

Vol. 1, No. 1, 2016

INFLUENCE OF DOBROTVIR THERMAL POWER PLANT ON ENVIRONMENTAL SPECIFICATIONS

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Received: 17.10.2015

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Abstract. The influence of the emissions of Dobrotvir TPP on the state of environmental pollution was evaluated: the state of air and soils and the state of waste management. The necessity to perform combined researches and ecological measures to reduce the negative impact of waste dumps on the environment was justified. It was established that the state of soils of ash and slag dumps was in crisis, the content of total forms of heavy metals in the soil is 2–10 times higher than TLV or a background concentration, large excesses of heavy metals of the I class of danger, namely Copper, Zinc and Lead were detected.

Key words: thermal power plant, ash and slag dumps, environmental pollution, heavy metals.

1. Introduction

Energetics is a branch of the economy, which covers energy resources, extraction, transformation, transmission and use of different types of energy. Electricity production in the world ranks an advanced place among all branches of production. There are three basic types of power plants that produce electricity. They are nuclear power plants (NPP), thermal power plants (TPP) and hydropower plants (HPP).

Thermal power plants (TPP) convert chemical energy of fuel (coal, oil, gas, etc.) sequentially to thermal, mechanical and electrical energy. By power equipment TPP are divided into steam, diesel and gas turbine power plants. Thermal power plants are the basis of power. The fuel which is used in thermal power plants is coal, natural gas, fuel oil, shale, wood. The increase of a single power of TPP determines the increase of absolute consumption of fuel consumption by individual power plants.

In different countries of the world the ratio of one or other particular type of power depends on the geographic location and scientific and technological potential of the country. Worldwide the thermal power plants produce 63 % of electricity, hydropower plants –

19 %; nuclear power plants – 17 % [1–4]. At the same time the structure of electricity production varies between regions. The share of nuclear power plants is much higher in Europe (27 %) and in Latin America there is a very high share of hydropower plants (75 %). Even more essential are the differences in structure between countries. The share of electricity production in Ukraine between the stations of different types is the following: TPP – 65,57; NPP – 25,83; GPP – 2,37; other power plants – 0,03.

Depending on the structural particularities of the world country, electricity producers can be divided into several groups. The first and fundamental group is consisted of countries where the principal part of the electricity produced is by the thermal power stations. Among those countries there are South Africa, the Netherlands, Poland, Russia, Ukraine, China, UK, USA and others. Overall, the share of thermal power plants in electricity production is growing, because their construction is cheaper, the terms of the construction are shorter, the power is great.

The presence of a large number of thermal power plants in Ukraine is due to huge reserves of coal during the Soviet times, which are mainly concentrated in Donetsk, Luhansk and Dnipropetrovsk regions even in Soviet times. When burning the solid types of fuel in the furnaces of thermal power plants the ash is generated in the form of residues similar to dust and lump slag as well as ash and slag mixtures. They are products of high-temperature treatment at temperatures of 1200... 1700 °C of the mineral part of the fuel. The chemical composition of ash and slag waste depends on the type of solid fuel (coal), which is subjected to burning, but the average of the waste includes the following oxides: SiO₂ – 55,3 %, Al₂O₃ – 17,3 %, Fe₂O₃ – 3,2 %, CaO – 3,59 %, MgO – 1,86 %, TiO₂ – 1,44 %, K₂O – 1,86, Na₂O – 0,72 %, and the oxides of vanadium, gallium and others. [5]. Ash slags which are formed as a result of the coal combustion in thermal power plants are large-tonnage waste. For their transportation the systems of hydraulic ash removal are used. Thus most of ash slags

is transported in a form of the slurry of low concentration slurry to place it the hydraulic ash dumps, which are one of the major sources of environmental pollution in the production of electric energy [5].

Modern industrial society is impossible without such not renewable energy sources as gas, oil and coal. Highly developed countries get 80 % of energy from them. Over the past 30 years at TPP, which are the largest producer of electricity, 76 billion tons of coal, 3 billion tons of oil fuel, 3 trillion m³ of gas. Despite of the large amount of produced electricity, a huge lack of TPP is environmental pollution in both a local and planetary scale [6–8].

The largest TPP are located in Donbass (Vuhlehirska, Starobeshevska, Myronivska, Kurahivska etc.), Prydniprovye (Prydniprovsk, Krivorozhsk), Kharkiv (Zmiyivska), Kyiv (Tripilsk), Ivano-Frankivsk (Burshtynska), Lviv (Dobrotvirsk) regions, in Zaporizhya, Odessa and others. Most of these power plants produce heat too (TPC). TPP are the major stations that provide electricity in half-peak and together with HPP and HNPP during peak hours.

In Lviv region five companies are included in the “List of 100 objects that are the major environmental polluters in Ukraine”: “Dobrotvirsk TPP”, OAO “Lviv Coal Company” Novorozdilsk State Mining and Chemical Enterprise (SMCE) “Sirka (Sulfur)”, Lviv communal enterprise “Zbyranka” Novoiavorivsk SE “Ecotransenergo”.

Dobrotvir TPP was launched in 1956 when the first phase of production capacities was put into operation. It had three boilers PK-19 of the plant № 1-3 with the release of flue gases station into the high-level smokestack № 1 (H = 101 m). Currently these boilers worked out and were removed, the smokestack № 1 is inactive. In 1961, the second phase of the station was put into operation, it had six boilers TP-10. These boilers run on two steam turbines K100-90-6 LMZ. The gas passages from six boilers № 5-10 are connected to a high-level smokestack № 2 (H = 105 m). In 1963 in the STPP the third phase of the station started to function, it was based on two power units of the station of 150 MWt. The release of flue gases from the boilers TP-92 is performing through the smokestack № 3 (H = 120 m). In the late 80's the construction of the fourth phase of Dobrotvir TPP (DTPP-2) began, it would consist of three power units of 225 MWt each. The high-level smokestack and partly an industrial building were constructed. In the early 90's, after the collapse of the USSR, in connection with the termination of financing the construction was stopped. In the strategic directions of the development of generating capacities of open JSC “Zahidenergo” for the period up to 2030 the completion of the construction of the shunting power unit № 9 of the capacity of 225 MWt and the construction of new power units № 10 and № 11 were planned for Dobrotvir TPP-2.

The average age of domestic TPP is 45... 50 years, because their main construction took place in 60's... 70's of the last century, that's why during this time the accumulation of solid waste (slag and ash) reached enormous sizes, 359 million tons, that in turn, takes a lot of land space for their storage. This leads to the disruption of the ecological situation both in the regions and in the country as a whole.

The emissions of thermal power plants in Ukraine in 5–30 times higher than European Union standards [9, 10], and they are the main gross air pollutant in the state.

Currently, there is no complex processing of ash and slag wastes, only their small number (10... 15 %) is used in the construction industry as a component in the production of bricks and a pavement. But the potential of slag wastes is much higher, it is due to the presence of large number of valuable components containing in the slags from TPP (vanadium, gallium, iron, silicon, etc.). Therefore, to improve the ecological situation in the country and to receive new sources of raw materials it is necessary to develop and implement a combined recycling of ash and slag wastes of TPP. The negative side of the function of TPP is an environmental pollution both by gaseous impurities and solid wastes in the form of ash and slag.

The aim of the work is to evaluate the influence of Dobrotvir TPP on the characteristics of the environment.

2. The presentation of the main material

Energy production in TPP is accompanied by a large amount of heat generation, that's why these plants are usually built near cities and industrial centers to use (utilize) this heat. Considering the limited world reserves of fossil fuel, scientists and engineers continue to work on improving the parameters of power units, increasing their coefficient of performance (COP), which provides economical fuel consumption. Further growth of the capacities of the power units is possible in the event of the introduction of so-called cryogenic generators that are refrigerated by liquefied helium. Burning fossil fuel is accompanied by strong environmental pollutions. Consider the main ones.

Air pollution by Dobrotvir TPP. Some issues of air pollution by Dobrotvir TPP were considered in the work [11]. The main air pollution by Dobrotvir TPP is performed by harmful substances that are emitted from the high-level smokestacks in the process of producing electricity and heat. The capacity of the reductions differ depending on the technological equipment of the station and it is constantly changing during the day, week, month and year, according to the controller load schedule.

In recent years, due to the significant rise in prices for natural gas and fuel oil and to the shortage of these types of fuel, the main fuel for STPP is coal of Lviv-Volyn, Donetsk coalfields. The increase in volume of used coal, in turn, leads to increased emissions of products of its

combustion in the air such as dioxide, carbon monoxide, sulfur dioxide, methane, vapors of sulfuric and hydrochloric acids, ammonia, carbon tetrachloride, carbon monoxide, vapors of mineral oil, solid particulates, heavy metals such as arsenic, chromium, copper, mercury, nickel, lead, zinc and greenhouse gases.

To reduce the emissions of pollutants from stationary sources into the atmosphere at Dobrotvir TPP the cleaning equipment from dust and gas is exploited. It means ash catching installations of station boilers, cyclones, dust sediment cameras.

“Wet” ash catchers with Venturi smokestacks were used for cleaning flue gases taken out from the furnace of the boilers in the boiler and turbine workshop; cyclones are used to reduce dust emissions of coal concentrate in the fuel and transport workshop and abrasive metal dust emissions in the repair and construction workshop; to reduce abrasive metal dust emissions in the repair and construction workshop dust sediment cameras are used.

Today “wet” ash catchers are replaced on ash catching installations (ACI) with emulsifiers of the second generation. The energy conversion efficiency of the previous ACI (“wet” ash catchers) was 94–95 %, the efficiency of the ash catching installation after installing the battery emulsifiers of the II generation according to the design data is ≥ 99 %, respectively, air emissions will be reduced by 85,7–86,7 % (from 1,4 – 1,96 g/Nm³ to 0,2 – 0,26 g/Nm³), herewith possible is cleaning of flue gases from sulfur oxides by 5–15 % without introducing special reagents.

Due to the combustion of hydrocarbon fuel in the furnaces of TPP carbon dioxide is emitted into the atmosphere, its concentration increases by about 0,25 % per year. This is dangerous because in the future it can cause warming of the atmosphere due to the greenhouse effect. From the smokestacks of TPP sulfur and nitrogen oxides are emitted into the atmosphere, which are the cause of acid rains. The case is complicated by the fact that the smokestacks of TPP began to grow up, their height reaches 250–300 and even 400 m, the amount of emissions are not reduced, but now they are scattered on vast areas (the emissions of TPP pollute the air with dust within a radius of 10–15 km). And during the rainy season, combining with water, gaseous toxic substances are converted into acid. These acid rains influence extremely harmfully on the environment: crop productivity is reduced due to damaging the leaves by acids; forests die; calcium, potassium, magnesium are washed out from the soil, causing degradation of flora and fauna; lakes and ponds water is poisoned, fish die, insects, waterfowl birds and animals which nourished by insects disappear (it is known in chemistry that the acidity is measured by the indicator pH. The change of pH by a unit means that the concentration of acid has changed in 10 times. For example, when pH of water system is 6,0–6,5 curls and shellfish die, and when pH is

5,0–6,0 most susceptible planktonic organisms, some types of fish die; air polluted with an acid mist causes respiratory and eye illnesses; the atmosphere is polluted as well with small solid particles of ash, slag incompletely burned fuel (soot).

To minimize the damage from these pollutions it is needed to clean coal from sulfur compounds before its combustion in TPP; to improve the quality of the coal blending it with the coal of ash content of 20–24 % coming from Poland; to capture sulfur and nitrogen oxides from the smoke of TPP using filters, to install electrostatic precipitators and desulphurization on the power unit №8 of Dobrotvir TPP according to order by the Ministry of Fuel and Energy № 300 from 22.08.06; to replace coal and fuel oil for TPP by environmentally friendly fuel, by gas (though at this stage it is not economically profitable). Due to the combustion of natural gas the single most significant air pollutant is nitrogen oxide, but it is produced 20 % less than due to burning coal.

Radioactive contamination. As into the furnaces of TPP with the coal get a lot of empty rocks (shales) containing impurities of natural radioactive elements – uranium-238 and thorium-232, ash particles emitted from the smokestacks of TPP, they are radioactive and cause additional exposure of the population at the territory close to the station, radioactive contamination of the atmosphere and the earth's surface. According to experts' data, the year of functioning TPP leads not only to a significant suppression of the immune system of humans and animals and anomalies of plants, but also to the shortening of life by 3200 person-years.

For electricity production they use fossil fuel, mostly coal, which like many other fossil materials contains a number of naturally occurring radionuclides, among which the most important is 40K, components of natural uranium and thorium radioactive series. During combustion in thermal power plants minerals melt and form glassy residue in a form of a slag, and volatile ash is taken out by hot gases and some part of it, depending on the effectiveness of the cleaning system of TPP gets into the atmosphere. With solid particles of volatile ash into the atmosphere get some natural radionuclides of uranium and thorium series, and 40 K, which are concentrated in it during coal combustion. As a result, thermal power plants are the source of getting natural radioactive isotopes in the environment, leading to its radioactive contamination and additional exposure of people.

To evaluate the influence of emissions of burning coal products by Dobrotvir thermal power station (STPP, Lviv region.) on radiological environmental state by gamma spectrometric method, the radionuclide composition and specific activity of coal that is burned on STPP as well as slags and volatile ash, which is produced due to coal burning were studied. The study was conducted at the accredited gamma spectrometer on the basis of spectrometric complex SU-01. The results of measurements are shown in the table.

Table
**The specific activity of radionuclides in coal,
 burned at Dobrotvir TPP, in ash and slag**

Radionuclide	Specific activity of radionuclides, Bq/kg		
	in coal	in ash	in slag
40K	338±35	558±53	625±55
214Bi	58±8	103±13	123±13
226Ra	105±15	192±18	247±22
208Tl	16±4	31±7	35±7
232Th	49±7	68±9	97±10
212Pb	57±8	100±11	122±12
214Pb	65±10	85±12	120±14
212Bi	45±7	71±10	116±13
228Ac	51±7	66±10	92±14

The obtained results showed that both in coal that is burned at STPP and in ash and slag which remain after the incineration, there are 40 K and radionuclides of uranium and thorium series, a range of values of specific activity of which in coal is in the range of 16 ± 4 to 338 ± 35 Bq/kg, in ash from 31 ± 7 to 558 ± 53 Bq/kg, and in slag from 35 ± 7 to 625 ± 55 Bq/kg. The concentration of radionuclides in the products of combustion was observed, in ash the specific activities of radionuclides are increasing in $1,6 \pm 0,3$ times, and in slag in $2,1 \pm 0,3$ times in comparison with coal.

For calculations such data on the activities of Dobrotvir TPP were used: the amount of coal that is burned at TPP is ~ 750 ths. tons per year; the emission of volatile ash into the atmosphere is ~ 768 tons per year; the amount of ash that remains after burning coal is ~ 80 ths. tons per year; the amount of slag that remains after burning coal is ~ 116 ths. tons per year; the project cleaning efficiency of solid particles at TPP is 98,5 %, and the actual one is 90 %.

The contributions of radionuclides activity in the total activity of coal, ash and slag were defined (Fig. 1–3).

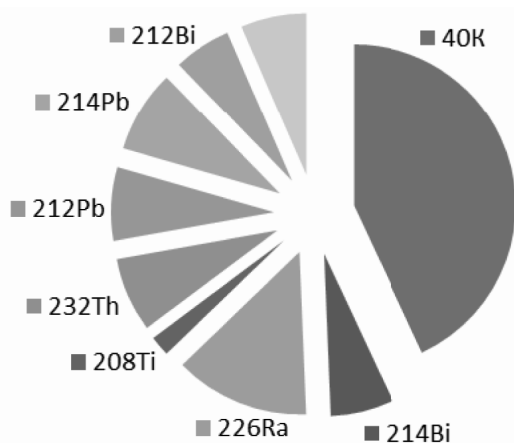


Fig. 1. The contributions of radionuclides activity in the total activity of coal

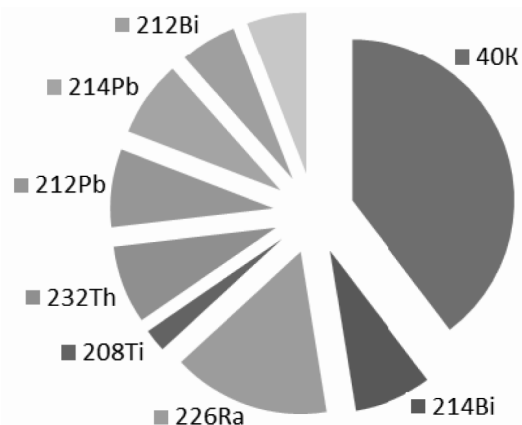


Fig. 2. The contributions of radionuclides activity in the total activity of ash

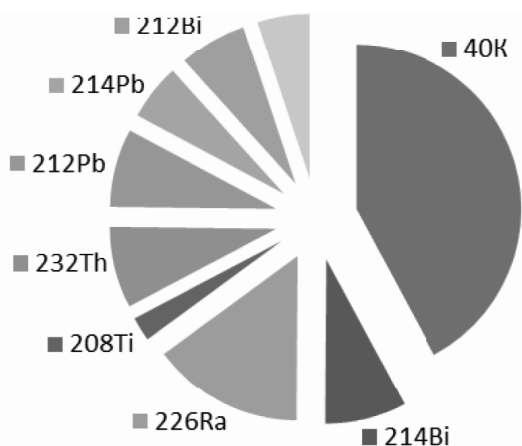


Fig. 3. The contributions of radionuclides activity in the total activity of slag at Dobrotvir TPP

Generally the configuration of this field depends on many factors such as the mass of ejected material and the size of ejected particles, the velocity of the emission of flue gases, the height of the smokestack, the total volume of flue gases of moving direction and wind speed, the changes of air temperature at different altitudes and some other parameters.

The management with the wastes of Dobrotvir TPP. In order to develop the cost-effective organizational and technical solutions the experience of developed countries on the issue of using ashes of TPP was studied.

The basic ideological difference: in developed countries ash and slag wastes are called an incident product of TPP and the power plants perform product presale preparation, improving its characteristics to the requirements of the official building regulations.

In Ukraine and Russia ash and slag wastes are officially called wastes and power plants offer exactly the waste to consumers but not a technologically refined product with characteristics corresponding to the requirements of building regulations.

In Western Europe and Japan ash dumps at TPP are almost eliminated. Dry ash enters the silos, built next to

the main buildings of TPP. For example, in Germany at many plants the capacity of the silos is 40-60 ths. tons and small silos are always built with a daily and two days capacity from which samples for a laboratory analysis of ash are taken, and in which it brings to the accordance to regulatory requirements by technological methods of mising and volumetric dosage in accordance with the fractional composition, then ash is reloaded in ash-storage silos.

In Germany, the largest company on the European continent on the use of ashes of TPP functions, Bau Mineral (BM) which is a subsidiary company of power system. This company is a link between TPP and the construction industry.

The production of BM meet the standards and guidelines of DIN, which are subject to external control by the institutions of testing building materials. The basis of quality assurance is continuous monitoring of products in its own well-equipped laboratories of testing building materials. From 4.3 mln. tons of volatile ash 3,5 mln. tons meet European standard of volatile ash for the materials of volatile ash. Combustion sand and granulated slag are utilized completely. Granulated slag is a substitute of sand in the sandblasting process. The main requirement is the homogeneity of ash properties. The areas of use are additives in concrete, mortar, cement, silicate products, the production of bricks, the underground and road construction. The main direction is the replacement of cement.

In Germany, there are no TPP without silos for ash. For example, at TPP "Molka" the total volume of silos is 60 ths. tons, the output of ash is 600 ths. tons/year. At TPP there are not any ash dumps. The incident products of TPP are exported to neighboring countries. For volatile ash a certificate is required if it comes to building and construction industry.

In Germany 3.1 mln. tons of cement are replaced by ash. Ash is recycled by an environmentally friendly method. The resources, the energy required for cement production are saved; the emissions of CO₂ are reduced by 3,1 mln. tons (during the production of 1 ton of cement the emissions of 1 ton of CO₂ are occurring), which is important according the requirements of the Kyoto Protocol on reducing the emissions of CO₂. The cost of silos, transport and wages are repaid. The power plant (TPP) is a producer of products but not waste. Uniformity is important for ash.

In the US, the builders are legally obliged to apply ash of TPP in concrete and mortars production. The violators are subjected to economic sanctions from the state. TPP often remunerate a consumer for the selection of ash. In China, ash and slag wastes of TPP are sold to consumers for free. In Poland, powerful economic levers, that stimulate the use of ash and slag wastes are used.

Conducting economic activities at Dobrotvir TPP, they create, temporarily store and remove such wastes as

waste fluorescent lamps (I class of hazard); they are stored in the central workshop, in the separately designated place; waste car oil which belong to the II-nd class of hazard are formed in motor workshop. Waste car oils are partially used for their own needs, for lubricating machinery; waste turbine oils (III class of hazard) are in the boiler and turbine workshop, they are stored in a tank of volume of 40 m³. The residue from washing vehicles (IV class of hazard), construction waste, solid household waste are removed to the city dump of the city Dobrotvir; oil sludge of mechanical purification of waste waters (III class of hazard) is transferred to the carriage depot of the city Drohobych; sludge of treatment plants (WTP) is removed to the sludge grounds of treatment plants of Dobrotvir TPP. Waste tires are passed to "Ivano-Frankivsk tire-repairing plant".

For softening and desalination of water at Dobrotvir TPP they use sulfuric acid, caustic soda and hydrazine-hydrate (levoksin) as an anticorrosive means for processing feed water in boilers and the conservation (the passivation) of the nourishing tract of inner surfaces of boilers. The average annual cost of these substances are respectively 160, 100, 2.5 tons. Contact mechanical sulfuric acid of the 1 grade is stored in three pressurized tanks of the type BNT-16 in a separate closed room, there is water to pour upon spilled acid and alkali and solutions to neutralize them.

Hydrazine hydrate, and its aqueous solutions are powerful reducing agents, containing up to 64 % of hydrazine and they are used as a corrosion inhibitor. Hydrazine-hydrate is stored in stainless steel tanks (2 m³, 0,5 m³, 0,3 m³) in the open acid workshop. Around the containers the territory is heaped round. Hydrazine hydrate is poured from the barrels into the receiver tank, half filled with water. The installation to preparing solutions of hydrazine-hydrate is located in the area of the power unit № 7 in an isolated room, which is equipped with ventilation and has a collector for collection and neutralization of drainage waters. In the room there is a required reserve of chlorinated lime to neutralize an accidentally spilled solution of hydrazine-hydrate.

The main wastes generated in production is ash and slag from coal combustion, primarily from the Lviv-Volyn basin with the content of ash of 24,85 %. During 2013 196,704.490 tons of ash and slag wastes were formed that belong to the waste of IV class of hazard. To build dams 23,733.600 tons were used, 20,354.000 tons were released for use to other owners, 152 616.890 tons were placed. Ash and slag waste is warehoused on two ash and slag dumps by the area of 56 hectares and 75 hectares of the volume of 4,5 mln. m³ and 8,057 mln. m³.

The determination of the coefficient of soil pollution by heavy metals in ash and slag dumps. Heavy metals get into the soils with the emissions of enterprises and transport, sewage, industrial waste, household waste, chemical fertilizers and pesticides. Typically, a signi-

ficant soil pollution occurs within industrial sites, household waste, roads.

To evaluate the degree of soil pollution according to the classification heavy metals of three classes of hazard were taken: the I class – very hazardous – Cd, Pb, Zn; the II class – moderately hazardous – Cr, Co, Cu, Ni; the III class – low-hazardous – Mn, Fe.

To control the technogenic pollution of soils they determine the gross amount of heavy metals in the soils, since the latter has the ability to bind metal compounds.

To evaluate the degree of pollution of heavy metals on the one hand, it is necessary to use the initial point of reference, which is the value of element background content, and on the other hand it is necessary to know the MAC of the element in the soil. Since the MPC of investigated heavy metals is approved only for gross contents of Mn (1500 mg/kg) and Pb (32 mg/kg), so for the evaluation of the level of pollution by gross contents of heavy metals their background concentrations should be taken.

Ecological condition of soils is determined by the following criteria:

- favorable – the content of gross forms of heavy metals in the soil is on the level of percent abundance;
- satisfactory – the content of gross forms of heavy metals in the soil is slightly higher than percent abundance; but does not reach the MPC or the background concentration;
- of a pre-crisis – the content of gross forms of heavy metals in the soil is on the level of MAC or of the background concentration;
- of a crisis – the content of gross forms of heavy metals in the soil is in 2–10 times higher than MAC or the background concentration;
- catastrophic — the content of heavy metals is in hundreds times higher than MAC or the background concentration.

Qualitative and quantitative composition of metals in the soil samples is determined using roentgen analyzer EXPERT 3L. In the Fig. 4–7 the graphs of pollution coefficient in ash and slag dumps are presented.

Was determined that the ecological state of soil pollution at Dobrotvir TPP is satisfactory. The soil state of ash and slag dumps is of a crisis (the content of gross forms of heavy metals in the soil is in 2-10 times higher than MAC or the background concentration), large excesses of heavy metal of the I class of hazard were found out, namely Cu – 4,00, Zn – 2,53 and Pb – 2,16. The soil state at a distance of 10 m and 100 m is satisfactory (the content of gross forms of heavy metals in the soil is slightly higher than percent abundance, but does not reach MAC or the background concentration). At a distance of 30 m from the dumps the significant excesses of the following elements were found out: Mn – 4,7 times, Cu – 3,11 times, Zn – 2,67 times, Pb – 2,24 times. Cadmium was not found in the samples. A significant deviation of the content of heavy metals at a distance of 30 m from th ash and slag dump can be explained by the difference of the relief on the area of Dobrotvir TPP.

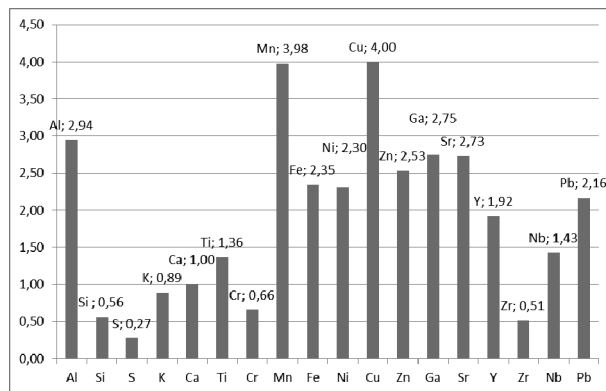


Fig. 4. Coefficient of pollution, ash and slag dump

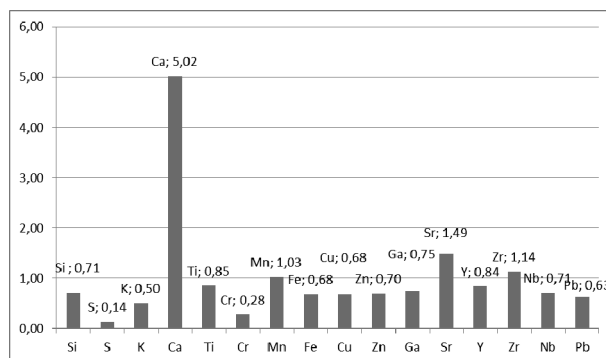


Fig. 5. Coefficient of pollution, distance of 10 m

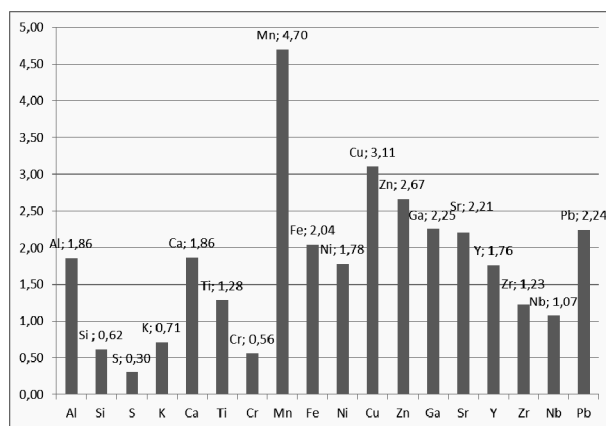


Fig. 6. Coefficient of pollution, distance of 30 m

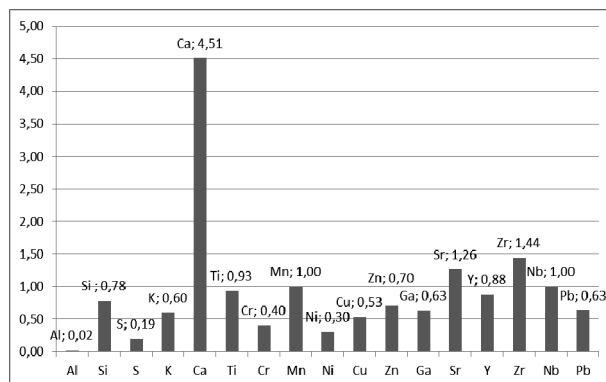


Fig. 7. Coefficient of pollution, distance of 100 m

3. Conclusions

The influence of emissions of Dobrotvir TPP Dobrotvir on the environment and the value of specific activity of radionuclides in coal that burned at Dobrotvir TPP, ash and slag. The installation of gas-cleaning equipment will reduce radioactive contamination of TPP in 100–200 times, ie to almost the background level.

The experience of developed countries on the issue of using ashes of TPP was studied. The state of management with wastes of Dobrotvir TPP was evaluated. The necessity to perform a combined research and environmental measures to reduce the negative influence of waste dumps on the environment was justified.

Ecological condition of soil pollution at Dobrotvir TPP is satisfactory, except ash and slag dumps themselves. The state of soils of ash and slag dumps is of a crisis (the content of gross forms of heavy metals in the soil is in 2-10 times higher than MAC or the background concentration), large excesses of heavy metal of the I class of hazard were found out, namely Cu – 4.00, Zn – 2.53 and Pb – 2.16. At a distance of 30 m from the dumps the significant excesses of the following elements were found out: Mn – 4.7 times, Cu – 3.11 times, Zn – 2.67 times, Pb – 2.24 times.

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