DETERMINATION OF THE RADIATION FROM THE WASTE OF RAW MATERIAL IN SOME INDUSTRIAL COMPOUNDS IN KOSOVO

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Abstract: In the paper there are presented the outcomes of determining the radiation of some remaining of radionuclide from raw material in the technologic aspect (TENORM-Technologically Enhanced Naturally Occurring Radioactive Materials),in some industrial plants in Kosovo, particularly in Feronikel and Power Plant Kosova-B. On-site measurements were carried out by detectors: Gamma Spectrometer Gr-130; Inspector–EXP-Radiation Alert, Spectrometer- TA-PUG-7A as well as Gamma monitor- SGM-29-246. Samples were taken at the above-mentioned locations and they were treated in the physic-chemical aspect at the Centre for Applied Nuclear Physics in Tirana. On-site measurements, respectively at the centers: Feronikel-Drenas, Trepçë – Mitrovica and TEC (PP) – Obiliq show that the level of annual radiation is around the interval from 75.45 nSv/h to the values 289.54 nSv/h. By spectrometric analysis conducted at the Centre for Applied Nuclear Physics in Tirana, the following radionuclide and its radiation concentration, expressed in Bq/kg: Waste from the convertor of industrial compound Feronikel – Drenas. Radioactive elements and their concentration (Bq/kg) :K–40--37 ± 7 Bq/kg; Ra–226--17 ± 4 Bq/kg; Ra–228--6 ± 1 Bq/kg; Th–228--5 ± 1; Th–232--5 ± 1 Bq/kg; U–238 --10 ± 3Bq/kg. Waste from phosphogypsum, industrial compound Trepça –Mitrovica. K-40--10 ± 3 Bq/kg; Ra–226-- 230 ± 30 Bq/kg; Ra –228--5± 1Bq/kg; Th –228--5 ± 1Bq/kg; Th–232-- 5 ± 1 Bq/kg; U–238-- 30 ± 5Bq/kg Ash waste from the Power Plant Kosova B- Obiliq- radioactive elements and concentration (Bq/kg) K–40 -- 150 ± 15 Bq/kg; Ra–226 -- 40 ± 10 Bq/kg; Ra–228 -- 20 ± 2Bq/kg; Th–228--20 ±2;Th–232-- 20 ± 2 Bq/kg; U–238--25 ± 5 Bq/kg. Based on the outcomes of measurements, it can be concluded that in two locations Feronikel-Drenas and PP – Obiliq the level is lower than the average of the natural background (200-250 nSv/Yr). Whereas in the location of Trepça-Mitrovica there are higher values and this is an indication that it requires a further and detailed study approach. After the final assessment we will conclude whether such waste can be used in practice for various needs. It will be concluded that what is the risk introduced by such waste in the aspect of radioactive contamination of living environment.

Key words: *Radioactive, Radiation, Cconcentration, Norm,Tenorm*

INTRODUCTION

In nature can be founded approximately around 340 nuclides and among them about 70 are radioactive (EISENBUD, 1997). Usually they are classified regarding their origin, which means primordial radioisotopes (for example 40K, 87Rb, 238U, 232Th), secondary radioisotopes and cosmogenic radioisotopes. The halved time of Primordial Radioisotopes is very long and they survived since their creation, and they are comparable to the age of the Universe. Secondary radioisotopes are the result of the diffraction of primordial radioisotope while cosmogenic radioisotopes are the result of continuous bombardment of stable nucleus by

cosmic rays (HOLMES-SIEDLER 2006). In the last two decades, the International Community Safety for example radiation protection IAEA, EC (IAEA 2003, EC 1999, EC 2002) have devoted a considerable attention in connection with Naturally Occurring Radioactive Materials (NORM) as defined in ICRP publications (ICRP 2007), or Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) , the exposures of workers during the handling of these materials may be of a very high level, in some cases even higher than the occupational exposure of workers dealing with the licensing of radiation sources. Being aware of the consequences, the International Community of Radiation Safety has published the safety standards primarily about norms that have been published in (IAEA 2004). In recent decades, with the development of new technologies it has also resulted the production of by-products and waste of so-called Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM). Therefore, the technical human activity can increase the radiation exposure, not only to persons directly involved in these activities, but also to the local population or even broadly. TENORM describes the sources, the content of radiation, the presence of radionuclide, and management of TENORM.

According to the Environmental Protection Agency, waste TENORM are divided into four categories;1.Mining waste 2.Waste of energyproduction: coal, oil,andnaturalgas, 3.Waste water treatment: waste water treatment and radioactive materials which are disposed legally in the system of sanitary waste water collection, and 4. Waste of consumer products. The International Atomic Energy Agency (7.IAEA) has published fully the radiation safety standards based on the recommendations of the International Commission on Radiation Protection, which are recommended for approval as the Basis Safety Standards (BSS), from all the European Union Member States. Based of these recommendations several countries have introduced their own Regulations for NORM and classification of TENORM by setting out rules and levels of treatment for those radionuclide that are selected for discharge.In the Basic Safety Standards (BSS) are recommended the exposure limits and exemptions from various sources of radioactivity, including the NORM. The most important limits are as follows: Maximum annual dose limit of 1 mSv (100 mrem) for the members of the public, with a provision to allow the highest doses in any single year, provided that the average for five consecutive years does not exceed 1 year mSv. The limit for an effective dose for exposed workers will be 100 mSv (10 rem) for five consecutive years, a period that is subject to a maximum effective dose of 50 mSv (5 rem) in any single year. The purpose of this study was the determination of some radionuclide, the level of radiation and their concentration, particularly in mineral processing waste in Ferronikel-Drenas and Trepca-Mitrovica and waste from the production of electricity PowerPlant - Kosovo - B, Obiliq.

MATERIAL AND METHODS

The investigations have been focused on direct measurement of industrial complexes and analysis of samples in the laboratory of Spectrometry at the Centre of Applied Nuclear Physics in Tirana. Our experimental work was conducted in the industrial complex of Ferronikel-Drenas, Trepca-Mitrovica and Power Plant Kosovo B in Obilic during 2010 to 2011. In the first part we have determined the basic level of radiation of raw materials as well as changing of these levels of radiation after the technological processes of radioactive materials, namely NORM / TENORM, ((NORM- Naturally Occurring Radioactive Materials and TENORM- Technologically Enhanced Naturally Occurring Radioactive Materials), hereinafter NORM / TENORM. 20-25 measurements have been made at a point of a material and is provided the average, at the same time, samples were taken from waste coal ash in the landfill of Power Plant in Kosovo-B -Obilic, waste from industrial Complex Trepca –

Mitrovica, Phosphogypsum landfill and waste dust from the Converter in industrial complex Ferronikel-Drenas. In direct measurements it is determined only the total radiation, we have analyzed the samples in the laboratory of Spectrometry at the Centre of Applied Nuclear Physics in Tirana. Levels of radiation of NORM are measured at a distance of 5cm from the ground while for the natural background 1m up the land. For this purpose we have used these radiation detectors: Gama-spectrometer Gr-130; Inspector-EXP-Radiation Alert, spectrometry-TA PUG-7A-and monitor-SGM-range 29-246. The samples for analysis were taken carefully, are taken in a surface of $1m^2$ and with a depth of surface from 5 cm. In the laboratory of spectrometry it was used the instrument Gamma spectrometry CANBERRA, Gama Spectrometer can handle a wide range of samples starting from the largest samples to the smallest one, in dishes from Marinell, in bottles, filters, Petri dishes, etc: CANBERRA Spectrometer is standardized in all aspects of spectrometer, detector, electronic shields and software, it has the following components to ensure optimal sensitivity. The instrument has available two standard gam-AN1 for routine counting and gam-AN2 for applications requiring increased sensitivity counting. The analyst Gamma CANBERRA is an instrument that gives results of high quality. It is determined the chemical composition of the material and concentration of the activity of these radioisotopes: K–40 Bq/kg; Ra–226 Bq/kg; Ra–228 Bq/kg; Th–228; Th–232 Bq/kg; U–238 Bq/kg.

Figure 1. Map of Kosovo –Location of measurement and taken of the measures

The Drenas Ferronickel (FeNi) Plant is located 30 km west of Pristina in the Drenas municipality, and consists of the smelting complex and two mines (1.5 km and 7.0 km far from

the smelter). Forthe moment the factory is operating just with one line due to the crisis and the so caused export low, but there is capacity for two lines. According to operator's information the main products are 25 kg ferronickel ingots with approx. 35% Ni content.

The Mitrovica Industrial Park is part of the Trepça Industrial Complex. Several industrial plants existed in the past in the complex as there was a lead smelter, a fertilizer production plant, a refinery,

a battery factory, a zinc electrolysis facility and a sulphuric acid plant (see Figure 1). The sulphuric acid, as by-product of the zinc electrolysis facility, was used in the fertilizer and the battery plant.

Most of the facilities are not operating for the moment because of heavy damage. According to operator´s information only 1% of the complex is currently operating. Nevertheless, some chemicals are still stored on site, as sulphuric acid. Because of the absence of maintenance most storages are in a bad condition and promote soil and groundwater pollution. The adjacent evaporite pond (phosphogypsum stack) has been polluted with residual heavy metals, too. Because of the large area the stack occupies and the related potential for release of radon gases this part of the plant must be considered as a major problem for the future that needs to be solved. For this reason the former production of phosphor fertilizers and the processing of bauxite have been identified as NORM/TENORM relevant processes on this site.

The Kosovo Energy Corporation (Energy Regulatory office- Kosovo, annual report 2005), with two major power plants is located in municipality Obiliq/Obilić northwest of Prishtinë/Priština on the main road to Mitrovicë/Mitrovica. The municipality was created in 1989, prior to which it was part of Prishtinë/Pristina.

RESULTS AND DISCUSSION

The results of direct measurements of radiation levels by Norm/Tenorm- in the above-mentioned complexes are in the interval from 75.45 nSv/h to the values 290 nSv/h. The natural background values in the Republic of Kosovo are around 2-2.5 mSv/year. In the industrial complex of Ferronikeli-Drenas the measured values of the general radiation are 75-110 nSv nSv/h. The measurements were performed close to the surface of materials. The results of measurements are given in Table 1. The factory is located in a low geographic region with a general natural background of radiation which is estimated to be about 60 -70 nSv / h. Samples are analyzed in the laboratories of Applied Nuclear Physics in Tirana, respectively, in the laboratory of spectrometry using Gamma spectrometry CANBERRA instrument. The results are presented in Table 4. From the results the nuclide compositions of the samples were calculated according to aiN = ai / (aU-238, max+ aTh-232,max) Here, ai is the activity concentration of a nuclide "i" and aU-238,max and aTh-232,max are the activity concentrations of those nuclides, which have the highest activity within the U-238 series and the Th-232series, respectively.

From the results obtained it is shown that the processed Ores in the Plant are characterized by a very low level of natural radioactivity. Therefore the Th-232 can be assessed as the average of Ra-228 and Th-228.From Table 4, we have the results of the waste from converter with these radionuclide and their concentration expressed in Bq/kg : K–40--37 $\pm$ 7 Bq/kg; Ra–226--17 $\pm$ 4 Bq/kg; Ra–228--6 $\pm$ 1 Bq/kg; Th–228--5 $\pm$ 1; Th–232--5 $\pm$ 1 Bq/kg; U–238 --10 $\pm$ 3Bq/kg.From the composition of radionuclide and their concentration it is shown that we have values with low concentrations, except that K-40 has higher value than K-40 in Trepça and lower from the Power Plant "Kosovo-B" The concentration of activity of U-238,

Ra-226, Ra-228, Th-228 is significantly lower than 100 Bq / kg. (100 Bq / kg appropriate dose of environment) Levels measured during the sampling are almost at the level of natural background. Therefore, these materials can be estimated being without radiological concerns. The activities are so low, that they meet the radiological criteria for various building materials without conditions.

Table 1.

Data of ambient gamma dose rate measurement of natural background, raw material and residues, at the NewCo Ferronikeli Complex L.L.C

Location	Sample ID	Distanc [m]	[nSv/h]
Natural background dose rate	**FN-1**	**1.0**	**70**
Ore (black and brown)	**FN-2**	**0.05**	**110**
Hard coal	**FN-3**	**0.05**	**75**
Converter slag	**FN-4**	**0.05**	**86**
Electro filter dust	**FN-5**	**0.05**	**107**

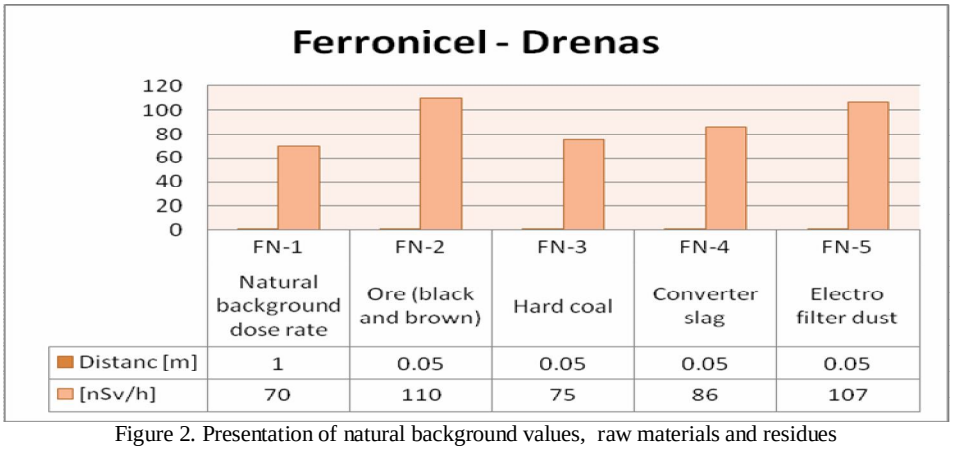

Figure 2. Presentation of natural background values, raw materials and residues

In the industrial complex Trepca in Mitrovica, the values of general radiation ranges from 75 nSv / h - 290 nSv / h, This is a temporary landfill within the industrial complex Trepca - Mitrovica, with an area of 10. 000 m^2 and with an estimation about 250,000 tone Phosphogypsum waste. The main source of radioactivity in Phosphogypsum landfill should be classified as TENORM.The spacies of the complex are located in a lower geographical region and has low values of natural background and the general radiation ranges in values 60-70 nSv/h. The results are presented in Table 4. The spectrometric analysis show that the nuclied of serie Th-232 is on the decrease of the balance. Therefore, Th-232 can be estimated as the average of Ra-228 and Th-228. The elaborated results from the residues of phosphogypsum show the presence of these radionuclide with this concentration (Bq / kg): K-40 - 10 + 3 Bq/kg; Ra-226-230 + 30 Bq/kg; Ra -228 - -5 + 1Bq/kg; Th -228 - 5 + 1Bq/kg; Th-232-5 + 1 Bq/kg, U-238-30 + 5Bq/kg. It is noted that Ra-226 and U-238, are with enhanced concentrations. We have increased levels of Ra-226-230 + 30 Bq / kg, which represents the concentration up to the natural background.

From the results the nuclide compositions of the samples were calculated according to aiN = ai/(aU-238,max+ aTh-232,max) Here, ai is the activity concentration of a nuclide “i” and aU-238,max and aTh-232,max are the activity concentrations of those nuclides, which

have the highest activity within the U-238 series and the Th-232 series, respectively.The waste of Phosphogypsum are thrown in locations close to the premises of the former processing, the values here are presented higher against the natural background and are up to 290 ns/h (see also Table 2). The survey results show that the temporay landfill of Phosphogypsum is a radiological concern and it is needed an environmental impact assessment. The results obtained are shown in Table 2.

Table 2.

Data of ambient gamma dose rate measurement of natural background, raw material and residues, at the Mitrovica Industrial Park – Trepça Industrial Complex

Location	Sample ID	Distanc [m]	[nSv/h]
Natural background dose rate	**TP-1**	**1.0**	**80**
Raw minerals	**TP-2**	**0.05**	**110**
Average value of measurements on the stack	**TP-3**	**0.05**	**75**
Landfill Phosphogypsum	**TP-4**	**0.05**	**290**

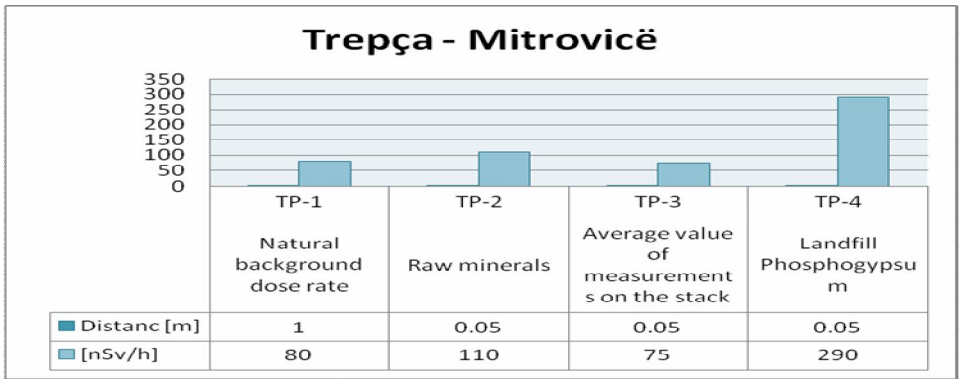

Figure 3. Presentation of natural background values, raw materials and residues

In the Republic of Kosovo the function of KEK for generating of electricity is performed by two Power Plants: Kosovo A (5 units) and Kosova B (2 units) and the production is based on the burning of coal. The overall Capacity of power plants is 1.478 MW, which would be sufficient to meet the current demands of electricity in Kosovo. However, due to the oldness, maintenance and inadequate operation during the years before and after the war, and due to the war damages, the reliability and overall capacity of the generation of these power plants is damaged seriously. The estimated lignite values are up to 14 billion tons. Currently there are in operation two open mining of lignite (Bardh and Mirash), supplying 6.5 million tons per year, generating units of electricity in KEK. (Energy Regulatory office- Kosovo, annual report 2005). The industrial Complex is located in a low geographic region, respectively in Fushe Kosova, on the huge reservoirs of coal (Lignite) with a general natural background, the radiation of which is estimated to be about 50 to 70 nSv / h. The measured values of general radiation of lignite and ash residues are from 75-110 NSV nSv / h. The measurements are performed near thesurface of materials. The results of measurements are given in Table 3.From the obtained results it is shown that the raw material -Lignite and ash residues are characterized by a very low natural radioactivity. The samples were analyzed in the laboratories of Applied Nuclear Physics in Tirana, respectively in the laboratory of spectrometry where is used the Gamma spectrometer CANBERRA. The results are presented in table 4.

The results of ash residues show the presence of radioactivity in this concentration: (Bq/kg):K–40 -- 150 ± 15 Bq/kg; Ra–226 -- 40 ± 10 Bq/kg; Ra–228 -- 20 ± 2Bq/kg; Th–228-- 20 ± 2 ; Th–232-- 20 ± 2 Bq/kg; U–238-- 25 ± 5 Bq. We have increased values K–40 -- 150 ± 15 Bq/kg where is represented the concentration on the natural background. The measured levels during the sampling are almost in the natural background; therefore these materials might be estimated to be without radiological concerns.

Table 3.

Data of ambient gamma dose rate measurement of natural background, raw material and residues, at the Power Plant "Kosova-B" Obiliq

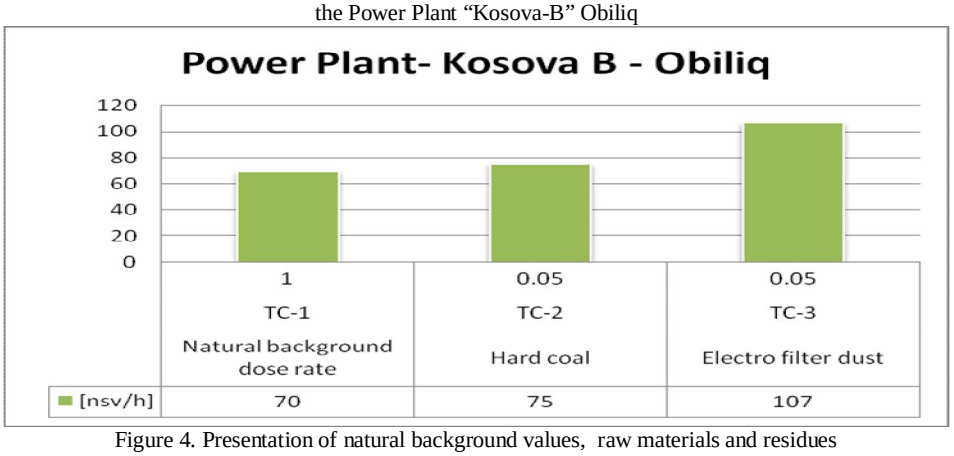

Figure 4. Presentation of natural background values, raw materials and residues

Table 4.

Summary of radionuclide analyses in solid samples [Bq/kg] at the Ferronickel Plant Drenas, Trepca Plant Mitrovica and the Power Plant "Kosova-B" Obiliq

Location	Radionuclide	K-40	Ra-226	Ra-228	Th-228	Th-232	U-238
Ferronickel – Drenas Electro filter dust	**Concentration, Bq/kg**	37 ±7	17 ± 4	6 ± 1	5 ± 1	5 ± 1	10 ± 3
Trepca - Mitrovica Landfill Phosphogypsum slag	**Concentration, Bq/kg**	10 ±3	230 ±30	5 ± 1	5 ± 1	5 ± 1	30 ± 5
Power Plant "Kosova-B" Obiliq Electro filter dust	**Concentration, Bq/kg**	150±15	40±10	20 ± 2	20 ± 2	20 ± 2	25 ± 5

CONCLUSIONS

The overall purpose of this research, in these above-mentioned industrial complexes was: the detection of the presence of radioactive elements (radionuclide), the level of radiation, the concentration (Bq/kg), analysis, review, information and the assessment of potential risks. The researches shown that in this industrial complex, on the radiological impact of radiation sources of technologically processed materials, especially processing mining and their waste, are of a high interest. From our results, the direct measurements it is shown that the radiation levels of natural materials (Norm), have low levels or radiation toward the natural background. Whereas as regards the waste of these materials following the technological processes (Tenorm) it is shown that we have an increased of a radiation level and especially the residues of Phosphogypsum. Also we may conclude that the dose of radiation to the members of the public resulting from these residues, is negligible compared to the average annual dose,

excluding the landfill of Phosphogypsum where is an increase on natural background. Effects on natural resources during the year are about 2.4 ms/year. Based on the allowed maximum of the activity, our predictions may lead to the conclusions that these residues can be used in a small amount of building materials or building products as for example, roof tiles, inner plaster, external plaster, stairs, road construction, filling in the levels. The utilization of these wastes can be used up to 10% of the general amount of construction.

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