UNIVERSITY OF NOVA GORICA
GRADUATE SCHOOL

# TECHNOLOGICALLY ENHANCED NATURALLY OCCURRING RADIOACTIVE MATERIALS (TENORM) IN SLOVENIA

MASTER'S THESIS

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## SUMMARY

TENORM, known as Technologically Enhanced Naturally Occurring Radioactive Material, is material containing radionuclides that are present naturally in rocks, soils, water, and minerals and that have become concentrated and/or exposed to the accessible environment as a result of human activities such as mining operations, manufacturing, or water treatment. In this thesis, a survey is made of the many sources of anthropogenic TENORM present in Slovenia, from past controlled practices (uranium mining and milling in the Žirovski vrh Uranium Mine), from practices that are not under radiological control (metal mining and smelting, phosphate industry, coal mining and power generation from coal, oil and gas drilling, rare earths and titanium oxide industry, zirconium and ceramic's industry, disposal of building materials) and from practices which would now be under control (e.g. applications of the natural radionuclides radium and thorium). The purpose of the thesis was identification of industries and activities handling TENORM and inventory of TENORM in Slovenia. In the thesis results of measurements of radioactivity at the locations of Idrija, Celje, Hrastnik, Jesenice, Kanižarica, Kidričevo, Kočevje, Lendava, Ljubljana, Ravne na Koroškem, Senovo, Šoštanj, Trbovlje, Vremski Britof and Žirovski vrh are presented. Measurements of gamma dose rate and/or sampling of the deposited materials for the analysis of $^{238}$U, $^{226}$Ra, $^{228}$Ra, $^{226}$Th, $^{210}$Pb, $^{40}$K and $^{137}$Cs gamma emitting radionuclides were performed. Based on results of measurement the estimation of annual doses and estimation of dose rates were made. It is conducted that annual effective doses in the vicinity of studied locations are lower than the average Slovenian natural background.



## POVZETEK

TENORM, znani kot tehnološko spremenjeni materiali, ki vsebujejo povišane vrednosti naravnih radionuklidov, ki so v naravi prisotni v kameninah, prsti, vod in mineralih, so v omenjenih materialih skoncentrirani in/ali so izpostavljeni spremembam kot rezultat človeških aktivnosti. Pri tehnoloških procesih izkoriščanja teh naravnih virov kot na primer z rudarjenjem in predelavo, pridobivanjem ali uporabo vode v različnih procesih nastanejo produkti s povečano radioaktivnostjo. Magistrsko delo predstavlja pregled antropogenih virov TENORM v Sloveniji, ki so rezultat preteklih dejavnosti, ki so pod radiološko kontrolo (rudarjenje in predelava uranove rude v Rudniku urana Žirovski vrh), dejavnosti, ki niso pod radiološko kontrolo (rudarjenje in predelava rud za pridobivanje kovin, fosfatna industrija, rudarjenje premoga in uporaba le-tega v termoelektrarnah, pridobivanje nafte in zemeljskega plina, redke zemlje in industrija titanovega dioksida, industrija cirkonija in keramična industrija, gradbeni materiali) in dejavnosti, ki bodo pod radiološko kontrolo (npr. aplikacija radia in torija). Namen dela je bila identifikacija industrije in inventarizacija TENORM v Sloveniji. Delo predstavlja rezultate meritev radioaktivnosti v Idriji, Celju, Hrastniku, na Jesenicah, v Kanižarici, Kočevju, Lendavi, Ljubljani, na Ravnah na Koroškem, v Senovem, Šoštanju, Trbovljah, Vremskem Britofu in na Žirovskem vrhu. Na omenjenih lokacijah so izmerjene hitrosti doze zunanjega sevanja gama in/ali opravljeno vzorčenje odloženih materialov za analizo vsebnosti vodilnih radionuklidov uran-radijeve, torijeve razpadne vrste, $^{40}$K in $^{137}$Cs. Na podlagi teh meritev je bila narejena ocena letnih doz in ocena hitrosti doz. Zaključeno je, da so letne efektivne doze v bližini omenjenih lokacij nižje od povprečne vrednosti naravnega ozadja v Sloveniji.

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## ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| ACPDR | Administration for Civil Protection and Disaster Relief of the RS (*Uprava Republike Slovenije za zaščito in reševanje*) |
| ALARA | As low as reasonably achievable |
| ARAO | Agency for Radioactive Waste Management *(Agencija za radioaktivne odpadke)* |
| ARSO | Slovenian Environmental Agency *(Agencija Republike Slovenije za okolje*) |
| BEIR | Biological Effects of Ionizing Radiation |
| CARE | Common approach for restoration of contaminated sites |
| CSRAO | Central Interim Storage for Radioactive Waste at Brinje (*Centralno skladišče radioaktivnih odpadkov Brinje*) |
| DNA | Deoxyribonucleic acid |
| DRSC | Directory of Radioactively Contaminated Sites |
| EPA | Environmental Protection Agency |
| GeLi | Lithium Drifted Germanium |
| GOV | Government of the Republic of Slovenia (*Vlada Republike Slovenije*) |
| HJM | Hydrometallurgical tailings |
| HPGe | High Purity Germanium |
| IAEA | International Atomic Energy Agency |
| IARC | International Agency for Research on Cancer |
| ICRP | International Commission on Radiological Protection |
| IJS | Jožef Stefan Institute (*Inštitut Jožef Stefan*) |
| LEPS | Low Energy Photon Spectrometry |
| MKGP | Ministry of Agriculture, Forestry and Food (*Ministrstvo za kmetijstvo, gozdarstvo in prehrano)* |
| MOP | Ministry of the Environment and Spatial Planning *(Ministrstvo za okolje in prostor)* |
| NAS | National Academy of Science |
| NCRP | National Council on Radiation Protection and Measurements |
| NORM | Naturally Occurring Radioactive Materials |
| NPP | Nuclear Power Plant |
| NRC | National Research Council |
| NRL | National Radiation Laboratory |
| OGRS | Official Gazette of the Republic of Slovenia (*Uradni list Republike Slovenije*) |
| PCBs | Polychlorinated biphenyls |
| RS | Republic of Slovenia (*Republika Slovenija*) |
| RŽV | Žirovski vrh Uranium Mine (*Rudnik urana Žirovski vrh*) |
| SIJ | Slovenian Steel Group (*Slovenska industrija jekla*) |
| SNSA | Slovenian Nuclear Safety Administration (*Uprava RS za jedrsko varnost*) |
| SRPA | Slovenian Radiation Protection Administration *(Uprava RS za varstvo pred sevanji)* |
| TEDE | Total Effective Dose Equivalent |
| TPP | Thermal Power Plant |
| TENORM | Technologically Enhanced Naturally Occurring Radioactive Material |
| UNSCEAR | United Nations Scientific Committee on Effects of Atomic Radiation |
| WHO | World Health Organization |
| ZVISJV | Act on Protection against Ionising Radiation and Nuclear Safety (*Zakon o varstvu pred ionizirajočimi sevanji in jedrski varnosti*) |
| ZVD | Institute of Occupational Safety (*Zavod za varstvo pri delu)* |

## QUANTITIES, UNITS, AND DEFINITIONS

**Absorbed dose (*D*)** Energy imparted by ionizing radiation per unit mass of irradiated material. The unit is $J\ kg^{-1}$, termed the gray (*Gy*).

**Activity (*A*)** The quantity *A* for an amount of *radionuclide* in a given energy state at a given time, defined as: $A(t) = dN / dt$
where $dN$ is the expectation value of the number of spontaneous nuclear transformations from the given energy state in the time interval $dt$. The SI unit of activity is the reciprocal second ($s^{-1}$), termed the becquerel (*Bq*).

**Critical group** A group of members of the public which is reasonably homogeneous with respect to its exposure for a given radiation source and given exposure pathway and is typical of individuals receiving the highest effective dose or equivalent dose (as applicable) by the given exposure pathway from the given source.

**Decontamination** The complete or partial removal of *contamination* by a deliberate physical, chemical or biological process.

**Dose** A measure of the energy deposited by radiation in a target. Absorbed dose, committed equivalent dose, committed effective dose, effective dose, equivalent dose or organ dose, depending on the context. All these quantities have the dimensions of energy divided by mass.

**Dose rate** The quantity of radiation absorbed per unit time. The ionizing radiation dose delivered per unit time. The unit of the dose rate is sievert per hour ($Sv\ h^{-1}$) or gray per hour ($Gy\ h^{-1}$).

**Effective dose (*E*)** A summation of the tissue *equivalent dose*s, each multiplied by the appropriate tissue weighting factor: $E = \sum_T w_T H_T$

where $H_T$ is the *equivalent dose* in tissue $T$ and $w_T$ is the tissue weighting factor for tissue $T$. From the definition of *equivalent dose*. The unit of effective dose is $J\ kg^{-1}$, with the special name sievert (*Sv*).

**Equivalent dose ($H_T$)** The equivalent dose is defined as:
$H_{T,R} = w_R\ D_{T,R}$
where $D_{T,R}$ is the *absorbed dose* delivered by radiation type $R$ averaged over a tissue or organ $T$ and $w_R$ is the radiation weighting factor for radiation type $R$. The unit of effective dose is $J\ kg^{-1}$, with the special name sievert (*Sv*).

**Exposure (*X*)** The act or condition of being subject to irradiation. Exposure can either be external exposure due to sources outside the body or internal exposure due to sources inside the body.

**Exposure pathway** A route by which radiation or radionuclides can reach humans and cause exposure. An exposure pathway may be very simple, for example external exposure from airborne radionuclides, or involve a more complex chain, for example internal exposure from drinking milk from cows that ate grass contaminated with deposited radionuclides.

**Half-life ($T_{1/2}$)** The time taken for the quantity of a specified material – a radionuclide – in a specified place to decrease by half as a result of any specified process or processes that follow similar exponential patterns to radioactive decay.

**Specific activity** The specific activity of a radionuclide is the activity per unit mass of that nuclide. The specific activity of a material is the activity per unit mass or volume of the material in which the radionuclides are essentially uniformly distributed. The unit is $Bq\ kg^{-1}$ or $Bq\ m^{-3}$.

**Secular equilibrium** The state of a radioactive decay chain (or part thereof) where the activity of each radionuclide in the chain (or part of the chain) is the same. This state is achieved when the parent nuclide has a much longer half-life than any of the progeny, and after a time equal to several times the half-life of the longest lived of the progeny.

# 1 INTRODUCTION

A radionuclide is a nuclear species with an unstable nucleus. There are over 1,500 different radioactive nuclides. Radionuclides are usually symbolised based on the element (atomic number) and on the atomic mass number, as in the case of radioactive hydrogen or tritium with an atomic weight of 3 is shown as $^{3}H$ or H-3. As another example, uranium with the atomic mass number of 235 would be shortened to U-235 or $^{235}U$. A radionuclide undergoes radioactive decay by emitting alfa, beta or/and gamma rays or their different modes of decay or undergoing internal conversion, hence becoming daughter nuclides.

Radionuclides are found naturally in air, water and soil. They are also found in human beings, given that we are the products of our environment. Everyday, we ingest and inhale radionuclides in our air, food and water. Natural radioactivity is common in the rocks and soil that make up our planet, in water and the oceans, and in our building materials and homes. There is nowhere on Earth where you cannot find natural radioactivity.

TENORM is known generally as technologically enhanced naturally occurring radioactive material. Before 1998, the term used for these materials was “Naturally Occurring Radioactive Materials” (“NORM”). The Committee on Evaluation of EPA Guidelines for Exposure to Naturally Occurring Radioactive Materials, National Research Council (NRC) of the National Academy of Sciences (NAS) and National Academy of Engineering, defines TENORM in its report as “*any naturally occurring material not subject to regulation under the Atomic Energy Act whose radionuclide concentrations or potential for human exposure have been increased above levels encountered in the natural state by human activities”* (NRC, 1999). The acronym “TENORM” is used throughout this thesis and is used in plural form. In general terms, TENORM are materials containing radionuclides that are present naturally in rocks, soils, water, and minerals, and that have become concentrated and/or exposed to the accessible environment as a result of human activities such as manufacturing, water treatment, or mining operations. Many TENORM contain only trace amounts of radioactivity and are part of our everyday landscape. Some TENORM, however, contain very high contents of radionuclides that can produce harmful exposure levels. TENORM are found in a wide variety of waste materials, some raw mineral ores, and in trace amounts in some consumer products where radionuclides may be bound to specific minerals used in the manufacturing process (zircon, for example, contains minute quantities of uranium and thorium and is used widely as a glaze for ceramics and metal moulds). Uranium, thorium and actinium radionuclides and their daughter products are also commonly found in TENORM. TENORM, because of human activity, may present a radiation hazard to people and the environment. Humans are exposed to radiation from external sources and by internal radiation from radionuclides incorporated into the body. The main routes of radionuclide intake are ingestion of food and water and inhalation. A particular category of exposure to internal radiation, in which the bronchial epithelium is irradiated by α particles from the short-lived progeny of radon, constitutes the major fraction of the human exposure from natural sources.

The European Commission (EC) report called Investigation of a possible basis for a common approach with regard to the restoration of areas affected by lasting radiation exposure as a result of past or old practice or work activity CARE (EC, 1999) subdivides sources of anthropogenic TENORM from industrial activities into three groups:

a) Past controlled practices:
   - uranium mining and milling (e.g., the former Uranium Mine and Mill at Žirovski vrh).

b) Practices not under radiological control:
   - metal mining and smelting (e.g., Acroni Jesenice, Metal Ravne);
   - phosphate industry (e.g., TKI Hrastnik);
   - coal mining and power generation from coal (e.g., the former Kočevje Coal Mine, …);
   - oil and gas drilling (Nafta Lendava ex-refinery);
   - rare earth and titanium oxide industry (e.g. Cinkarna Celje);
   - zirconium and ceramics industry (e.g., in Celje);
   - extraction or use of water in industrial processes (e.g., geothermal water, drinking water, waste water)
   - disposal of building materials.

c) Practices which would now be under control:
- applications of the natural radionuclides radium and thorium.

Sites where minerals and materials (e.g. those made by extraction, processing or in manufacturing industries with the potential for radioactive contamination) are present which are not radioactively contaminated, should be considered as potentially contaminated, and should be treated as a potential environmental hazard (EPA, 2003). The same should be valid for sites where TENORM are deposited, unless it is proven that radiation emitted to the surroundings is higher than that permitted by law.

TENORM represent one source of ionising radiation impacting the population. Because of that, the Government of the Republic of Slovenia and other institutions are preparing new regulations for the field of radioactivity and for controlling radiation exposures of the public, to specific sources or practices (e.g. discharge to the environment, International Atomic Energy Agency (IAEA) – basic safety standards, European Union basic safety standards …). Slovenia has a law, termed the Act on Protection against Ionising Radiation and Nuclear Safety (Zakon o varstvu pred ionizirajočimi sevanji in jedrski varnosti – ZVISJV) (Off. Gaz RS, No. 102/2004). Slovenian research institutes have already made some analysis of TENORM. Measurements were performed in the area of the Žirovski vrh Uranium Mine, Slovenian thermal power plants (e.g., Šoštanj, Trbovlje, Ljubljana), the Kočevje Coal Mine, the Mercury Mine Idrija, Cinkarna Celje (production of $TiO_2$), the Kanižarica Coal Mine, the Hrastnik Phosphate industry (so-called TKI Hrastnik), Talum Kidričevo, Nafta Lendava, the iron and steel industry in Jesenice and Ravne na Koroškem, the Vremski Britof Coal Mine, and in industry which uses zirconium minerals (EMO Kemija in Celje, Martex in Šmartno ob Paki, Gorenje Keramika in Velenje). Holistic studies investigating what the real effects of TENORM are, have not yet been made. Knowledge of the influence of TENORM on people and on the environment is needed.

This thesis presents information about the existence of TENORM in Slovenia, based on historical data on mining and other industrial activities in past centuries (18. – 20. Century) and based on studies that have already been made by Slovenian research institutes. Slovenian results from such measurements are compared to results from other countries. The study summarizes sources of TENORM in Slovenia, divided into different activities, and a previous estimation of the influence of TENORM on people's health and on the environment.

# 2 AIMS OF THE THESIS

The objective of this thesis is to make an inventory of TENORM in Slovenia. Experimental studies, research reports made by different research institutions in Slovenia, results published in scientific publications and other media, and historical information on past industrial activities in Slovenia were basis for inventorying, surveying and evaluating available data. Collected data are in forms as they were available (e.g., as dose rate, specific activities, effective dose, and concentration). Based on these data average annual doses, that may be received by the population, were be calculated. Inventory includes information about existence of TENORM in Slovenia, results of measurements that were already made, compared to results from other countries studies. The thesis presents sources of TENORM in Slovenia divided on different industrial activities and makes draft assessment of impact to human health and to the environment.

# 3 LEGISLATION

## 3.1 EU legislation – Council Directive 96/29/EURATOM

EU legislation treats the issue of natural sources of radiation in the EU Basic Safety Standard (Council Directive No. 96/29/EURATOM) and states:

- that the directive applies to activities, which can increase exposure to ionizing radiation because of artificial sources or natural sources of radiation with natural radionuclides, processed because of their radioactive decay or fertile properties,
- that the directive covers work activities involving the presence of natural radiation sources, which may cause a significant increase in the exposure of the population and workers', which is not negligible from the radiological aspect,
- that every EU member must on it's own initiative identify work activities with materials and storage of materials which contain natural radionuclides, that could cause an increased exposure of workers or of the population, and those working activities which produce residues of these activities that can significantly increase the exposure of the population and of workers due to the presence of natural radionuclides.

In the case an EU member identifies a potentially problematic work activity, they must implement monitoring the exposure and use intervention measures to decrease this exposure. To implement this directive Slovenia adopted Regulation on radioactivity monitoring (Off. Gaz. RS, 20/2007).

Specific work activities are not covered by the Directive, if the activities or concentrations of them relevant radionuclides do not exceed the limits set in columns 2 and 3 given in Table 8, or the individual limits of the EU members, set by the proper authority and that are within those laid down in the Council Directive 96/29/EURATOM.

Mining, mineral processing and extraction industries can be placed under radiological supervision, if the competent authority so orders. The limits laid down allow exceptions only if the concentration or the complete activity of a certain radionuclide (together with its descendants) does not exceed the limits set. That means that materials such as, for example, 1 kg of phosphogypsum or 2.5 kg of phosphatic fertilizer or 11 kg of granite, because of their total activity, can easily exceed the limits implemented by the Council Directive 96/29/EURATOM.

## 3.2 Slovenian legislation

### 3.2.1 Act on Radiation Protection and Nuclear Safety (Zakon o varstvu pred ionizirajočimi sevanji in jedrski varnosti)

The Act on Protection against Ionising Radiation and Nuclear Safety (Off. Gaz. RS, No. 102/2004) regulates ionising radiation protection with the aim of reducing the detrimental effects on human health and reducing to the lowest possible level radioactive contamination of the living environment resulting from the use of sources of ionising radiation, while at the same time enabling the development, production and use of radiation sources and employing radiation practices. With regard to radiation sources intended for producing nuclear energy, this act regulates the implementation of nuclear safety measures and also, in the case of the use of nuclear materials, special protection measures.

Articles 45 and 46 concern exposure due to the presence of natural radiation sources or precisely about systematic surveillance of the living and working environment and about measures to reduce the exposure of workers and members of the public.

As defined in Article 45 of this Act, the ministry competent for health shall ensure protection against increased exposure of workers and members of the public to radiation resulting from

natural radiation sources by systematic surveillance of the living and working environment. Such protection shall be ensured:
- where workers or members of the public are exposed to radon or thoron progeny, gamma radiation or any other exposure resulting from natural radiation sources in the living and working environments, such as for example spas, caves, mines, underground locations and in certain areas on the surface,
- where materials or waste, which are usually not considered radioactive but do contain naturally present radio-nuclides, accumulate or are stored or disposed,
- during air transport.

This article also states that the government shall adopt a programme of systematic surveillance of the living and working environments, and of raising awareness among the population on the importance of measures for the reduction of the presence of natural radiation sources.

Article 46 states that, if on the basis of the systematic surveillance referred in Article 45, it is established that the exposure of individuals due to natural radiation sources exceeds dose limits for members of the public, the ministry competent for health shall order the employer or operator of the facility and devices in question to implement measures for reducing the exposure of workers and members of the public, as well as measures for the protection of exposed workers within the scope of and in a way applying to persons carrying out radiation practices.

Article 90 states that the minister competent for the environment and the minister competent for health and, in the case of foodstuffs and feedstuffs, also the minister competent for agriculture and the veterinary service, shall determine the plan of emergency monitoring in cases of increased radioactive contamination of the air, drinking water, water, ground, foodstuffs, feedstuffs or individual products or materials, as well as the method to be used for reporting and informing the public.

Article 123 determines that the ministry competent for the environment, air, water and the ground, as well as for some products; the ministry competent for health, foodstuffs and drinking water, and the ministry competent for agriculture and feedstuffs shall ensure the monitoring of radioactivity in the environment. On the basis of the results such monitoring of radioactivity in the environment shall be established trends of population exposure due to radioactivity of the environment; the provision of data needed for prompt action in the case of a sudden increase of radioactivity in the environment shall be ensured, and an evaluation of the doses received by the population shall be drawn up. The article defines that the monitoring of radioactivity in the environment shall include permanent and occasional measurements of:
- open air radioactivity levels,
- external gamma radiation,
- the presence of radionuclides in surface waters and subterranean waters,
- radioactivity of the ground and of precipitation, and
- radioactivity of feedstuffs, drinking water, foodstuffs and individual products.

In 2004 the adoption of implementing regulations expedited the enforcement of the Act and the following regulations and decrees were issued:
- Regulation on health surveillance of exposed workers (Pravilnik o izvajanju zdravstvenega nadzora izpostavljenih delavcev) (Off. Gaz. RS, 2/2004),
- Regulation on the obligations of the persons carrying out radiation practices and persons possessing ionizing radiation sources (Pravilnik o obveznostih izvajalca sevalne dejavnosti in imetnika vira ionizirajočih sevanj) (Off. Gaz. RS, 13/2004),
- Regulation on empowerment of experts performing professional tasks in the field of ionising radiation (Pravilnik o pooblaščanju izvajalcev strokovnih nalog s področja ionizirajočih sevanj) (Off. Gaz. RS, 18/2004),
- Regulation on the method of keeping records of personal doses due to exposure to ionizing radiation (Pravilnik o načinu vodenja evidenc o osebnih dozah zaradi izpostavljenosti ionizirajočim sevanjem) (Off. Gaz. RS, 33/2004),

- Decree on areas of spatial limitations due to a nuclear facility and the conditions of facility construction in these areas (Uredba o območjih omejene rabe prostora zaradi jedrskega objekta in o pogojih gradnje objektov na the območjih) (Off. Gaz. RS, 36/2004),
- Decree on radiation practices (Uredba o sevalnih dejavnostih) (Off. Gaz. RS, 48/2004, 9/2006),
- Decree on dose limits, radioactive contamination and intervention levels (Uredba o mejnih dozah, radioaktivni kontaminaciji in intervencijskih nivojih) (Off. Gaz. RS, 49/2004),
- Regulation on inputs from and outputs into EU member states and on import and export of radioactive waste (Pravilnik o vnosu in iznosu v države članice Evropske unije ter uvozu in izvozu radioaktivnih odpadkov) (Off. Gaz. RS, 60/2004),
- Regulation on the use of potassium iodide (Pravilnik o uporabi tablet kalijevega jodida) (Off. Gaz. RS, 142/2004).

Several other decrees and regulations (15) were in the process of preparation and harmonization from the year 2004. Some of them are shortly presented in next subchapters.

### 3.2.2 Decree on Radiation Practices (Uredba o sevalnih dejavnostih)

The Official Gazette of the Republic of Slovenia, No. 48/2004 and 9/2006 lays down a Decree on Radiation Practices and in article 3 and annex 1 discusses technologically enhanced naturally occurring radioactivity. In this decree there are also set out exemption levels (Table 3.1), and regulatory control of source materials exceeding the exemption levels (reporting, licensing).

***Table 3.1: Set exemption values – concentration of activity for selected radionuclides (Decree on Radiation Practices. Off. Gaz. RS, No. 48/2004, 9/2006).***

| Radionuclide | Quantity (Bq) | Concentration (Bq $g^{-1}$) |
|---|---|---|
| $^{226}Ra^{+}$ | 10,000 | 10 |
| $^{228}Ra^{+}$ | 100,000 | 10 |
| $^{228}Th^{+}$ | 10,000 | 1 |
| $^{232}Th^{sec}$ | 1,000 | 1 |
| $^{238}U^{+}$ | 10,000 | 10 |
| $^{238}U^{sec}$ | 1,000 | 1 |

Nuclides carrying the suffix '+' or 'sec' in Table 3.1 represent parent nuclides in equilibrium with their correspondent daughter nuclides as listed in Table 3.2. In this case the values given in Table 3.1 refer to the parent nuclide alone, but already take account the daughter nuclide(s) present.

***Table 3.2: List of nuclides in secular equilibrium as referred to in legend of Table 3.1 (Decree on Radiation Practices, Off. Gaz. RS, No. 48/2004, 9/2006).***

| Parent radionuclide | Daughter radionuclide |
|---|---|
| $^{226}Ra^{+}$ | $^{222}Rn$, $^{218}Po$, $^{214}Pb$, $^{214}Bi$, $^{214}Po$, $^{210}Pb$, $^{210}Bi$, $^{210}Po$ |
| $^{228}Ra^{+}$ | $^{228}Ac$ |
| $^{228}Th^{+}$ | $^{224}Ra$, $^{220}Rn$, $^{216}Po$, $^{212}Pb$, $^{212}Bi$, $^{208}Tl$, $^{212}Po$ |
| $^{232}Th^{sec}$ | $^{228}Ra$, $^{228}Ac$, $^{228}Th$, $^{224}Ra$, $^{220}Rn$, $^{216}Po$, $^{212}Pb$, $^{212}Bi$, $^{208}Tl$, $^{212}Po$ |
| $^{238}U^{+}$ | $^{234}Th$, $^{234m}Pa$ |
| $^{238}U^{sec}$ | $^{234}Th$, $^{234m}Pa$, $^{234}U$, $^{230}Th$, $^{226}Ra$, $^{222}Rn$, $^{218}Po$, $^{214}Pb$, $^{214}Bi$, $^{214}Po$, $^{210}Pb$, $^{210}Bi$, $^{210}Po$ |

### 3.2.3 Decree on dose limits, radioactive contamination and intervention levels (Uredba o mejnih dozah, radioaktivni kontaminaciji in intervencijskih nivojih)

The Decree on dose limits, radioactive contamination and intervention levels (Off. Gaz. RS, No. 49/2004) in articles 22, 23 and 32 considers naturally occurring radioactivity, which is enhanced technologically. The Decree also considers indoor radon, building materials and contamination.

# 4 RADIOACTIVITY IN THE ENVIRONMENT

Naturally occurring radionuclides of terrestrial origin (also called the primordial radionuclides) are present in various degrees in all media in the environment, including the human body itself. Only those radionuclides with half-lives comparable to the age of the earth, and their decay products, exist in significant quantities in these materials. Irradiation of the human body from external sources is mainly a result of gamma radiation from radionuclides in the $^{238}$U and $^{232}$Th series and from $^{40}$K. These radionuclides are also present in the body and irradiate the various organs with alpha and beta particles, as well as gamma rays.

Natural radioactivity or background radioactivity is the activity of naturally occurring radionuclides that are present under ambient conditions in the environment which are in no way influenced by human activity. Natural radioactivity in the environment can vary over a range of concentrations and exposure rates from a variety of causes. The magnitude of variation can be significant over a short distance and can vary in the same place from time to time. The background variation can be a result of natural causes as well as human activities. Understanding the characteristics of background, radiation and the wide range of background values encountered in the field is beneficial when designing and conducting surveys. Variations due to geology, chemical and physical mobility and deposition, temporal, and human effects should all be considered.

Worldwide, we can find areas of high natural background. There are various causes of these elevated exposure levels. Some result from monazite sand deposits, which have high levels of thorium, including Guarapari in Brazil, Yangiang in China, the states of Kerala and Madras in India, and the Nile delta in Egypt. Some result from volcanic soils such as Mineas Gerais in Brazil, Niue Island in the Pacific, and parts of Italy. The Central Massif in France has granitic and schistic rocks and sands, and an area in the southwest of that country is mainly associated with uranium minerals in soil. The areas of Ramsar and Mahallat in Iran are influenced by $^{226}$Ra deposited from waters flowing from hot springs. It should be noted that exposures in high background areas can vary in time as deposits or springs and tides replenish beach sands. Road construction and urbanization of these areas have led to moderate decreases in the background levels (United Nations Scientific Committee on Effects of Atomic Radiation, UNSCEAR, 2000).

In Slovenia, higher natural backgrounds are a result of higher uranium concentrations in native ore/soil and a result of deposited TENORM. Outdoor concentrations of radon in the populated part of the valley below the Žirovski vrh Uranium Mine reach up to 40 – 60 Bq m$^{-3}$ under stable meteorological conditions, and 10 – 15 Bq m$^{-3}$ in disturbed ones (Brajnik et al., 1988). Some areas in Slovenia, mainly in the Dinaric region, could be classified as radon prone areas (Križman et al., 1996a). Higher concentrations of radon were measured in Kočevje, whit an annual average of 30 – 68 Bq m$^{-3}$, with daily peaks above 100 Bq m$^{-3}$ (Jovanović and Konda, 2001). The annual average radon concentration in the Idrija valley is nearly 30 Bq m$^{-3}$, with maximal outdoor radon concentrations (estimated via $^{218}$Po) reaching up to 100 Bq m$^{-3}$ (Križman et al., 1996c). In the last three cases, increased concentrations are also the result of uranium and coal mining, and result of enhanced natural radioactivity in the environment. Emission of radon in the range of 20 – 200 Bq m$^{-3}$ was estimated near Trbovlje (above the tailings) in controlled stable weather conditions (Brajnik et al., 1988). Cinnabarite ore in Idrija has a high uranium content, with an average of more than 100 mg kg$^{-1}$ (40 – 400 mg kg$^{-1}$) (Križman et al., 1996c). The average uranium concentration in the Žirovski vrh Uranium Mine ore was about 715 grams per ton of ore (Rojc and Jovanović, 2005). The measurements show that the uranium contents in soil in Slovenia ranges from 0.11 to 16.79 µg g$^{-1}$, an average of 3.3 µg g$^{-1}$ (41 Bq kg$^{-1}$). Raised levels of uranium in soil are still found on Pohorje and are mostly found in the Idrija – Škofja Loka area, which is rich with cases of uranium mineralization, and in Dinaridi in the area of carbonated rock, characteristic of the Karstic relief (Andjelov, 1993). Thorium appears in soil in ranges of 0.31–21.86 µg g$^{-1}$, an average of 8.47 µg g$^{-1}$ (35 Bq kg$^{-1}$). The highest levels are found in the northeast part of the Dinaridi, in the Idrija–Škofja Loka area and in Pohorje (Andjelov, 1993).

## 4.1 Sources of radioactivity

According to NCRP (National Council on Radiation Protection and Measurements) from 1994, four major components constitute "background sources" of radiation:

- cosmic,
- cosmogenic,
- terrestrial (most TENORM are associated with terrestrial sources, but other types may interfere in measuring levels of TENORM),
- man-made.

### 4.1.1 Cosmic radiation

This type of background refers to both the primary energetic particles of extraterrestrial origin that strike the Earth's atmosphere and to the secondary particles generated by their interaction with the atmosphere. Primary radiation itself consists of two components, designated as galactic or solar depending on origin. The primary energetic particles or galactic energetic charged particles that originate in outer space and impinge isotropically on the top of the Earth's atmosphere are mostly protons (87 %), alpha particles (11 %), nuclei of elements of atomic number 4 – 26 (about 1 %), and electrons (about 1 %). Their energy extends up to about $10^{20}$eV (EC, 2004). The interactions of the primary particles with atmospheric nuclei produce electrons, gamma rays, neutrons, pions and muons. At sea level, muons account for about 80 % of the cosmic-radiation charged-particle flux, and electrons account for about 20 %; or in other words, galactic energetic charged particles interact with the atmosphere producing secondary radiation, which together with the primary incident particles give rise to radiation exposure throughout the atmosphere, decreasing in intensity with depth from the altitude of supersonic aircraft down to sea level (EC, 2004). The dose from galactic energetic charged particles varies not only with altitude but also with the geomagnetic coordinates (longitude and latitude) being larger towards the poles and smaller near the equator. It also depends on the solar activity, which varies according to a cycle of about 11 years. Solar energetic charged particles are produced by sudden, sporadic releases of energy in the solar atmosphere and by coronal mass ejections.

### 4.1.2 Cosmogenic radiation

Cosmogenic radionuclides arise from the collision of highly energetic cosmic ray particles with stable elements in the atmosphere and in the ground. The entire geosphere, the atmosphere, and all parts on the Earth that directly exchange matter with the atmosphere contain cosmogenic radionuclides. The major production of cosmogenic radionuclides (Table 4.1) results from the interaction of cosmic rays with atmospheric gases. The outermost layer of the Earth's crust is another area where reactions with cosmic rays occur. However, the rate at which they occur is several times smaller than the atmospheric component because most of the cosmic rays are attenuated in the atmosphere. The result is that the contribution to background dose is minimal. The most important radionuclide produced is $^{14}$C. However, many others, such as $^{3}$H, $^{22}$Na, and $^{7}$Be, occur.

***Table 4.1: Some common cosmogenic nuclides.***

| Nuclide | Symbol | Half-life |
|---|---|---|
| Carbon-14 | $^{14}$C | 5730 a |
| Tritium-3 | $^{3}$H | 12.3 a |
| Beryllium-7 | $^{7}$Be | 53.28 d |
| Beryllium-10 | $^{10}$Be | 1.51 $10^{6}$ a |
| Sodium-22 | $^{22}$Na | 2.6 a |
| Aluminium-26 | $^{26}$Al | 7.4 $10^{5}$ a |
| Silicon-32 | $^{32}$Si | 172 a |

Continued …

**Table *4.1*: *Continuation.***

| Nuclide | Symbol | Half-life |
|---|---|---|
| Phosphorus-32 | $^{32}P$ | 14.26 d |
| Phosphorus-33 | $^{33}P$ | 25.34 d |
| Sulphur-35 | $^{35}S$ | 87.51 d |
| Chlorine-36 | $^{36}Cl$ | $3.01\ 10^5$ a |
| Argon-37 | $^{37}Ar$ | 35.04 d |
| Argon-39 | $^{39}Ar$ | 269 a |
| Krypton-81 | $^{81}Kr$ | $2.29\ 10^5$ a |

It is clear that the cosmogenic radionuclides produced in the stratosphere with half-lives short compared with the stratospheric residence time are likely to decay in the stratosphere and do not have a significant effect at the Earth's surface.

### 4.1.3 Terrestrial radiation

Terrestrial radionuclides fall into two groups:
- those that occur singly (non-series nuclides) and decay directly to a stable nuclide, and
- those that occur in decay chains (series nuclides) and decay to a stable isotope of lead through a sequence of radionuclides of wide-ranging half-lives.

Primordial radionuclides are also terrestrial radionuclides and are remain from the approach when the world and the universe were created. They are typically long lived, with half-lives often on the order of hundreds of millions of years (Table 4.2). Some other primordial radionuclides are $^{50}V$, $^{87}Rb$, $^{113}Cd$, $^{115}In$, $^{123}Te$, $^{138}La$, $^{142}Ce$, $^{144}Nd$, $^{147}Sm$, $^{152}Gd$, $^{174}Hf$, $^{176}Lu$, $^{187}Re$, $^{190}Pt$, $^{192}Pt$, $^{209}Bi$ and $^{222}Rn$.

***Table 4.2: Content of primordial radionuclide in soil.***

| Radionuclide | Symbol | Half-life | Concentration in soil (UNSCEAR, 2000) |
|---|---|---|---|
| Uranium-235 | $^{235}U$ | $7.04 \times 10^8$ a | / |
| Uranium-238 | $^{238}U$ | $4.47 \times 10^9$ a | 16 – 110 Bq $kg^{-1}$ |
| Thorium-232 | $^{232}Th$ | $1.41 \times 10^{10}$ a | 11 – 64 Bq $kg^{-1}$ |
| Radium-226 | $^{226}Ra$ | $1.60 \times 10^3$ a | 17 – 60 Bq $kg^{-1}$ |
| Potassium-40 | $^{40}K$ | $1.28 \times 10^9$ a | 140 – 850 Bq $kg^{-1}$ |

a) Non-Series Radionuclides

Non-series radionuclides that contribute to the background dose are listed in Table 4.3. $^{40}K$ emits beta particles (89 % – mass percentage) and gamma particles (11 % – mass percentage) and contributes to both internal and external doses. Natural potassium contains 0.0117 % $^{40}K$ (UNSCEAR, 2000). Its contribution to external dose is variable, depending on its concentration in rocks and soil. Its average concentration is about 600 Bq $kg^{-1}$ in crustal rock. Rubidium–87 is a pure beta emitter and is found in crustal rocks in concentrations of about 70 Bq $kg^{-1}$. It is not an external hazard and is rarely considered in dose calculations.

***Table 4.3: Principal natural radionuclide decay series – non-series radionuclides.***

| Radionuclide | Half-Life | Major Radiations |
|---|---|---|
| Potassium–40 | $1.28 \times 10^9$ years | beta, gamma |
| Argon–40 | stable | none |
| Calcium–40 | stable | none |
| Rubidium–87 | $4.9 \times 10^{10}$ years | beta |
| Strontium–87 | stable | none |

The remainder of the non-series radionuclides have combinations of half-lives, isotopic abundances, and elemental abundances such that they have negligibly small specific activities and are not significant in background calculations. Potassium–40 is found particularly in building materials (bricks, cinder blocks). Potassium is metabolically regulated by the body and its levels is not controlled by intake.

b) Series Radionuclides

There are three naturally occurring decay series, headed by the radionuclides $^{238}U$, $^{235}U$, and $^{232}Th$. These series are commonly called the uranium, actinium and thorium chains. Each radioactive chain includes α, β and γ active radionuclides with half-lives varying from small fractions of a second to thousands of years. In Figure 4.1, Figure 4.2 and Figure 4.3 are listed decay products of the uranium, thorium and actinium chains and their half-lives. Generally, the actinium chain does not play a significant role in industrial TENORM due to its very low abundance – in the Earth's crust, $^{235}U$ constitutes 0.72 % of uranium by mass (EPA, 1999). Some other terrestrial radionuclides such as $^{87}Rb$, $^{138}La$, $^{147}Sm$, $^{176}Lu$, and including those of the $^{235}U$ series, exist in nature but at such low levels that their contributions to the dose in humans are small (UNSCEAR, 2000).

If not subjected to chemical or physical separation, each of these series attains a state of secular radioactive equilibrium. TENORM as well as natural physical and chemical reactions often interfere with this balance. Crustal concentrations of $^{238}U$, $^{235}U$, and $^{232}Th$ are extremely small (parts per million); the short-lived decay progeny are present in such exceedingly minute concentrations that their behaviour does not always follow chemical (mass action) rules.

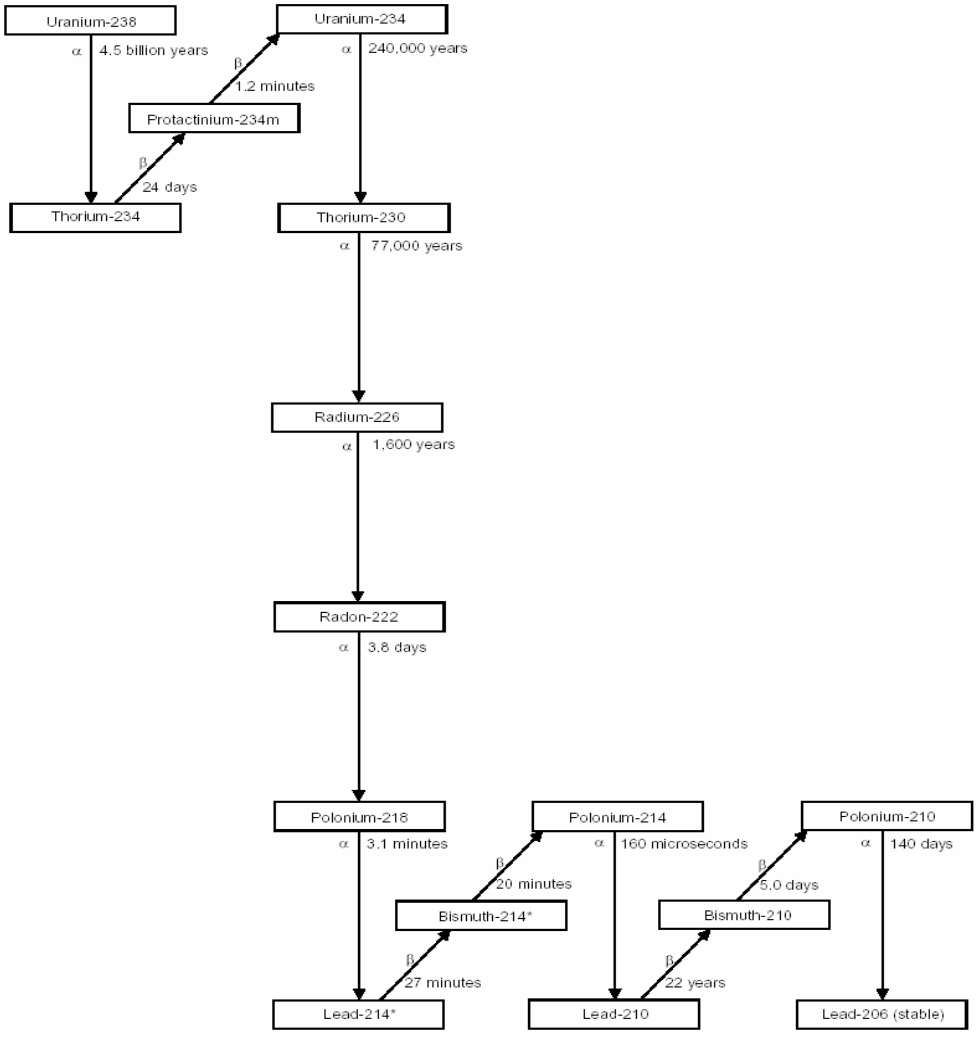


***Figure 4.1: Uranium decay series – $^{238}U$ series (Natural Decay Series, 2005).***

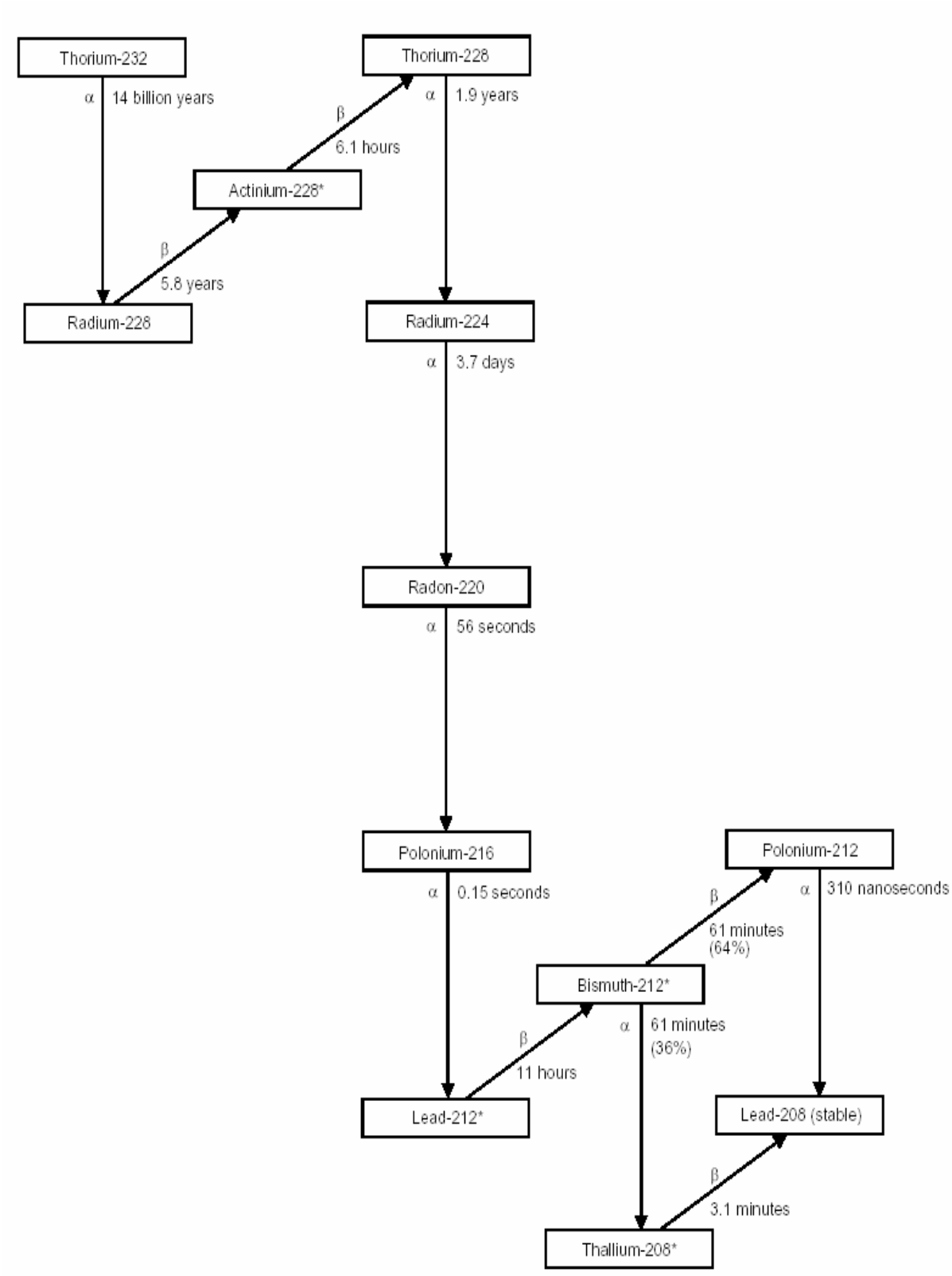


**Figure 4.2: Thorium decay series – $^{232}$Th series *(Natural Decay Series, 2005).***

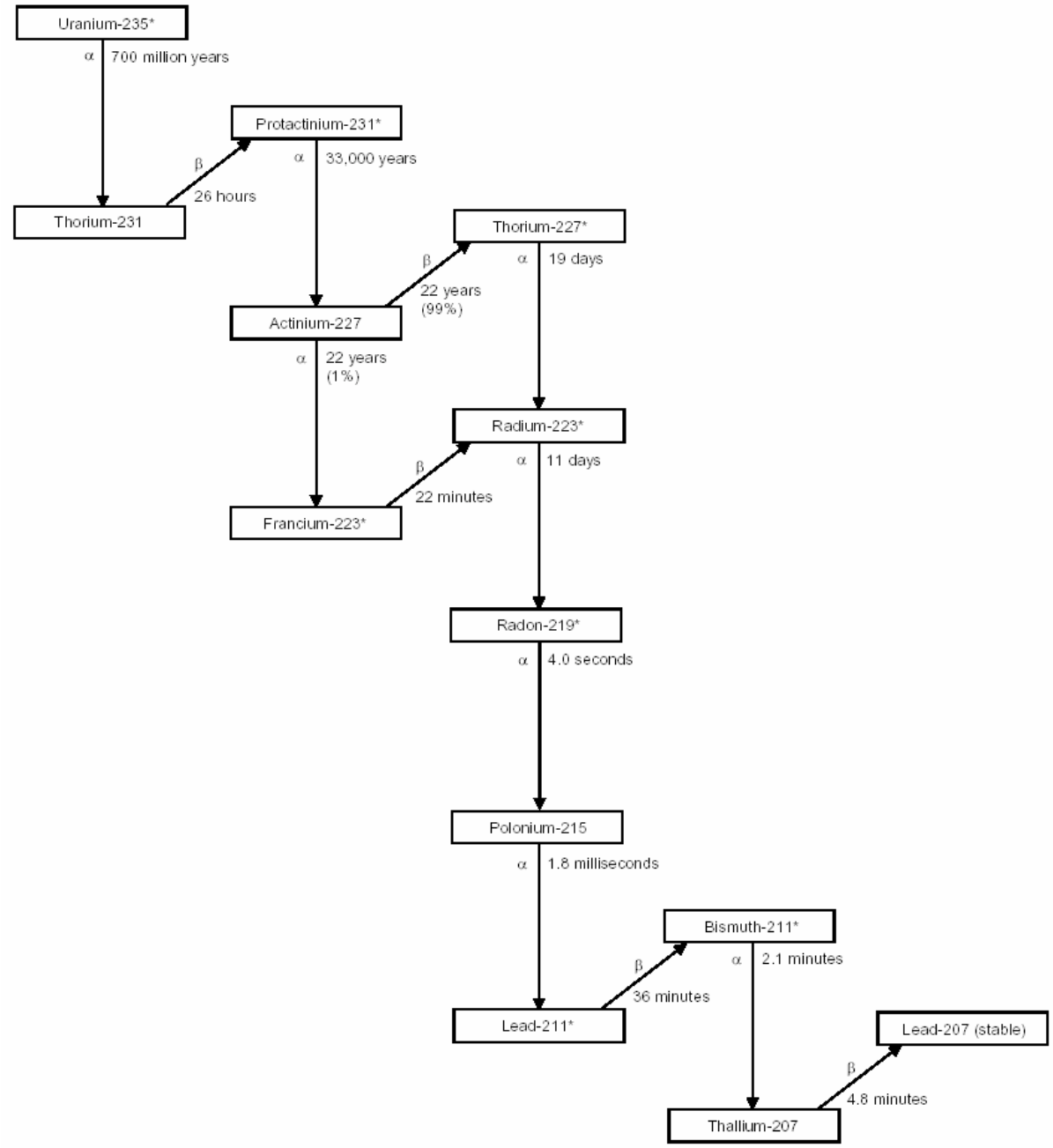


**Figure 4.3: Actinium decay series – $^{235}$U series *(Natural Decay Series, 2005).***

### 4.1.4 Man-made sources of radioactivity

Activities that have contributed and still contribute to the dispersion of radionuclides in the environment are:

- production processes (e.g., radioisotope production and use, research reactors)
- releases under normal operations (e.g., nuclear reactors; nuclear reprocessing or fuel reprocessing to recover uranium and plutonium from spent fuel for reuse in reactors; disposal of radwaste; hospitals, industry and research)
- accidental releases (e.g., reactor accidents (Chernobyl), waste repositories, lost submarines, lost nuclear weapons and radiation sources, satellites)
- nuclear explosions (e.g., Hiroshima and Nagasaki; military test explosions; civilian nuclear explosions)

Most anthropogenic radionuclides are short-lived, but some have half-lives of many years (Table 4.2).

***Table 4.2: Examples of anthropogenic radionuclides with short and long half-lives.***

| Radionuclides | Half-life |
|---|---|
| Long lived radionuclides | |
| $^{137}$Cs | 30 a |
| $^{90}$Sr | 28.1 a |
| $^{85}$Kr | 10.73 a |
| Short lived radionuclides | |
| $^{67}$Ga | 78.3 h |
| $^{201}$Tl | 73.1 h |
| $^{123}$I | 13.2 h |
| $^{99m}$Tc | 6 h |

The discharges from nuclear reactors to the atmosphere mostly consist of noble gases (Table 4.3). All these radionuclides are short-lived except $^{85}$Kr with half live of 10.8 years and they are not of radioecological interest, the main route of intake being inhalation and external radiation from the clouds. During the operation of nuclear reactors, several fission noble gases are released, as is the activation radionuclide $^{41}$Ar. Among the more prominent fission noble gases are $^{133}$Xe (but short-lived radionuclides such $^{135}$Xe are also present) from pressurized water reactors (e.g., in Slovenia the Krško Nuclear Power Plant) and $^{85}$Kr, $^{87}$Kr, $^{88}$Kr, $^{133}$Xe, $^{135m}$Xe, $^{135}$Xe and $^{138}$Xe from boiling water reactors, while for other components release, e.g. $^{14}$C or $^{131}$I, there may be no inherent differences between reactor types (UNSCEAR, 2000). Much of the dose from these (and other) radionuclides is delivered by the pathway of cloud shine and immersion As most of the fission-product noble gases and the activation gas $^{41}$Ar are short-lived, attention has been focused on exposures to nearby residents. More interesting are releases of tritium and $^{14}$C, also because they may contribute to exposure of the population due to their biologically importance as internal irradiators when incorporated in an organism. Releases of tritium in airborne effluents from pressurized water reactors and boiling water reactors are identical; the distribution from gas cooled reactors is somewhat higher; the distribution from heavy water moderated reactors is much higher, reflecting the large amounts of tritium produced in the moderator of these reactors (UNSCEAR, 2000). $^{131}$I is radioecologically the most important fission product released with airborne effluents from nuclear reactors. The distribution of $^{131}$I releases in airborne effluents is quite wide; such releases are somewhat higher from boiling water reactors and heavy water moderated reactors than from pressurized water reactors (UNSCEAR, 2000). The dominant radionuclide in liquid effluents from nuclear reactors is tritium. Typical releases from reactors are $^{90}$Sr and $^{137}$Cs.

***Table 4.3: Noble gases released from reactors.***

| Radionuclide | Half-life |
|---|---|
| $^{41}$Ar | 1.827 h |
| $^{85m}$Kr | 4.48 h |
| $^{85}$Kr | 10.72 a |
| $^{87}$Kr | 76.3 m |
| $^{88}$Kr | 2.84 h |
| $^{131m}$Xe | 11.9 d |
| $^{133m}$Xe | 2.188 d |
| $^{133}$Xe | 5.245 d |
| $^{135}$Xe | 9.09 h |
| $^{138}$Xe | 14.17 m |

Hospitals are the main users of unsealed radionuclides outside the nuclear fuel cycle. Most of these radionuclides (e.g. $^{67}$Ga, $^{99m}$Tc, $^{123}$I and $^{210}$Tl) are fairly short-lived and thus of little environmental concern. Others, such as $^{3}$H, $^{14}$C, $^{32}$P, $^{35}$S and $^{131}$I may be detected in the effluents from hospitals. Research and educational institutions use primarily $^{3}$H, $^{14}$C, $^{32}$P and $^{35}$S and in industry $^{147}$Pm is applied in relatively large quantities. Beside these applications of

unsealed isotopes, there is also use of sealed sources e. g. $^{60}$Co, $^{137}$Cs, $^{226}$Ra and $^{241}$Am, which in case of accidents may contaminate the environment. The UNSCEAR report (UNSCEAR, 2000) revealed that the dominant contributors to the collective effective dose are $^{14}$C (90 % of the dose), $^{131}$I (9 % of the dose) and $^{3}$H (1.5 % of the dose). Seven hospitals or clinics in Slovenia use unsealed sources (radiopharmaceuticals) for diagnostics and therapy in nuclear medicine departments: the Ljubljana Medical Centre – the Department of Nuclear Medicine, the Institute of Oncology and general hospitals in Maribor, Celje, Izola, Slovenj Gradec and Šempeter near Gorica. In 2004, in the nuclear medicine departments for diagnostics and therapy applied 10,292 GBq of the radionuclide $^{99m}$Tc, 1,469 GBq of $^{131}$I, 300 GBq of $^{133}$Xe and minor activities of $^{67}$Ga, $^{111}$In, $^{18}$F, $^{90}$Y, $^{186}$Re, $^{51}$Cr, $^{125}$I, $^{123}$I, $^{153}$Sm and $^{87}$Sr (Slovenian Nuclear Safety Administration, SNSA, 2005). In 2005, these nuclear medicine departments applied 6,215 GBq of $^{99m}$Tc, 1,318 GBq of $^{131}$I, 217 GBq of $^{133}$Xe and minor activities of $^{67}$Ga, $^{111}$In, $^{18}$F, $^{90}$Y, $^{186}$Re, $^{51}$Cr, $^{125}$I, $^{123}$I, $^{153}$Sm and $^{89}$Sr for diagnostics and therapy (SNSA, 2006). Global usage of $^{131}$I in nuclear therapy is approximately 600 TBq (UNSCEAR, 2000). The Jožef Stefan Institute or the Institute of Occupational Safety inspects the nuclear medicine departments twice a year, and until now, no major deficiencies have been found.

## 4.2 Environmental behaviour of radionuclides

The environmental behaviour of deposited radionuclides depends on the physical and chemical characteristic of the radionuclides, path of deposition, size and shape of particles and the environment. When radionuclides are released to the environment, they are exposed to dispersion and transfer in the terrestrial and aquatic environment. The most active short lived radionuclides (e.g., $^{137}$Cs, $^{90}$Sr) also have more mobility in ecosystem and their radioactivity can be lost from the ecosystem by radioactive decay.

In the aquatic environment radionuclides are subjected to advection and dispersion, solubility, sorption and desorption, remobilisation from the sediments, resuspension … Some radionuclides have strong tendency to associate to the solid phase while other radionuclides enter solution and remain in a dissolved form. The transport is determined by chemical reactivity of the radionuclide, the biogeochemical properties of the receiving medium, and the physical processes that redistribute radionuclide and those that can contribute to its dispersion and dilution. The accumulation of radionuclides by aquatic organisms depends upon physical, chemical and biological factors. Radioactivity can be transferred from water bodies to man either directly via drinking water or swimming in the water or indirectly via fish or other aquatic organisms.

In terrestrial environment radionuclides are subjected to atmospheric dispersion and deposition (e.g., dry deposition, wet deposition – rainout and washout, occult deposition), resuspension processes, migration (in soil – advection, dispersion, adsorption; to water; in/to atmosphere), leaching and transfer to food chain (bioaccumulation). Radionuclide mobility and bioavailability in soil depends on controlling factors: radionuclide, soil type and characteristic, agricultural practice (ploughing, fertilizer applications). Radionuclides are initially deposited on the upper surface of the soil, but they quickly weather into the first centimetre of soil, especially if they are deposited via rainfall. The weathering effect and also the fact that the soil surface is not a smooth plane reduce the radiation field at the generally used reference height of 1 m above the soil surface (UNSCEAR, 2000). Mechanisms, like ploughing and fertilising (e.g., application of potassium fertiliser and lime to contaminated soils can reduce uptake by crops of $^{137}$Cs and $^{90}$Sr) can reduce the exposure rate. In general, the elements uranium, actinium and thorium, and hence their decay products, show enormous variations in activity throughout the environment and have high concentrations in igneous rocks; certain sedimentary rocks, e.g. some shale and phosphate rocks also show high concentrations. The natural radionuclides, together with other trace constituents, may be transported and redistributed by weathering processes and water movements, which will disturb the concentrations of their decay products from their equilibrium values. The process of root uptake of radionuclides from soil is indirect pathway for the contamination of plants. $^{131}$I can transfer relatively rapidly through the food chain (UNSCEAR, 2000). Direct pathway of plant contamination, which is more important than root uptake, are deposition of

radionuclides from the atmosphere (dry or wet deposition) to the vegetation surface. For people consuming vegetables grown in contaminated soil, washing and peeling of vegetables can reduce the potential intake of radionuclides. Consumption of fruit and vegetables (direct radiation exposure) or, consumption of products from animals fed on contaminated vegetable matter (indirect radiation exposure) represent significant pathway (e.g., $^{137}Cs$, $^{90}Sr$) for human exposure.

Behaviour of radionuclides and their content in the atmosphere vary with time and location. Variations are day-to-day, seasonal, longitudal, and sunspot-cycle related. The concentrations of some cosmogenic radionuclides, such as $^{3}H$, $^{14}C$, $^{22}Na$, and $^{37}Ar$, are increased during nuclear tests. Nuclear reactors also generate $^{14}C$ that eventually will be distributed in the atmosphere, but is estimated to be two orders of magnitude lower than the natural concentration. $^{14}C$ produced in the atmosphere is quickly oxidized to $^{14}CO_2$. The equilibrium concentrations of $^{14}C$ in the atmosphere are controlled primarily by the exchange of $CO_2$ between the atmosphere and the ocean. The oceans are the major sink for removal of $^{14}C$ from the atmosphere. Most of the other cosmogenically produced radionuclides in the atmosphere are oxidized and become attached to aerosol particles. Aerosols with adsorbed cosmogenic radionuclides act as condensation nuclei for the formation of cloud droplets and eventually coagulate to form precipitation. The mechanisms for transferring aerosols with adsorbed radionuclides to the Earth's surface include:

- wet deposition as:
  - formation of clouds by small particles (condensation nuclei) with their subsequent production of rain,
  - scavenging of aerosol particles by rain drops (or other forms of precipitation) during their fall,
- dry deposition on surface by diffusion, impaction and gravitational processes.

The radionuclides $^{3}H$ and $^{14}C$ tend to behave in a different manner. The $^{3}H$ nuclei produced exchange with stable hydrogen atoms and become incorporated into $H_2$ molecules, after which it is converted to water known as tritiated water (HTO). As tritiated water it enters the natural cyclic movements of water over the Earth's surface. Its principal reservoir is in the oceans. Releases of $^{3}H$ and $^{14}C$ are important because they may contribute to exposure of the population due to their biologically importance as internal irradiators when incorporated in an organism.

Artificial radionuclides generally enter forest ecosystems (tree overstorey, understorey, organic layer, soil) from the atmosphere as a result of nuclear waste discharges or nuclear weapon testing, via surface run-off through discharges and leaching from shallow disposal sites, or from ground water leaching from waste repositories to aquifers where roots may penetrate. To be incorporated into plants, the radionuclides must be transported through the temporary storage reservoir (organic layer) into the root zone. Trees act as filters for airborne aerosols. Radionuclides can be removed from the vegetation surface by several mechanisms such as washoff, throughfall, stemflow, etc. Foliar absorption and root uptake lead to radionuclide incorporation into the internal plant components and can be removed from the plant by leaf fall, root exudation, volatilization. These redistribution processes have characteristic rates which depend on the type of forest, season, specific radionuclide, etc. Removal from the plant surface is rapid, while radionuclides incorporated into structural components of the vegetation are very difficult to remove, resulting in a much longer residence time

In addition to the geological weathering of rock and soil, radionuclide concentrations and exposure rates vary because of physical and chemical processes, both natural and anthropogenic. Mobilization of radionuclides can happen because of human activities, intentional or unintentional activities. If mobilized, the radionuclides are available for transport. When radionuclides are dissolved in groundwater, the radionuclides tend to travel with the water until redeposition takes place. It happens also in air, when air flow serves to transport fine particulates, combustion or volatilization products. Usually, however, the TENORM are mobilized along with some other mineral of interest. Generally, redeposition involves the same factors as mobilization. Changes in any of the parameters of a stream of material may result in reduced mobility and subsequent redeposition.

For instance the major atmospheric exposure in the vicinity of the tailings (for by-products from uranium mining and milling) comes from the inhalation of $^{222}$Rn and $^{230}$Th, $^{226}$Ra, $^{238}$U, $^{210}$Po and $^{232}$Th on dust and aerosols. $^{226}$Ra is generally the radionuclide of major concern in the aquatic pathway. Doses to the public can result from consuming contaminated aquatic biota or water or through ingestion of plants irrigated with contaminated water. Where fish is a major source of food, this pathway can dominate. Since radium migration through groundwater is retarded by soil, exposure through this pathway is generally unimportant. Doses from radionuclides such as $^{210}$Pb, $^{210}$Po, uranium and thorium are usually less than those from $^{226}$Ra. However, under some circumstances, the release of these radionuclides can be of the same order of magnitude or even higher than for $^{226}$Ra (e.g. U-migration under oxidising conditions) and should be considered separately.

## 4.3 Background environmental radioactivity and monitoring of environmental radioactivity in Slovenia

### 4.3.1 Background radioactivity in the environment in Slovenia

The radioactive rocks on the Earth and radiation coming from space (cosmic rays) cause natural exposure. According to UNSCEAR report (UNSCEAR, 2000), the average annual effective dose from natural sources to a single individual is 2.4 mSv, ranging from 1 to 10 mSv. From the existing data on external radiation and radon concentrations in dwellings and outdoors, it can be concluded that this value in Slovenia is somewhat higher than the world average, i.e. about 2.5 to 2.8 mSv per year. About 50 % of this is due to internal exposure from inhalation of radon and its progeny (Table 4.4). Particularly people from the Northern Hemisphere are exposed to ionising radiation from global contamination of the environment as the consequence of past nuclear bomb tests and the nuclear accident in Chernobyl. Estimation of this exposure showed that in 2003 the average individual dose to the population from this source in Slovenia was around 9 μSv and in year 2004 near 9 μSv, the annual effective dose of external radiation originating from soil radioactivity, building material in dwellings and from cosmic rays together being estimated at 800 to 1,100 μSv, and the amount due to intake of food and water being equal to about 400 μSv (SNSA, 2004; SNSA, 2005). The biggest contribution come from external radiation, while food and water consumption contributed only 2 μSv. Due to lower contamination of the ground with $^{137}$Cs, the population in urban areas is less exposed than that in the rural environment.

Maps of natural radioactivity in Slovenia were elaborated in 1994 and are based on results of in-situ gamma-spectrometry measurements and analyses of soil samples: dose rate levels, uranium equivalent, contents of thorium and potassium (Andjelov, 1993). An average value of 57 nGy $h^{-1}$ was derived from terrestrial data with a range from 32 to 112 nGy $h^{-1}$.

***Table 4.4: Annual effective dose from natural sources to a single individual in Slovenia (SNSA, 2004).***

| **Transfer pathway** | **Annual effective dose (mSv)** |
|---|---|
| External radiation (soil, building materials, cosmic rays) | 0.8 – 1.1 |
| Intake of food and water | 0.4 |
| Inhalation of radon and its progeny | 1.2 – 1.5 |
| Ionizing radiation from global contamination of the environment | 0.009 |
| **Average effective dose** | **2.5 – 2.8** |

The highest exposures of the population are observed for individuals living in the surroundings of the former uranium mine at Žirovski vrh, being slightly below one tenth of the exposure due to natural sources. The population is to some extent also exposed to some other human activities. These are exposures from deposited materials with enhanced natural radioactivity originating from past industrial or mining activities, related mostly to mining and

processing of raw materials containing uranium and thorium (in Slovenia: mining and processing of mercury ore, processing of bauxite, phosphates, coal combustion). Data exist on various types of materials, their amounts, and higher contents of natural radionuclides. The only exception is the Šoštanj TPP (Thermal Power Plant) operation were public exposure for a reference group, based on results of environmental measurements and model calculations, was assessed to be of some micro-sieverts per year (in 2002: 7 μSv) (Mljač and Križman, 2004).

### 4.3.2 Monitoring of environmental radioactivity in Slovenia

Environmental monitoring due to global radioactive contamination has been carried out in Slovenia for more than four decades. Two long-lived fission radionuclides ($^{137}$Cs and $^{90}$Sr) are followed, as the consequence of nuclear bomb tests (1951 – 1980) and of the Chernobyl accident (1986). They are measured in the atmosphere, water, soil and in the food chain. Results for the years 2003 – 2005 show that concentrations of both long-lived fission products in samples of air, precipitation, soil, milk and grass are further slowly decreasing and are mostly lower than before the Chernobyl accident in 1986. Only the specific area activity of $^{137}$Cs in the upper layer of uncultivated soil is still enhanced: at the time of the Chernobyl accident an approximately five times higher contamination (20–25 k*Bq* $m^{-3}$) was measured compared to the contribution of all nuclear bomb tests in the past (SNSA, 2000). The highest contamination of the ground was measured in the Alpine and forested regions, resulting in enhanced contents of $^{137}$Cs in forest fruits, mushrooms and game, and in Alpine milk and cheese. A part of the monitoring programme also comprises measurement of river water contamination with $^{131}$I due to medical use of this radionuclide. In all samples other gamma emitters are also measured, as well as tritium ($^{3}$H) in water samples. In 2004 monitoring of radioactivity in feedstuffs was not performed because the relevant ministry did not provide the financial resources to fulfil its legal obligations. The biggest contribution to radiation exposure of members of the public comes from external radiation and from food ingestion, while inhalation dose due to aerosols with fission radionuclides is negligible. In 2003 the effective dose from external radiation of $^{137}$Cs was estimated to be 6.5 *μSv*, which is a little less than in the year before (2002: 6.8 *μSv*). The annual dose from ingestion (food consumption) was 2.1 μSv; the radionuclide $^{90}$Sr accounting for 78 % of the dose, while the contribution of $^{137}$Cs was 22 %. The annual contribution due to inhalation of both radionuclides is negligible if compared with radiation exposure from other transfer pathways. In 2003, the total effective dose to an adult individual of Slovenia arising from the global contamination of the environment with fission products was estimated to be 8.6 *μSv*, as shown in Table 4.5. This is approximately a three hundred times lower dose compared to the annual exposure from natural radiation in the environment (2.5–2.8 m*Sv*). In 2004 no radioactive contamination of the environment was detected related to any nuclear or radiation event on the globe.

In 2004 the effective dose to an adult from external radiation of $^{137}$Cs was estimated to be 6.4 μSv, which is similar to previous years. The annual dose from ingestion (food and drinking water consumption) was 2.1 μSv, just as in the year before; the radionuclide $^{90}$Sr accounted for 60% of the dose, while the contribution of $^{137}$Cs was 40%. The annual contribution due to inhalation of both radionuclides was below 0.01 μSv, which is negligible if compared with radiation exposure from other transfer pathways. In 2004, the total effective dose to an adult individual of Slovenia arising from the global contamination of the environment with fission products was estimated to be 8.5 μSv, as shown in Table 4.5. This is approximately a three hundred times lower dose compared to the annual exposure from natural radiation in the environment (2.5–2.8 mSv). The effective dose for drinking water, taking into account natural and artificial radionuclides was estimated. It was shown that the limit value of 0.1 mSv per year due to water ingestion from any local water supply was not exceeded. Dose limits are listed in Table 4.6.

***Table 4.5: Radiation exposure of the population in Slovenia due to global contamination of the environment in the period 2003 – 2004 (SNSA, 2004; SNSA, 2005; SNSA, 2006; SNSA, 2007).***

| Transfer pathway | Effective dose (μ*Sv* per year) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 2003 | 2004 | | 2005 | | 2006 | |
| | Adults | Adults | Children (up to 12 years) | Adults | Children (up to 12 years) | Adults | Children (up to 12 years) |
| Inhalation ($^{137}$Cs, $^{90}$Sr) | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| Ingestion -food ($^{137}$Cs, $^{90}$Sr) | 2.1 | 2.1 | 2.2 | 2.1 | 2.2 | 1.5 | 2.7 |
| -drinking water ($^{137}$Cs, $^{90}$Sr; tap water Ljubljana, 2 litres daily) | 0.02 | 0.04 | 0.05 | 0.04 | 0.05 | 0.03 | 0.06 |
| External radiation | 6.5 | 6.4 | 6.4 | 4˙8 | 4.8 | 1.5 | 1.5 |
| **Total (rounded)** | **8.6** | **8.5** | **8.6** | **6.9** | **7.0** | **3.0** | **4.2** |

In 2006 the effective dose for an adult from external radiation of $^{137}$Cs (mainly from the Chernobyl accident) was estimated at about 1.45 μSv, which is 0.06 % of the dose received by an average Slovenian from natural background radiation (SNSA, 2007). This value is smaller than the one measured and calculated for the previous year (4.8 μSv) not because of a decrease in radioactivity but because of the inconsistency of soil sampling on different pedologic basements: before 2006 "Ljubljansko barje", after that "Ljubljansko polje". Before 2005 the sampling site was at Cesta dveh cesarjev, but in 2006 a new location at the Reactor Centre Brinje was chosen, where soil permeability for radioactive contaminants is higher.

***Table 4.6: Dose limits for members of the public (IAEA, 1996).***

| Dose | Level |
|---|---|
| Effective dose | 1 mSv in a year; in a special circumstances up to 5 mSv in a single year provided that he average dose over five consecutive years does not exceed 1mSv per year |
| Equivalent dose to the lens of the eye | 15 mSv in a year |
| Equivalent dose to the skin | 50 mSv in a year, averaged over 1 cm$^2$ of the most highly irradiated area of the skin |

The Institute of Occupational Safety also measured radioactive contamination of imported and exported food samples. Altogether about 200 measurements of specific activities of radionuclides were performed. Measurements of natural radioactivity were carried out mainly within research studies or natural surveys, supported by the Ministry of Health, Ministry of Environment and Spatial Planning and Ministry for Science and Technology.

### 4.3.3 Automatic on-line radiation monitoring

The first automatic stations for dose rate measurements in Slovenia were installed after the Chernobyl accident around the Krško NPP (Nuclear Power Plant), and in the year 1992 on-line measuring stations were installed gradually over the whole country. At the moment there are 45 stations located throughout Slovenia managed by four different organisations: the Krško NPP, the Slovenian Environmental Agency (ARSO) (Agencija Republike Slovenije za okolje), the Slovenian Nuclear Safety Administration (SNSA) (Uprava RS za jedrsko

varnost), and the Milan Vidmar Electrical Institute (for TPPs). Since 1996, real-time measurement data from all networks have been collected at the SNSA, the body responsible for monitoring and data exchange. All the data are transmitted at half-hour intervals on the internet and are also available on the SNSA homepage. As an example is presented Figure 4.4 which shows that real time gamma dose rate levels on 19th January 2007 in Slovenia were 0 – 200 nSv $h^{-1}$ and 100 – 200 nSv $h^{-1}$.


***Figure 4.4: Map of Slovenia with measurement locations for external radiation (External gamma radiation, 2007).***

The data are graphically presented in the form of a map of Slovenia where the different colours of the spots indicate the information on the gamma dose rate level in real time. The year 2006 marked the end of a large PHARE project at the SNSA, in which the national system for early warning was upgraded. 35 new measuring sites were added to the network, equipped with radiological as well as sophisticated meteorological equipment. The new system now consists of 77 sites for measurement of gamma dose rate.

### 4.3.4 National survey on radon

Nation-wide radiation measurements were performed in the early 1990s, including mapping of natural radioactivity and indoor radon concentrations in dwellings. Slovenia was one of the first countries that carried out a national survey on radon concentrations in all kindergartens and schools. Numerous research projects dealt with elevated radon concentrations in different environments, e.g. in Karst caves, natural spas etc. Some pilot projects were also performed to gain a deeper insight into specific subjects related to industry and mining. National surveys and research studies were supported by the ministries responsible for health, science and the environment.

Radon ($^{222}Rn$) is a chemically inert, naturally occurring radioactive gas without odour, colour or taste. The concentration of radon in the home depends on the amount of radon-producing uranium in the underlying rocks and soils, the routes available for its passage into the home and the rate of exchange between indoor and outdoor air. Radon enters houses through openings such as cracks in concrete floor-wall junctions, gaps in the floor, small pores in hollow-block walls, and through sumps and drains. Consequently, radon levels are usually higher in basements, cellars or other structural areas in contact with soil. Due to dilution in the air, outdoor radon levels are usually very low. Radon can also be found in drinking water,

the concentration depending on the water source, and this can sometimes present a hazard. Radon levels are higher indoors, and much higher radon concentrations can be found in places such as mines, caves and water treatment facilities. Health effects have been found in, for example, miners. However, the lower concentrations – found, for example, in normal buildings and to which large populations are exposed – also carry health risks. For most people, by far the greatest exposure to radon comes in the home. Radon escapes easily from the ground into the air and disintegrates through a chain of short-lived decay products ($^{218}$Po, $^{214}$Pb, $^{214}$Bi, $^{214}$Po). The short-lived progeny, which decay emitting heavily ionizing radiation called alpha particles, can be electrically charged and become attached to aerosols, dust and other particles in the air we breathe. As a result, radon progeny may be deposited on the cells lining the airways where the alpha particles can damage DNA (deoxyribonucleic acid) and potentially cause lung cancer.

The Slovenian radon programme started in period 1990 – 1992 with measurements of indoor air radon concentrations in 730 kindergartens (Vaupotič et al, 1994a; Vaupotič et al, 1994b) and 890 schools (Vaupotič, Šikovec, Kobal, 2000). Concentrations higher than 400 Bq m$^{-3}$ have been found in 45 kindergartens and 78 schools, and concentrations higher than 1,000 Bq m$^{-3}$ in 6 kindergartens and 24 schools. In the period 1994 – 2002 attention was focused on schools with elevated levels (Vaupotič and Kobal, 2005).

Systematic measurements of radon in dwellings started in winter 1993/1994 in the framework of a national monitoring programme of indoor radon measurements: concentrations were measured in 892 (out of 1,000) randomly selected homes (Križman et al. 1996a). In about 10 % of dwellings radon concentrations were higher than 200 Bq m$^{-3}$ and in about 1 % of dwellings they exceeded 400 Bq m$^{-3}$. The arithmetic mean of the results was 87 Bq m$^{-3}$ and the geometric mean 60 Bq m$^{-3}$. The survey showed that the south-western part of Slovenia (the Karst territory) could be recognised as a radon prone area since indoor concentrations were highly above average, concentrations of radon in towns were lower than in the countryside and concentrations of radon were higher in old houses than in new houses. Based on this programme an intervention level of radon concentration in dwellings of 400 Bq m$^{-3}$ has been set. This level was exceeded in 42 homes included in the measurements. In all new-built houses the intervention level should not exceed a concentration of 200 Bq m$^{-3}$ (Križman et al. 1996a).

Screening of radon concentrations was made in Slovenian spas (in air and in thermal water) (Vaupotič and Kobal, 2001). The results showed that levels are relatively low and only in one or two spas was the exposure of personnel likely exceed the limit for the public of 1mSv per year. In a systematic radium survey in the year 1997 (Popit el al., 2004) concentrations in 115 spring waters were below the limit for drinking water of 1,000 Bq m$^{-3}$. The survey showed that there is no enhancement of $^{226}$Ra concentrations due to use of phosphate fertilizers in agriculture and it was proven that $^{226}$Ra concentration is related to the rock type at the spring and to the lithological composition of the aquifer. In survey levels exceeding 36 Bq m$^{-3}$ were found on acid, intermediate, and basic igneous and metamorphic rocks, while values above 36 Bq m$^{-3}$ were found in 10 springs from aquifers composed of limestone, dolomite, flysch and sandstone. The situation is not so favourable in the case of tourist caves where periodical measurements (Vaupotič, 2003) showed that radon levels were of the order of several thousand Bq m$^{-3}$. This was the first time in Slovenia that the regulatory body identified work activities in the presence of elevated natural radiation and considered tourist guides as radiation workers. Radiation exposures of guides have been recorded in the central dose register for almost a decade.

All these studies have shown that radon concentrations within the home vary with the time of year, from day to day and from hour to hour. Because of these fluctuations, estimation of the annual mean concentration of radon in indoor air requires reliable measurements of mean radon concentrations for at least three months and preferably longer. Short-term radon measurements give only limited information.

# 5 SOURCES OF TECHNOLOGICALLY ENHANCED NATURALLY OCCURRING RADIOACTIVE MATERIALS

## 5.1 Uranium mining and milling

Uranium mining can take place using conventional (underground and open pit) mining methods or the leaching process. In milling, the ore from the mine is crushed and is then subject to a leaching process. The solvent is usually $H_2SO_4$, or NaOH for carbonate-rich rocks. After the uranium minerals (typically pitchblende, $UO_{2(s)}$) have been dissolved, the pregnant solution is separated from the residual solids (tails). Typically, the solids are washed in several steps with fresh solvent until the desired level of metal recovery is attained. The dissolved uranium is recovered from the pregnant solution by neutralization, followed by precipitation, non-aqueous solvent extraction or ion exchange. The final product is termed yellowcake. Every 0.1 % of uranium in intact uranium ore contains approximately 12.4 Bq per 1 gram of ore of each descendant of the $^{238}U$ in the decay type, or 174 Bq of total radioactivity (EC, 1999). The waste that is created in production is mining waste and the waste from the uranium ore processing procedure. In a typical uranium ore processing procedure, approximately 90–95 % of uranium and approximately 15 % of the initial total radioactivity is contained in the final product, i.e. in the yellow cake, while the rest stays in the waste. The initial 85% of the activity decreases quickly to 70 % as short-lived daughters, such as $^{234}Th$, decay (EC, 1999).

Cumulative uranium production in the western world to the end of 1990 was around 1 Mt. World uranium resources found in 49 countries of the world have been classified in 1996 by the IAEA into fifteen major geological deposit categories (EC, 1999). Of the 582 entries in the IAEA database used to create a world uranium distribution map, 159 (25.1 %) were in Europe, 167 (29 %) in North America, 111 (19.2%) in Asia, (of which 78 (12 %) were in Central Asia (primarily Kazakhstan and Uzbekistan)), 34 (6%) in Australia, 61 (10%) in Africa, 18 (3 %) in South America, and 32 (5%) in the Russian Federation. Estimated cumulative world production of uranium up to 1999, based on information provided in the IAEA Guidebook from 1996, amounted to approximately 1,966,900 tons (IAEA, 1996a). With these data, it is estimated that 33.1% came from North America, 28.2 % from Europe, 13.5% from Asia (including the Central Asian states), 17.1% from Africa, 4.8% from the Russian Federation, 3.1 % from Australia and 0.2 % from South America (IAEA, 2003a).

European uranium mining and milling was mainly carried out in Germany, the Czech Republic, France, Bulgaria, Romania, Hungary, Spain and Slovenia. Most mining and milling sites in France and Spain are closed and remediated or remediation is in progress. There are also many abandoned sites in Eastern Europe; but none are remediated. Many of these sites pose serious problems because preservation and protection of the environment has often been neglected and also because they are, in many cases, situated close to human populations. The most prominent case of environmental contamination due to mining activities is in the former East Germany. In the final report of an European Commission (EC, 1999), it is stated that the barren rock (3–30 ton per ton ore for open pit mines) contains on average between 15 and 25 mg $kg^{-1}$ uranium with a total activity of 2–5 kBq $kg^{-1}$; while cut-off grade rocks generated in comparable amounts to the ore contain, on average, 150 mg $kg^{-1}$ uranium with a total activity of 30 kBq $kg^{-1}$. Relatively low grade ore was excavated and treated in the Žirovski vrh Uranium Mine in Slovenia (1.2 % $U_3O_8$) (Logar, 1996). The Žirovski vrh Uranium Mine waste has an average uranium content of 70 mg $kg^{-1}$ and consists of mine waste material under 300 mg $kg^{-1}$, mill reffinated neutralization filter cake and some building construction material (Logar, 1996). For static and dynamic leaching residues, the uranium concentration and total activity are 20 mg $kg^{-1}$ and <40 kBq $kg^{-1}$ and 50 mg $kg^{-1}$ and 300 kBq $kg^{-1}$, respectively. The sands which contain 20 % of the initial radium (1–4 kBq $kg^{-1}$ $^{226}Ra$) contain on average 0.004–0.01% $U_3O_8$ and 2–22 kBq $kg^{-1}$ $^{230}Th$. The fines have a similar $^{230}Th$ content but contain 80 % of the initial $^{226}Ra$ (5–20 kBq $kg^{-1}$) and 0.016–0.04 % $U_3O_8$ (EC, 1999).

## 5.2 Mining and metal production

Mining, which can take place on the surface, underground or by leaching, creates large quantities of waste material. Through industrial processing procedures, waste products containing even higher radionuclide activities can be obtained.

There are three categories within the category of mining and ore processing for the production of metals, rare metals, metals of special application and metals which industry requires in large amounts. Among the special application metals are metals with unique commercial and industrial use, such as hafnium, tin, titanium and zirconium. Metals needed in industry in large amounts include aluminium, copper, iron, lead, zinc and precious metals such as silver and gold. The presence of NORM, found in mining for metals depends mostly on the geological constitution or the geographical area in which a certain mineral is mined, so the activities can vary significantly.

In Australia bauxite is mined in large amounts and is the raw material input for the acquisition of aluminium oxide, which is called hydrated alumina and which can be used for electrolytic production of aluminium. It may contain significant concentrations of $^{238}U$ as well as $^{232}Th$ and of their descendants, which result from the presence of the minerals monazite and illmenite. The production process using the Bayer procedure of melting bauxite to an alloy with sodium hydroxide creates an insoluble precipitate, which contains iron, silicon and titan and is called red sludge. It contains up to 60 % of iron hydroxide and has a great affinity to bind cations, heavy metals and radionuclides (IAEA, 2003a). The red sludge may also contain up to three time's higher radionuclide levels than bauxite. Important by-products of aluminium production are vanadium and gallium. The bauxite ore can contain significant concentrations of radioactivity, as shown in Table 5.1. This radioactivity can be due to either or both $^{238}U$ and $^{232}Th$, depending on the ore gangue mineralogy.

***Table 5.1: Content of radionuclides in bauxite and red mud (IAEA, 2003a).***

| Radionuclide | Specific activity (Bq $kg^{-1}$) | |
|---|---|---|
| | **Bauxite** | **Red mud** |
| U - Ra decay series | 10 – 9,000 | 100 – 3,000 |
| Th decay series | 35 – 1,400 | 100 – 3,000 |
| Actinium decay series | 120 – 130 | – |
| $^{40}K$ | 10 – 600 | 10 – 100 |

Iron ore contains iron oxides, the primary forms of which are magnetite ($Fe_3O_4$) and haematite ($Fe_2O_3$). Due to their geochemical characteristics, the iron ores, particularly when subjected to disintegration, are good collectors of radionuclides and heavy metals. As raw material the iron ore contains approximately 15 Bq $kg^{-1}$ of uranium and its decay products. The presence of uranium in the raw material input (ore, coke, lime) in the processing of iron ore leads to pre-concentration of the volatile radionuclides $^{210}Pb$ and $^{210}Po$ on fine dust particles, which, combined with inappropriate cleaning systems, can lead to an increased exposure of people and wide contamination of the environment. Important sources of $^{210}Pb$ to air are the elementary phosphorus and iron and steel production industries; cement production and brick and tile installations may also be of importance because they are so numerous (UNSCEAR, 2000). A sediment is created from the coal added in the processing procedure and it may contain increased activity of $^{210}Pb$ (~100 Bq $kg^{-1}$) and $^{210}$ Po (~300 Bq $kg^{-1}$); is usually deposited at the landfill, along with scoria (EC, 1999). Most of the uranium descendents remain in the products and waste scoria (98 % of the raw material input), and approximately 2 % can be found in fine dust particles. The radionuclide concentrations are relatively low, if the presence of radionuclides in the ore itself is low (save for the exceptions mentioned in the example). Because of the mineralogical, vitrified structure of the scoria, the probability of mobilization of the radionuclides it contains is negligible. Table 5.2 includes ranges for the specific activity of radionuclides in different residues from iron production.

***Table 5.2: Content of radionuclides in aerosols and slag; data for Netherlands and United Kingdom (Leopold et al, 2002).***

| Material | Specific activity (Bq kg$^{-1}$) | | |
|---|---|---|---|
| | $^{226}$Ra | $^{232}$Th | $^{210}$Pb / $^{210}$Po |
| Slag | 64 – 380 | 30 – 98 | – |
| Filter dust | – | – | 15,000 / 30,000 |
| Sludge | – | – | 12,000 / 4,000 |

## 5.3 Phosphate industry

Waste in the phosphate industry is created during the mining and processing of phosphate ore (phosphorite) into phosphorous acid or elementary phosphorus. These two products can then be used for the production of phosphatic fertilizers, detergents, feedstuffs, alimentary additives, plant protection products and other phosphorus–containing chemicals. The phosphatic ore is processed in two processes; sour leaching for the production of phosphorous acid, or a thermal process for the production of elemental phosphorus.

Leaching with sulphuric acid is the most common creating phosphogypsum ($CaSO_4 \times H_2O$). Phosphogypsum generally contains 80 % of $^{226}$Ra, 30 % of $^{232}$Th and 14 % of $^{238}$U, although the values may vary significantly. It is normally deposited on phosphoric gypsum landfills or is discharged into watercourses or seas (EC, 1999).

In the thermal processing procedure of phosphate ore for the production of elemental phosphorus, the waste product, calcium silicate ($CaSiO_3$) is created, which contains the main share (approximately 93 %) of the uranium and radium. The amount of fine ashes created by the thermal process is below 1 % of the raw material ore and contains high activities of $^{210}$Pb and $^{210}$ Po (~1,000 Bq kg$^{-1}$) (IAEA, 2003a). Radionuclide concentrations in the gypsum range from background to 1,853 Bq kg$^{-1}$, depending on radionuclide and country (Table 5.3).

***Table 5.3: Example of radionuclide concentrations in phosphogypsum (IAEA, 2003a).***

| Country | Specific activity (Bq kg$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $^{226}$Ra | $^{238}$U | $^{210}$Pb | $^{210}$Po | $^{232}$Th |
| USA | 270 – 1,358 | 22 – 451 | 348 – 1,853 | 355 – 1,765 | 11 |
| Europe | 15 – 1,700 | 500 | 1,300 | 900 | 10 |
| Australia | 280 – 350 | 10 – 24 | 320 – 440 | 150 – 360 | 4 – 7 |
| Slovenia* | 520 | 263 | 482 | – | 7.9 |

**Source: Križman et al., 1989 and SNSA, 2006..*

Phosphogypsum is the principal waste by-product generated during the phosphoric acid production process (wet process), and phosphate slag is the principal waste by-product generated from the production of elemental phosphorus (thermal process). During the wet process, there is selective separation and concentration of radionuclides. About 80 % of the $^{226}$Ra follows the phosphogypsum, while about 86 % of the uranium and 70% of the thorium are found in the phosphoric acid (EC, 1999).

## 5.4 Coal mining and incineration in thermal power plants

Fossil fuels (coal, lignite, peat) contain the naturally present radionuclides of the uranium-radium, thorium decay series and $^{40}$K. The radionuclide concentrations in the coal, tailings and waste waters depend on the geological formation of coal layers. Mining is connected with the production of comparable amounts of tailings and drainage water, which may contain increased radionuclide concentrations. Depending on the hydrogeological conditions, the coal can be accompanied by drainage waters with high mineralization and high radium levels, which can cause the accumulation of $^{226}$Ra and $^{228}$Ra in sediments, when discharged into local watercourses or holding ponds. As an example, specific activities of $^{226}$Ra in coal ash from 5 locations in Slovenia, are shown in Figure 5.1.

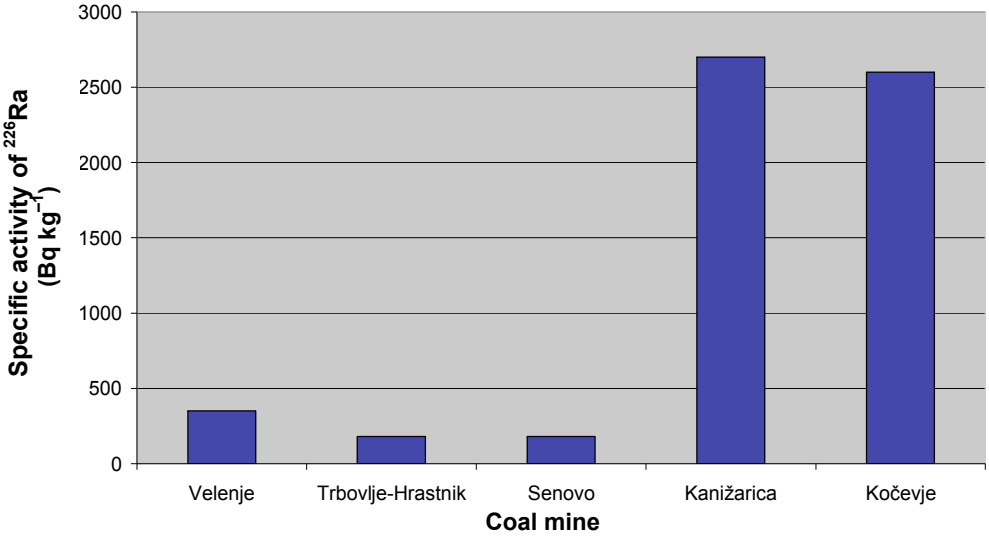


***Figure 5.1: Radioactivity of coal ash from different coal mines in Slovenia (based on Vokal et al, 2004).***

In the process of incineration, ashes and fine ashes are created. Because the radionuclides are concentrated in the ashes during incineration, the content of radionuclides in the ashes and other residue is directly related to the concentration in coal. Typical concentration factors in the ashes are 1 – 10 for $^{238}$U, 5 – 15 for $^{226}$Ra, 30 – 200 for $^{210}$Po, 20 – 120 for $^{210}$Pb, 1–10 for $^{230}$Th and 10 – 50 for $^{40}$K (Martin et al., 1997). Volatile radionuclides such as $^{210}$Pb and $^{210}$Po are concentrated primarily in the fine fly ashes. The arithmetic mean of the reported values of radionuclides in fly ashes is 265 Bq kg$^{-1}$ $^{40}$K, 200 Bq kg$^{-1}$ $^{238}$U, 240 Bq kg$^{-1}$ $^{226}$Ra, 930 Bq kg$^{-1}$ $^{210}$Pb, 70 Bq kg$^{-1}$ $^{232}$Th, 110 Bq kg$^{-1}$ $^{228}$Th and 130 Bq kg$^{-1}$ $^{228}$Ra. Radon emanation from ash is a possible exposure pathway from both ash disposal piles and use of fly ash as a concrete aggregate (EPA, 2000a).

Table 5.4 give examples of typical radionuclide concentrations found in residues resulting from coal combustion in a number of countries. These concentrations, however, can vary widely depending on the mineral content of the coal, which, in turn, can vary with mining location and region of the country.

Most of the waste from coal mining is deposited on the surface. In mine water catchments sediments with increased radioactivity that precipitate in the catchments area can mix with tailings and be used for filling abandoned mineshafts. Due to the high consumption of fossil fuels, large quantities of ashes are produced and deposited on surface landfills or used to fill mineshafts. From the radiological point of view, the use of ashes in building construction can lead to an increased exposure of the population due to gamma radiation, with the most significant contribution from radon and its decay products.

***Table 5.4: Content of radionuclides in ash and slag (IAEA, 2003a; Brajnik et al., 1988).***

| Country | Specific activity (Bq kg$^{-1}$) | | |
|---|---|---|---|
| | $^{238}$U decay series | $^{232}$Th decay series | $^{40}$K |
| Hungary [a, b] | 200 – 2,000 | 20 – 300 | 300 – 800 |
| USA [a] | 100 – 600 | 30 – 300 | 100 – 1,200 |
| German | 6 – 166[a]<br>68 – 245[b] | 3 – 120[a]<br>76 – 170[b] | 125 – 742[a]<br>337 – 1,240[b] |
| *Slovenia, Trbovlje [a] | 120 – 300 | 80 | – |
| *Slovenia, Šoštanj [a] | 250 | – | – |

[a] ash and fly ash, [b] slag

** Source: Brajnik et al., 1988.*

Due to the presence of NORM in most soils and rocks, underground mining activities can lead to enhanced levels of radioactive dust, and radon isotopes and their radioactive

progeny, unless careful attention is given to the design and use of suitable ventilation systems in these mines. In open-cast mines, NORM can also be produced, and since the ventilation cannot be controlled, work practice has to be carefully regulated to minimise the radiological risk to the on-site work-force.

## 5.5 Acquisition of natural gas and oil

In this area by-products created containing TENORM can appear in the form of sediments, sludge and deposits in the piping system, and are mostly created when the mixture of oil-gas-water is brought to the surface, or during the separation process itself. Salty formation water with a low sulphate concentration contains the most dissolved radium in comparison with uranium and thorium. The amount of this water also increases with the time of exploitation of the bore, which means that the amount of TENORM also increases with time. Sediments are created by changes in the pressure, temperature and salinity, when the water surfaces and are typically mixtures of carbonates and sulphates. One of the sulphate minerals is barite ($BaSO_4$), with which, because of its similar chemical characteristics, radium can co-precipitate. Compared to the other by-products, these sulphates contain the most $^{226}Ra$, the activity of which increases significantly in comparison with the activities found in nature. The short-lived descendants of radon, as well as $^{210}Pb$ and $^{210}Po$, are concentrated in the layers coating the piping system used for acquisition of natural gas.

Table 5.5 includes illustrative ranges for the activity concentrations of radionuclides in different residues associated with oil and gas production. The largest concern in terms of radionuclide activity concentrations for NORM in the oil and gas industry involves the hard scales which form on the inside of the downhole tubing. At many oilfield sites the downhole tubing can become coated with scale deposits that contain radium. Because of the loss of flow capacity in the downhole tubing, these scales must be removed occasionally. When they are removed, they become a waste management concern. Repinc et al. (2004) measured specific activities of 29 – 270 Bq $kg^{-1}$ on piping scale from Nafta Lendava.

Managing waste materials depends on radionuclide activities and expenses normally grow in proportion with radioactivity. Waste waters are discharged either to nearby watercourses or to evaporation reservoirs (holding ponds), and the low-activity sludge is used in agriculture or is attenuated with soil to the activity allowed by legislation. Waste material with high specific activity demands isolation, either by underground deposition in a repository for low-radioactivity wastes; in an underground mine, and so on.

***Table 5.5: Representative specific activities of oil and gas residues (IAEA, 2003a).***

| **Material** | **Specific activity (kBq $kg^{-1}$)** |
|---|---|
| Scale in downhole tubing, pipes and other equipment for handling oil/gas and formation waters | $^{226}Ra$: Background – 15,000 |
| Sludges in separations and production equipment | $^{226}Ra$: 10 – 1,000 |
| Sludges, films in natural gas supply equipment | $^{210}Pb$: Background – 40 |
| Sludges from soils beneath holding ponds | $^{226}Ra$: 10 – 40 |

## 5.6 Rare earths and titanium oxide

Rare-earth metals are used to improve the mechanical properties of steel. Lanthanum, cerium, praseodymium and samarium are used as components in welded carbon electrodes (studio lighting). Cerium, praseodymium and neodymium are used in glasses and lenses for special purposes. Europium and gadolinium are used for achieving phosphorescence in TV tubes. Samarium, europium, dysprosium and gadolinium are used in instruments for checking the fuel sticks in nuclear reactors, as catalysts in oil refineries, in the equipment for controlling emissions from motor vehicles, as catalysts in self-cleaning ovens (cerium) and in permanent magnets. Also Ce is used widely in pyrophoric alloys with iron in lighter flints and sparking devices. Minerals such as ilmenite, monazite, zirconium, rutile and so on, are used

as input raw materials in the process for extracting rare-earths, zirconium, titanium, thorium and tin.

The concentrations of radionuclides may vary greatly, depending on the origin of the minerals and the extraction process that was used. Titanium minerals have lower concentrations than zirconium minerals, and most of the activity comes from thorium and its descendants. Radioactivity can be significantly influenced by the presence of smaller quantities of other minerals such as monazite, which contains high concentrations of $^{232}$Th and its descendants. The presence of radionuclides in products and waste is caused by the presence of the radionuclides $^{238}$U and $^{232}$Th and their descendants. Thorium is the main component of monazite and pyrochlore, and in smaller amounts in xenotime and zirconium. In the ore (mainly rutile, illmenite, monazite) $^{238}$U and $^{232}$Th concentrations range between 30–600 and 35–6,000 Bq kg$^{-1}$ $^{228}$Ra and $^{226}$Ra (EC, 1999). In the processing procedure, an increase of radionuclide concentrations in side and waste products occurs. Barium sulphate from the extraction process may contain 3000 and 450 Bq kg$^{-1}$ $^{228}$Ra and $^{226}$Ra (EC, 1999).

## 5.7 Zirconium and ceramics industry

Zircon (ZrSiO4) is a zirconium ore used mainly for high temperature purposes in steel and iron foundries, in refractory materials, as well as in fine ceramics. Minor quantities are used as additives in special types of glass. Other uses of zircon and the associated minerals of zirconia and zirconium include abrasive products, catalysts, paints, fuel cladding and structural materials in nuclear reactors (UNSCEAR, 2000). Zirconium is found in nature in pegmatite, where the concentrations of the $^{238}$U decay series nuclides can be up to 74 kBq kg$^{-1}$ (average 3 kBq kg$^{-1}$) and $^{238}$U in bricks can reach 10 kBq kg$^{-1}$ (average 600 Bq kg$^{-1}$) (UNSCEAR, 2000). The activity of $^{238}$U in bricks can reach 10 kBq kg$^{-1}$, while the activities in ceramic products reach 6 kBq kg$^{-1}$ (EC, 1999). Zirconium silicate is used for production of ceramic isolators and for special fire-proof ceramics.

## 5.8 Building materials

All building materials contain radionuclides of the uranium and thorium decay series and $^{40}$K, as a result of the natural content of these in rocks and soil. The presence of radionuclides can also be caused by the presence of industrial by-products (zirconium sand) and waste products (gypsum, ashes, and scoria). This process of recycling waste materials is desirable, but often problems arise because of the content of radionuclides in the recycled product. Natural radionuclide concentrations in building materials as final products are collected in Table 5.6. Specific activities in building materials are typically around 50 Bq kg$^{-1}$ both for $^{238}$U and $^{232}$Th (EC, 1999). In fly ash bricks from the Velenje TPP (coal ash was used as an additive) $^{226}$Ra specific activity was 300 Bq kg$^{-1}$ (Kobal et al., 1990).

***Table 5.6: Content of radionuclides in construction materials (IAEA, 2003a).***

| Material | Specific activity (Bq kg$^{-1}$) | | |
|---|---|---|---|
| | $^{226}$Ra | $^{232}$Th | $^{40}$K |
| Concrete | 1 – 250 | 1 – 190 | 5 – 1,570 |
| Aerated concrete | 9 – 2,200 | < 1 – 220 | 180 – 1,600 |
| Red brick | 1 – 200 | 1 – 200 | 60 – 2,000 |
| Natural stone | 1 – 500 | 1 – 310 | 1 – 4,000 |
| Natural plastering materials | < 1 – 70 | < 1 – 100 | 7 – 280 |
| Cement | 7 – 180 | 7 – 240 | 24 – 850 |

## 5.9 Applications of radium and thorium

In the past, natural radionuclides such as radium were used for decades for their special properties, such as luminescence, in radium baths, as radioactive sources for

chemotherapy. Radium paint was used in the mid 1900s to paint the hands and numbers of some clocks, watches and other instruments. The paint was composed of radium salts and a phosphor and glowed in the dark. Radium emits α, β, and γ rays and when mixed with beryllium produces neutrons. Inhalation, injection, or body exposure to radium can cause cancer and other diseases. Radium is an alkaline earth metal, white but tarnishes black upon exposure to air, luminesces, decomposes in water, emits radioactive radon gas and disintegrates radioactively until it reaches stable lead. Exposure to radium can cause cancer and other illnesses. Radium is over a million times more radioactive than the same mass of uranium.

Thorium is a silvery-white metal which is air-stable and retains its lustre for several months. When contaminated with the oxide, thorium slowly tarnishes in air, becoming grey and finally black. The physical properties of thorium are greatly influenced by the degree of contamination with the oxide. The principal use of thorium has been in the preparation of the Carl Auer von Welsbach gas mantle, used for portable gas lamps. These mantles, consisting of thorium oxide with about 1% cerium oxide and other ingredients, glow with a dazzling light when heated in a gas flame. Thorium is also used as additive to magnesium alloys, tungsten fibres, ceramic products, as a catalyst and so on. It is an alpha emitter. The specific activity of the feed material is in the range of 1,000 – 10,000 Bq $kg^{-1}$ (EC, 1999).

# 6 MANAGING TENORM IN SLOVENIA

Managing waste is one of the least satisfactorily solved tasks within the framework of environmental protection in Slovenia. Disposal to local landfills is practically the only way of managing municipal and most industrial wastes, while these landfills are very often at inappropriate locations, technically unsuitable (non-sealed, non-degassed, flooded or in reach of underground waters) and on top of that, mostly full. Industry mostly deposits its waste together with municipal waste, except in some cases, where the companies maintain their own depositories for certain types of hazardous wastes or individual mono-landfills, e.g. scoria, ashes and tailings disposal sites.

## 6.1 Strategic objective of Slovenia in the field of waste management

An important step in the direction of improvement of the situation is the document Strategic objectives of the Republic of Slovenia in the field of waste management – Problems and specificity in the process of approximation to Europe (adopted by the Government of Republic of Slovenia on August 1st, 1996) (Strateške usmeritve Slovenije na področju ravnanja z odpadki – Problemi in specifičnost pri približevanju Evropi), which determines the basic objectives and goals in the field of waste, and a hierarchy of possible ways of waste management, while taking into account economic development and inclusion in European integration processes (MOP, 1996). The strategic objectives are an integral part of the National Environmental Protection Plan – NPVO (Nacionalni program varstva okolja), which in its programme only recapitulates the main objectives and goals and measures for improvement of current conditions. The goals of waste management focus mostly on the steps necessary for long-term beneficial effects on the environment and on the sources of problems and decisions regarding activities for their reduction or the prevention of negative effects.

The general goals of waste management are among others:

- waste deposited in landfills should not represent a danger potential for future generations
- making an inventory of landfills and other old burdens and creating a prioritized order of rehabilitation and remediation using criteria which take into account unfavourable influences on the environment, the risk for the environment, future intended purpose of the site, remediation costs and its acceptability to the local population,
- old burdens, particularly abandoned landfills, older parts of still active landfills, industrial wastes, polluted soil in certain areas within factories and abandoned industrial buildings, shall be rehabilitated on the basis of a risk analysis and established influences on the environment, with technical measures which shall prevent or lower to a satisfactory level any further burden on the environment and enable a new, environment- friendly intended purpose of the site.

Wastes created through research, processing and exploitation of mineral raw materials (hereinafter: mining wastes) are classified within the framework of the European list of wastes, which entered into force with its last amendment in the beginning of the year 2002 in Slovenia, but have not yet been discussed in detail in the EU legal system (ARSO, 2002). In accordance with the Mining Act two types of waste are created by research, exploitation and processing of mineral raw materials or by carrying out mining works: tailings or overburden, created by the winning or acquiring of ore, and waste produced in the process of enrichment and storing of mineral raw material. Managing of these is planned and carried out in accordance with technical documentation (mining projects, long-term and annual programmes of mineral raw material exploitation, documentation on the effects of mining work on the environment, etc.) and in addition, the mining operator, i.e. the producer of waste, has to provide for suitable monitoring of the effects of these works on the environment.

According to information provided by the Environmental Agency of the Republic of Slovenia (ARSO, 2002), there were approximately 70,000 tons of industrial waste registered in the

year 2000, of these, about 10 % was dangerous. The principal reason for this must be that this issue is not dealt worth within the mining sector, since in most cases there is no monitoring of one's own wastes, which are processed integrally within the production process, including the deposition in their own landfill. Most of the waste material, particularly that which is produced by the construction of infrastructural facilities in underground mines (i.e. accessible underground shafts) or the upper layers at surface exploitation (i.e. humus, useless overburden), are used for either refilling excavated underground sites or for improvement of degraded areas on the surface (i.e. for rehabilitation). Filling underground sites has been established especially within the framework of so-called friendly mining. Substantial changes in this area are expected in the next few years, after the new European Directive on management of these wastes is adopted. In October 2000 in its communication, the European Commission has already taken an initiative regarding the next safe steps in mining in Europe, taking into account the principle of substantiated development (non-energy) of extraction activities. The main demand is to reduce potential effects on the environment after mines cease their operation.

The urgency of a united solution to this issue has given rise to many projects. One of them (while taking into consideration regulations and the situation in the field of mining wastes in the EU) is intended to provide a suggestion of criteria for safe removal of mining wastes in the candidate states, or for the sanitation of the areas already polluted by mining wastes. In this context, Slovenia is treating 8 locations (Velenje, Trbovlje–Hrastnik, Žirovski Vrh, Zagorje, Senovo, Kanižarica, Idrija and Mežica). "Energy waste" is primarily waste from oil refineries, petroleum oil purification, coal pyrolysis, while the biggest share comes from ashes, scoria, and products of flue gas purification from thermal power plants and cogeneration plants (and also boiler rooms).

According to information gathered from the year 1999, the wastes from industry and energy generation are deposited on mono-landfills or industrial landfills at 27 locations in Slovenia (Table 6.1), including the Barje landfill, where scoria and ashes are deposited, from Ljubljana TPP and the landfill for dangerous waste in Metava (Drava, 1999; Drava, 2000).

***Table 6.1: List of industrial disposal facilities covered by analysis (Drava 1999; Drava, 2000).***

| No. | Waste holder | Title of disposal facility |
|---|---|---|
| 1. | Šoštanj Thermal power plant– old | Landfill for ash, slag and products of additive desulphurisation of flue gases |
| 2. | Šoštanj Thermal power plant– new | Landfill for products of desulphurisation of flue gases |
| 3. | Trbovlje Thermal power plant | Landfill for ash and slag |
| 4. | Zagorje Coal Mine in the process of closure | Filling in mine tunnels by Kotredeščica stream |
| 5. | Slovenian steel group– ACRONI, Javornik | Javornik tailings disposal site |
| 6. | Slovenian steel group– ACRONI, Bela | Bela tailings disposal site |
| 7. | Slovenian steel group – Metal Ravne | Ravne tailings disposal site |
| 8. | Štore Steel | Restoration of gravel-pit Vrhe above Štore |
| 9. | TDR – Metalurgija | Industrial disposal facility |
| 10. | Mežica Mine – MPI | Landfill for metallurgical slag and crushed artificial substances |
| 11. | Talum Kidričevo – active | Ash landfill |
| 12. | Talum Kidričevo – non active | Red mud landfill |
| 13. | IMP Livar | Suhi most Polževo landfill |
| 14. | ETA Cerkno | Industrial disposal facility in Novaki |
| 15. | Snaga public enterprise | Landfill for special wastes in Metava |
| 16. | Salonit Anhovo construction materials | Landfill for waste asbestos-concrete materials |

Continued ...

***Table 6.1: Continuation***

| No. | Waste holder | Title of disposal facility |
|---|---|---|
| 17. | LKI Lesonit | Landfill for wooden wastes |
| 18. | IGM Sava | Stari grad gravel pit |
| 19. | Paloma | Industrial disposal facility |
| 20. | IUV (Vrhnika leather industry) | Landfill for wastes from Šmartno Rakovnik Tannery |
| 21. | Sugar industry (green offal) | Landfill – compost of green offal |
| 22. | Sugar industry (solid wastes) | Landfill for soil and stones |
| 23. | Petrol | Landfill for tar |
| 24. | TKI Hrastnik | Unično industrial disposal facility |
| 25. | TOK in bankruptcy | Landfill for factory of organic acids |
| 26. | Cinkarna Celje – Bukovžlak | Bukovžlak landfill for plaster |
| 27. | Cinkarna Celje – Žepina | Landfill for solid wastes with soil partition wall |

# 7 INDUSTRIAL AND MINING ACTIVITIES IN SLOVENIA

The oldest known production of TENORM in the country was related to mercury processing (Idrija, from 1490): roasted residues of Hg ore were deposited everywhere in urban areas, resulting in high radon concentrations (up to 15,000 Bq $m^{-3}$) and enhanced dose rates (Križman et al., 1996). Past coal mining in southern Slovenia (e.g. Kočevje Coal Mine and Kanižarica Coal Mine) produced mine wastes and coal ash which contain relatively high levels of radionuclides of the uranium series (up to 2 kBq $kg^{-1}$). Phosphate ore processing (at Hrastnik) resulted in production of radioactive phosphogypsum, in several cases used also in building construction and disposed into the local stream or to the nearby site. Titanium oxide production from ilmenite ore, containing thorium, resulted mostly in highly radioactive scales and increased dose rates on filters and pipelines in the working area. Past aluminium production (at Kidričevo) resulted in a wide area of deposited processed bauxite with enhanced thorium and uranium contents. Production of fly ash concrete bricks (in Velenje) ended in the middle of the eighties: several measurement campaigns showed moderately high radon concentrations and dose rate levels. Zircon sand was identified as a potential source of occupational exposure in the ceramic industry (in Celje) but due to the applied technology is not of mud concern. Two coal-fired thermal power plants (Šoštanj, 750 MW, lignite and Trbovlje, 200 MW, brown coal) produce fly ash with U–Ra contents of 350 and 180 Bq $kg^{-1}$ respectively (Vokal et al., 2004). The environmental impact of fly ash disposal is mainly related to chemical water pollution and some minor radiological impact (dose to the population is of the order of magnitude of 10 μSv per year) (Mljač, 2001). Contamination at nearby hilly sites with $^{210}$Pb due to stack emissions is under current investigation.

## 7.1 Industrial and mining activities in the territory of Slovenia in the past

Historical data on various activities in the territory of Slovenia reach back to antiquity periods, the Migration Period, the Middle Ages and later industrial periods. The greatest leap in the economic development of the country could be observed in the time after the Napoleonic Wars. The period before the March Revolution witnessed the advent of the first machine factories on Slovenian territory, use of the first steam engines, construction of railways, establishment of the iron industry as an important branch of the economy, flourishing of mining and the search for new deposits of ore, etc. The rapid spread of the railway network in Slovenia facilitated the development of industry and mechanisation, as well as uniting Slovenian lands into a single market. The largest amount of data on ore excavation and processing comes from the period between the 18$^{th}$ and 20$^{th}$ century (see Annex 1), and with it data on the coal and iron industry. Unfortunately, historical literature on industrial activities holds no data on the management of industrial wastes from these activities.

There were numerous deposits of lead, zinc, iron, mercury, copper, antimony and manganese ore, and many coal mines in the Slovenian territory between the 18$^{th}$ and 20$^{th}$ century (Figure 7.1). This was the time when ore excavation and processing was a remunerative business, which led to the exploitation of many smaller ore deposits in addition to large ones, which were not as rich with ore (these are not included in the report) or had very complicated and uneven locations of their ore veins. In the time before 1848 the iron industry constituted a leading branch of the economy in the Slovenian territory. In the Pre-March Period ironworks and blast furnaces could be found in Upper Carniola (Gorenjska – Karavanke mountain range), Lower Carniola (Dolenjska – of importance was the blast furnace plant in Dvor at Žužemberk), Styria (Štajerska – Štore) and Carinthia (Koroška – Prevalje). The iron industry in the Pre-March Period was still based on charcoal and only later switched to coal during a process of modernisation. The mining industry in Carniola had retained its position in 1886 and even made a little progress, while the value of blast furnace and mining production in Styria dropped by 18 %. The year 1888 was particularly critical for the mining industry. Production was in a state of decline almost everywhere, followed by numerous cutbacks in the workforce. This was the era when mines had already become significant consumers of mining and structural timber, fuel and other working material. Production of non-ferrous metals declined considerably in 1893, but the production of brown coal grew steadily and was progressively successful from year to year. Excavation of coal

remained a lucrative business throughout these years. A coal mine in Leše was also among the more important coal mines during the 1830s, while the Styria region played the most significant part, with its numerous workings. The Laško–Hrastnik–Trbovlje district was the most important of all the coal mining districts.

The demand for manganese in the Slovenian territory grew in 19th century after the discovery of ferromanganese. This increased the extraction of other non-ferrous metals, but production never the less started to lessen after the turn of 19th century. The main manganese mine was located at Mount Begunjščica, where more than 80 % of the entire Slovenian production had been acquired at this site in Carniola. Other lesser mining activities were conducted in Styria.

There was only one large excavation of mercury ore in the Slovenian territory in the period between the 18$^{th}$ and 20$^{th}$ century that was located in Idrija, along with much smaller exploitations in the vicinity of Litija and Tržič. These locations were also the site of the extraction of mercury itself, which was used in Idrija in the production of cinnabar. Ore excavation was ample in this period, as was the activity of smelters. Idrija was of the greatest importance with its large ore excavation site and the biggest extraction of the metal itself.

The extraction of zinc and zinc ores constituted a large share of mining activities in the Slovenian territory. Slovenian zinc plants were productive, so that another zinc plant in Celje started operating in 1875. Rich deposits of zinc could be found in the areas that were rich in lead ore (Carinthia), while large zinc plants were located in the region of Celje. Numerous excavations of zinc ore were conducted in Carniola, but their production started to decline considerably towards the end of 19$^{th}$ century, which led to their eventual closure, as well as the closure of zinc plants from that region (e.g., in Šentjanž). The only successful Carniolan zinc plant was located in Zagorje, since it enjoyed a sufficient stockpile of ore that was being provided from Austrian Styria. The largest share of lead ore excavation and processing in 19th century was located in Carinthia (the area of Mežica). From 1872 zinc ore was separated during the excavation of lead ore in the Mežica area, while before that it had been removed along with tailings. There were many important ore deposits in the Litija region of Carniola, which saw a significant increase in production after the opening of a smelter in that area. In Carniolan smelters from Zagorje and Šentjanž lead was also being extracted as a by-product from zinc plants. Production of lead in Carniola was profitable up to 1883, while production in Carinthia from the period between 18$^{th}$ and 20$^{th}$ century was registered as acceptable and gave the desired results. A smaller share of Slovenian extraction of lead ore and lead from this period was also registered in the region of Celje. In most cases of past activities in Slovenia the impact to the environment has not been entirely investigated (Vokal et al., 2004). The content of radionuclides in mining materials has been determinated at five locations (Table 7.1).

***Table 7.1: TENORM from past activities and their impact on the environment (Vokal et al,, 2004).***

| TENORM | Coal mine tailings and coal ash | Coal ash (landfill) | Mercury ore ignited residues | Red mud (bauxite processing) | Phospho-gypsum |
|---|---|---|---|---|---|
| Location | Kočevje | Ljubljana | Idrija | Kidričevo | Hrastnik |
| $^{226}$Ra (Bq kg$^{-1}$) | 300 – 500<br>2100 – 2600 | 450 | 300 – 1100 | 200 ($^{226}$Ra)<br>400 ($^{228}$Th) | 400 |
| $^{222}$Rn (Bq m$^{-3}$) | 80 (daily average),<br>150 (daily peaks) | / | ~30 (daily avg.)<br>100 (daily peaks) | / | / |
| Gama dose rate (μSv h$^{-1}$) | 0.15 – 0.3 | 0.25 | 0.15 – 0.4 | 0.3 | 0.25 |

## 7.2 Industrial and mining activities in Slovenia at present

Slovenia is a country with very long and strong mining tradition. Even though the extent of mining activities has continuously decreased and only represented a small part of the total

industrial production, it is still an important part of Slovene industry because of the profits and employment it provided. The total production of industrial mineral raw materials, construction materials and aggregates is not very large, but it mostly covered almost all national needs. Figure 7.2 shows the present most important sources of enhanced natural radioactivity in Slovenia. Coal production covers 90 % of home consumption. Home production of oil and petroleum oil only covers a small portion of needs and Slovenia depends mostly on imports, and the same applies to metals and ores for home production of aluminium, iron and steel. The stocks of lignite and brown coal in Slovenia are relevant, but their production in the future depends very much on market economics and increasingly strict environment protection requirements. As the most important domestic energy source, Slovenia currently produces lignite and brown coal in two operating mines – coal mines, and their total production, mainly because of environmental requirements, is used exclusively in the energy sector, in thermal power plants. Reorganization of Slovene coal mines began in the early nineties of the 20$^{th}$ century. Thus in 1995 three coalmines started the process of shutting down on the basis of the adopted parliamentary acts and shut-down programmes, and have in fact ceased production in the middle of 1996. The funds for shutting down are provided from the national budget, within the framework of planned programmes for closing pits, environmental rehabilitation of areas degraded by mining works, public relations and provision of funds for restructuring employment. In 2000 state funds from the national budget were provided to gradually shut down the Trbovlje – Hrastnik coalmine, with run-down operation until the year 2007. Production of oil and petroleum oil in Slovenia is practically non-existent, as most of the supplies is already exploited. Greater production would only be possible by implementation of new technologies, which are too expensive. In 1999 the funds for remediation of over 200 old deserted pilot and production drilling wells, pipelines and devices in the north-east part of Slovenia that in fact represent a burden on the environment. The rehabilitation programme is to be completed within the next 10 years. The Žirovski vrh Uranium Mine, which was also meant as a source for the production of fuel for the Nuclear power plant in Krško, ceased to operate in 1990. Today, on the basis of the adopted act, programme and funds shut down works are being carried out, which, due to stricter measures for radiological protection are focused mostly on the rehabilitation of areas degraded by the mining works. This includes uranium ore processing devices, and especially the landfills of hydrometallurgical tailings at Boršt and the spoil tailings at Jazbec. These closure works are to be completed by 2007. The Idrija Mercury Mine and Mežica Zinc Mine operated for several centuries. The first ceased production in 1987, and the second in 1988, they are both currently in the process of closing. The production of industrial mineral raw materials is expected to cover the needs of Slovenian industry for the next period. The stocks of mineral raw materials for the production of cement, lime and brick products are also satisfactory.

The precise amounts of waste produced at the present day are not known. Since closing the lead and zinc mines in Mežica, the mercury mine in Idrija and the uranium mine in Žirovski vrh, Slovenia has no underground mineral mining industry. In all of these locations, closure activities, including ecological rehabilitation of above and underground surfaces, are taking place. After the closing of the lignite mines in Zagorje, Senovo, Kanižarica and Laško, only two mines are left, namely the lignite mine in Velenje and the Trbovlje–Hrastnik lignite mine with a production of about 3.6 million tons of lignite, or 0.6 million tons of coal per year, which are intended for the production of electricity in the thermal power plants at Šoštanj and Trbovlje.

The zinc production plant in Celje (Cinkarna Celje) is the only producer of titanium dioxide in Slovenia and imports the raw material (ilmenite). The beginning of production, the basic programme of which is the production of titanium dioxide pigments, goes back to the year 1973. The combined capacities of all the titanium dioxide pigment producers in the world, using both procedures, sulphate and chloride, amount to approximately 4.5 million tons in the year 2003: the share of Cinkarna Celje represents approximately 1 % (GOV, 2004).

It seems that the aluminium production in Kidričevo will not yet cease to operate, although production has been stopped in many locations in Europe for various reasons. As the production of bauxite ceased in 1991, the input raw material (bauxite) is imported, and waste such as red sludge and ash is no longer produced. The plans look to the future, and one of

the most advanced modern aluminium factories with a capacity of 155,000 tons Al per year is being built (Company Talum, 2006).

Slovenian independence from Yugoslavia in 1991 caused one of the worst economic crises of the Slovenian iron industry, suddenly losing the traditional market in ex Yugoslavia. Due to the at the time self-governing system, non-market economy system in its own economic environment, and the rapid development of the western economy, it was completely unprepared for the competition it had to face in the international market. Thus in 1991 and 1992 the Slovenian government adopted a concept of remediation and restructuring of Slovenian iron fundries by principles of nationalisation – remediation – privatisation. By nationalising in 1991 the Republic of Slovenia became the sole owner of the Slovenian iron industry. Presently the trust Slovenian Steel Group is the only producer of steel in Slovenia. Steel production is based on scrap iron and steel waste (Production programme, 2006).

An overview of TENORM in Slovenia, the total quantity of deposited waste and specific activities of significant radionuclides are given in Table 7.3, while Table 7.2 gives an overview of radiation levels in mines in Slovenia. Radon concentration in the mercury mine amounted to 700-1100 Bq $m^{-3}$ and radon progeny average concentration was 250 Bq $m^{-3}$ (EEC) (Križman et al., 1996c).It can be estimated from the measured values in Table 7.2 that exposure to short-lived radon progeny hardly exceeded 1 mSv per year (Vokal et al., 2004).

***Table 7.2: Radiation levels in mines and ores in Slovenia (Vokal et al., 2004).***

| **Mine** | **$^{222}$Rn (Bq $m^{-3}$)** | **Gamma dose rate (μGy $h^{-1}$)** | **$^{222}$Rn (Bq $m^{-3}$)** |
|---|---|---|---|
| Uranium mine Ventilated | 1500 500 EEC | 5 | average 8,700 |
| Mercury mine | 200 – 1000 250 EEC | 0.5 | 700 – 1,100 |
| Lead and zinc mine (natural ventilation) | up to 5200 up to 4000 EEC | 0.05 | less than 10 |
| Coal mine | 100 – 300 | / | 50 – 550 |

** EEC – equilibrium equivalent concentration of $^{222}$Rn*

***Table 7.3: Survey of activities where TENORM are produced in Slovenia (Repinc et al., 2004).***

| **CATEGORY** 1. Feed material 2. Product 3. Wastes and by-product | **Scale of extraction, production and waste generation** | **Specific activities of radionuclides in by-products and wastes (Bq $kg^{-1}$)** | **Area of deposited materials** |
|---|---|---|---|
| **URANIUM MINING AND MILLING** Uranium Mine Žirovski vrh | | | |
| 1. Uranium ore | 1. Total consumption was 0.6 mega tons uranium ore | | Disposal facility Žirovski vrh: a. Boršt landfill of hydrometallurgical tailings, 38000$m^2$ b. Jazbec Landfill (mill tailings, red mud, filter cake) 36,500 $m^2$ |
| 2. Yellow cake | 2. 452 tons of yellow cake | | |
| 3.a Mill tailings<br>3.b Red mud | 3.a 3.5 Mton<br>3.b 48,518 tons | 3.a 70 g $U_3O_8$ $ton^{-1}$<br>3.b 60,000 $^{230}$Th, 500 $^{238}$U, 200 $^{226}$Ra, < 200 $^{210}$Pb, < 200 $^{210}$Po | |
| 3.c Hydrometallurgical tailings | 3.c 600,000 tons | 3.c 900 $^{238}$U and 8,600 $^{226}$Ra | |
| 3.d Filter cake from treatment plant | 3.d 3,000 tons | | |

Continued …

*Table 7.3: Continuation*

| **CATEGORY**<br>1. Feed material<br>2. Product<br>3. Wastes and by-product | **Scale of extraction, production and waste generation** | **Specific activities of radionuclides in by-products and wastes (Bq kg$^{-1}$)** | **Area of deposited materials** |
|---|---|---|---|
| **STEEL INDUSTRY**<br>Slovenian Steelworks Acroni Jesenice | | | |
| 1.a Metal and non-metal input | 1.a 1148 kg ton$^{-1}$ of steel | | Jesenice: Tailings disposal site at Javornik, 2.2 ha |
| 1.b Alloys | 1.b 63 kg ton$^{-1}$ of steel | | |
| 1.c Flame-retarding material | 1.c 26 kg ton$^{-1}$ of steel | | |
| 2. Steel | 2. 260,000 tons a$^{-1}$ | | |
| 3.a Slag (white + black) | 3.a 36,000 tons a$^{-1}$ | 3.a 93–219 $^{210}$Pb, 52–486 $^{238}$U, 56–634 $^{226}$Ra, 18–53 $^{228}$Ra, 18–52 $^{228}$Th, 137–358 $^{40}$K | |
| 3.b Slag (white) | 3.b 8,200 tons a$^{-1}$ | | |
| 3.c Flame-retarding material | 3.c 950 tons a$^{-1}$ | | Jesenice: Tailings disposal site at Javornik, 2.2 ha |
| 3.d Dust from re-dusting installation | 3.d 4,160 tons (for year 2003, take to modification | | |
| Metal Ravne Steelworks | | | |
| 1. Waste and scrap metal of iron or steel falling alloys thereof falling, ferro-alloys | | | Ravne na Koroškem: Industrial zone, Ravne tailings disposal site, 100,000 m$^2$ |
| 2. Steel (steel profiles and casts) | 2. ~ 88 % regarding input material | | |
| 3.a Slag | 3.a 135 kg ton$^{-1}$ liquid steel | 3.a < 30 $^{238}$U | |
| 3.b Steel falling and scale | 3.b 54 kg ton$^{-1}$ liquid steel | 3.b ~ 49 $^{210}$Pb, ~ 25 $^{238}$U (scale) | |
| **ALUMINIUM PRODUCTION**<br>Talum Plc, Kidričevo | | | |
| 2. Bauxite | | | Talum Kidričevo: – landfill of red mud (covered by layer of soil) 42 ha – landfill of ash (50 % grassed) 8 ha |
| 3.a Red mud<br>3.b Ash | 3.a 6,500,000 tons<br>3.b 1,500,000 tons primary aluminium production 75,000 tons a$^{-1}$ (for year 2000) | 3.a 340 $^{228}$Th, 175 $^{226}$Ra, 125 $^{238}$U<br>3.b 64 $^{228}$Th, 341 $^{226}$Ra, 456 $^{238}$U | |
| **MERCURY MINING AND MILLING**<br>Ex-mine Idrija | | | |
| 1. Mercury ore | | | ~ 7.25 ha |
| 3.a Tecnological tailings | 3. ~ 5 mega tons | 3. ~ 95–1404 $^{238}$U, 41–1364 $^{226}$Ra, 51–1089 $^{210}$Pb, 11–75 $^{232}$Th | |

Continued …

***Table 7.3: Continuation***

| **CATEGORY**<br>1. Feed material<br>2. Product<br>3. Wastes and by-product | **Scale of extraction, production and waste generation** | **Specific activities of radionuclides in by-products and wastes (Bq kg$^{-1}$)** | **Area of deposited materials** |
|---|---|---|---|
| **PHOSPHATE INDUSTRY**<br>TKI Hrastnik d.d. | | | |
| 1. Phosphate rock | | 1. 508 $^{226}$Ra | Unično disposal facility :<br>Wastes from TKI Hrastnik, 5,000 m$^2$ |
| 3.a Phosphogypsum | 3.a 200,000 tons (inactive) | 3.a 263 $^{238}$U, 520 $^{226}$ra, 482 $^{210}$Pb | |
| 3.b Phosphate mud | | | |
| **COAL MINING AND POWER PRODUCTION FROM COAL** | | | |
| Šoštanj Thermal power plant (TEŠ) | | | |
| 1. Lignite | 1. consumption 4 million tons a$^{-1}$ | 1. 78–105 $^{238}$U, 85–92 $^{226}$Ra | Ash landfill, 50 ha |
| 3.a Slag | | 3.a 320–410 $^{238}$U, 280–420 $^{226}$Ra, 420–490 $^{210}$Pb, 44–72 $^{232}$Th | |
| 3.b Ash | 3. 800,000 tons a$^{-1}$ | 3.b 230–340 $^{238}$U, 250–390 $^{226}$Ra, 60–140 $^{210}$Pb, 33–63 $^{232}$Th | |
| Ljubljana Thermal power plant (TE–TOL Ljubljana) | | | |
| 1. Coal | 1. consumption 500,000 tons a$^{-1}$ | 1. < 10 $^{238}$U, 12 $^{232}$Th, 7 $^{226}$Ra, < 10 $^{210}$Pb | Disposal facility of municipal wastes for city of Ljubljana – at Barje; ash is used for stabilisation of tips |
| 3. Ash and slag | 3. 24,000 tons a$^{-1}$ (for year 2003) | 3. ash: 31–54 $^{238}$U, 58–98 $^{226}$Ra, < 120 $^{210}$Pb, 42–82 $^{232}$Th | |
| Trbovlje Thermal power plant (TET) | | | |
| 1. Coal | 1. consumption ~ 620,000 tons a$^{-1}$ | 1. < 10 $^{238}$U, 12 $^{232}$Th, 7 $^{226}$Ra, < 10 $^{210}$Pb | Prapretno disposal site |
| 3. Ash and slag | 3. 195,000 tons a$^{-1}$ (70 % ash, 30 % slag), ~ 40,000–60,000 tons a$^{-1}$ are used for production of building materials and in case of need used in mine | 3. ash: 31–54 $^{238}$U, 58–98 $^{226}$Ra, < 120 $^{210}$Pb, 42–82 $^{232}$Th | |
| Kanižarica Coal Mine in closure | | | |
| 2. Coal | | 1. 1420–1909 $^{238}$U and $^{226}$Ra, 69–98 $^{232}$Th | 20,000 m$^2$ |
| 3. Tailings | 3. 100,000 m$^3$ Annually there are 1,000 m$^3$ of deposited clay, soil for managing the field | 3. 358–777 $^{238}$U, 245–544 $^{210}$Pb | |
| Senovo Coal Mine in closure | | | |
| 2. Coal | | 1. ~ 200 $^{238}$U and $^{226}$Ra | 80,000 m$^2$ |
| 3. Tailings | 3. no more deposition | 3. in average 57 $^{238}$U, 70 $^{226}$Ra, 57 $^{210}$Pb, 42 $^{232}$Th | |
| Zagorje Coal Mine in closure | | | |
| 3. Tailings | 3. 30,000 tons a$^{-1}$ | 3. ~ 55–94 $^{238}$U, 55–95 $^{226}$Ra, 67–91 $^{210}$Pb, 30–54 $^{232}$Th (data from Ruardij) | Backfilling of mine tunnels by Kotredeščica stream |

Continued …

***Table 7.3: Continuation***

| **CATEGORY**<br>1. Feed material<br>2. Product<br>3. Wastes and by-product | **Scale of extraction, production and waste generation** | **Specific activities of radionuclides in by-products and wastes (Bq kg$^{-1}$)** | **Area of deposited materials** |
|---|---|---|---|
| **TITANIUM ORE MILLING**<br>Cinkarna Celje | | | |
| 1. Ilmenit | 1. 44,000 ton a$^{-1}$ | 1. 80–170 $^{238}$U, 150–260 $^{226}$Ra, 50–260 $^{228}$Ra | Landfill Za Travnikom, 6,600,000 m$^2$, 38.5 ha |
| 3.a Gypsum/plaster | | 3.a 66 $^{228}$Th, 79 $^{210}$Pb | |
| 3.b Deposit formed in pipes | 3.b no information | 3.b 160,000 $^{238}$U, 52,000 $^{226}$Ra | |

***Figure 7.1: Past industrial activities in Slovenia which are sources of enhanced natural radioactivity.***

**Figure 7.2: Present industrial activities in Slovenia which are sources of enhanced natural radioactivity.**

# 8 IMPACT OF TENORM ON HUMAN HEALTH

Natural radioactivity is so widespread that it cannot be avoided. Humans are exposed to natural radiation from external sources and by internal radiation from radionuclides incorporated into the body. The point above which special attention must be paid to radioactivity of any material, including TENORM is that when it involves exposure to the public.

Radioactivity below minimal levels is considered to be of no importance in terms of potential effects on individuals or ecosystems. Materials whose radioactivity does not exceed these levels do not require any labelling to identify their content of radionuclides.

The relevance of exposure to TENORM depends very much on local or regional circumstances and behavioural patterns (types of homes, amount of time spent at home, or contaminated areas etc.). For example, a mine located in an unpopulated, remote area poses less of a risk for potential exposures to the general public than similar facilities located near a populated area.

The levels of radioactivity found in TENORM do not produce doses large enough to cause any immediate physical changes, or in other words, with regards to TENORM, acute exposures are not possible. The other type of exposure beside acute is chronic, which involves low-dose delivered to an individual over long periods. Cancer is the principal health effect that has been associated with low-dose radiation (World Health Organization, WHO, 2005). Everyone is chronically exposed to radiation because of the natural background radiation that surrounds us. Chronic exposures do not lead to immediate illness – the doses are just too low. But they can increase a persons risk at forming a cancer sometime in the future. Chronic exposure to TENORM is related to very low levels of radioactivity over a long time. However, through appropriate working practices, the risks from working with TENORM can be easily controlled. For the general public, the effective dose limit concerning artificial exposure is 1 mSv per year. This dose limit serves as an orientation for exposure limits concerning cosmic radiation as well as other natural radiation sources (WHO, 2005).

The presence of TENORM can lead to radiation doses that are not insignificant from a radiation protection point of view. Occupational exposure from natural radiation, in the Report of the UNSCEAR to the General Assembly with scientific annexes (2000) is estimated to contribute more than 80 % of the world-wide annual collective dose from occupational exposure, uranium mining excluded. Also individual doses of workers exposed to TENORM in industry can be significant. When the operator of a practice, or the regulatory authority, is not aware of the problems associated with enhanced levels of TENORM in raw materials, products or residues, and when no protective actions are taken, the doses to workers may even exceed the occupational dose limit. The relevant routes of exposure of workers to TENORM are external radiation and internal exposure, either by inhalation of radon in workplaces or by inhalation of aerosols in dusty working conditions. The use of buildings as dwellings and workplaces can also lead to exposure to TENORM, as well as the use and disposal of waste materials (e.g. mine tailings, fly ash) that can pose significant radiological problems.

The pathways by which TENORM can move through the environment and impact on humans, animals and biota can be divided into on-site pathways and off-site pathways. On-site pathways tend to be direct and usually result in external exposure to gamma radiation or internal exposure resulting from inhalation of radioactive dust or radon progeny. Off-site pathways, on the other hand, are exposures or potential exposures to humans living near a site where TENORM is produced or deposited, and to animals and plants which may be exposed to these technologically enhanced levels of radioactivity; off-site exposures can result from the transfer of TENORM via environmental pathways or from the use of industrial wastes containing TENORM. Environmental pathways tend to be much more indirect and more complex, such as transfer of radionuclides through the food chain by riverine and oceanic transport, by atmospheric dispersion, by resuspension of radioactive dust, etc. These external exposures to the public can result from exposures to gamma radiation resulting from the passage of a cloud of radioactive material through the atmosphere (cloud

shine), or exposure to gamma radiation from material deposited on the surface of the ground (ground shine).

We must stress that the dominant exposure pathways in most situations are external gamma radiation, inhalation of radon gas and its decay products, inhalation of radioactive dust and ingestion of contaminated food and water. Important characteristics that also contribute to risks of developing cancer are the inherent radiosensitivity and exposure history of a person. Parameters that contribute to inherent radiosensitivity include the capabilities for biological defence and repair and cell repopulation and specialisation.

Exposure pathways may be generalised as follows:
- inhalation: atmospheric pathways which lead to irradiation by inhalation of radon/thoron and its daughters, inhalation of airborne radioactive particulate;
- ingestion: atmospheric and terrestrial pathways which can cause doses from ingestion of contaminated foodstuffs, drinking water, and soils and sediments; aquatic pathways which can result in ingestion of contaminated water, ingestion of food produced using irrigation, fish and other aquatic biota and sediments;
- external exposure: from contaminated water bodies, soils and sediments, urban surfaces, other materials and due to passage of a radioactive cloud.

The exposure of every inhabitant of planet may be summarised in terms of exposure to radiation from several radiation sources in the environment:
- natural radiation of terrestrial and cosmic origin,
- nuclear bomb tests and accidents with large amounts of radioactive materials released to the atmosphere,
- human activities carried out in inhabited environments, increasing the concentrations of natural radionuclides

Besides this some of the population is additionally exposed to sources of ionising radiation:
- at work if they are dealing with radiation sources or in a radiation field,
- in medical examinations if they are exposed to ionising radiation.

The radionuclides of most concern for the atmospheric pathways are gaseous $^{222}$Rn and $^{220}$Rn and their solid daughters which become attached to aerosols, and airborne particulates containing $^{230}$Th, $^{226}$Ra and $^{210}$Pb, as well as $^{238}$U. The exposure resulting from airborne particulates is primarily through the inhalation of respirable particles and/or eating food which has become contaminated by $^{230}$Th, $^{226}$Ra and $^{210}$Pb (EC, 1999).

The radiological impact on humans (and plants and animals) can depend strongly on the process that produces TENORM and the pathways by which it is transferred from the source to humans. TENORM can reach humans via several pathways, including the food chain, inhalation or ingestion of airborne radioactive dust and the inhalation of radon isotopes and their progeny which reach the atmosphere as a result of the exhalation of radon isotopes from the surface of the ground surface or from building materials. The radiological impact of internal exposures is usually assessed by means of direct measurement of the body burden and calculation of the dose to a particular organ or group of organs. It is assessed by the use of faecal or urine analysis or, if the intake is known, by the use of a model (e.g. ICRP (International Commission on Radiological Protection) respiratory tract model, ICRP biokinetic model) which simulates the behaviour of the radionuclide in vivo.

Although silica has been identified as a carcinogen more than 10 years ago (International Agency for Research on Cancer, IARC, 1997), the historical neoplasm/cancer hazard among miners is a result of exposure to radon (ICRP, 1994). The suspicion that working in underground mines is associated with cancer goes as far back as the mid 1500s when Georgius Agricola wrote about the high mortality of miners in the Carpathian Mountains of Eastern Europe (Craven and Smit, 2006). Later autopsy studies of miners in the 1800s in that region demonstrated that chest tumours, later demonstrated to be primary lung cancer, were a common cause of death (Frumkin and Samet, 2001). In the early 20$^{th}$ century, mines in the present Czech Republic were found to have high radon levels and researchers suspected that this exposure was the cause of the miners´ lung cancer. In the 1950s, radiation scientists recognized that particulate radon progeny and not radon gas delivered

the radiation dose ultimately responsible for causing cancer. Several epidemiological cohort studies of radon-exposed underground miners with relatively high exposures during the 1950s and 1960s confirmed the association between radon exposure and lung cancer (NRC, 1998).

It is known that the doses involved with TENORM will not cause any immediate health impact. We don not know exactly what the risks of getting cancer are from a low-level radiation dose, primarily because the few effects that may occur cannot be distinguished from normally occurring cancers. However, we can make estimates based on extrapolation from the extensive knowledge resulting from scientific studies on high dose effects. The uncertainty associated with this risk estimate does not rule out the possibility of higher risk, or the possibility that the risk may even be zero at low occupational doses and dose rates. The radiation risk incurred by a worker depends on the amount of dose received.

# 9 RADIATION MEASUREMENTS

In the literature, measurements (EPA, 2000b) of external gamma radiation and measurements of radionuclides in soil are presented as:

- direct measurements for alpha, beta and gamma emitting radionuclides (e.g., *in situ* gamma spectrometry),
- scanning surveys for alpha, beta and gamma emitting radionuclides.

To conduct direct measurements of alpha, beta, and gamma surface activity, instruments and techniques providing the required detection sensitivity are selected. The type of instrument and method of performing the direct measurement are selected as dictated by the type of potential contamination present, the measurement sensitivity requirements, and the objectives of the radiological survey. Direct measurements are taken by placing the instrument at the appropriate distance above the surface, taking a discrete measurement for a pre-determined time interval (e.g., 10 s, 60 s, etc.), and recording the reading. Measurements at several distances may be needed. Near-surface or surface measurements provide the best indication of the size of the contaminated region and are useful for model implementation. Gamma measurements at 1 m provide a good estimate of potential direct external exposure. A one minute integrated count technique is a practical field survey procedure for most equipment and provides detection sensitivities that are below most DCGLs. However, longer or shorter integrating times may be warranted. Direct measurements may be collected at random locations in the survey area. Alternatively, direct measurements may be collected at systematic locations and supplement scanning surveys for the identification of small areas of elevated activity. Direct measurements may also be collected at locations identified by scanning surveys as part of an investigation to determine the source of the elevated instrument response. Professional judgment may also be used to identify locations for direct measurements to further define the areal extent of contamination and to determine maximum radiation levels within an area, although these types of direct measurements are usually associated with preliminary surveys (i.e., surveying, characterization, remedial action support). All direct measurement locations and results should be documented.

Scanning is the process by which the operator uses portable radiation detection instruments to detect the presence of radionuclides on a specific surface (i.e., ground, wall, floor, equipment). The term scanning survey is used to describe the process of moving portable radiation detectors across a suspect surface with the intent of locating radionuclide contamination. Investigation levels for scanning surveys are determined during survey planning to identify areas of elevated activity. Scanning surveys are performed to locate radiation anomalies indicating residual gross activity that may require further investigation or action. Small areas of elevated activity typically represent a small portion of the site or survey unit. Thus, random or systematic direct measurements or sampling on commonly used grid spacings may have a low probability of identifying such small areas. Scanning surveys are often relatively quick and inexpensive to perform. For these reasons, scanning surveys are typically performed before direct measurements or sampling. In this way time is not spent fully evaluating an area that may quickly prove to be contaminated above the investigation level during the scanning process. Scans are conducted which would be indicative of all radionuclides potentially present, based on the Historical Site Assessment, surfaces to be surveyed, and survey design objectives. Documenting scanning results and observations from the field is very important. For example, a scan that identified relatively sharp increases in instrument response or identified the boundary of an area of increased instrument response should be documented. This information is useful when interpreting survey results.

High penetration power of gamma rays almost limits their detection and measurement by solid state detectors (Knoll, 1989). Scintillation detectors provide one alternative to the detection and measurement of gamma rays. Poor resolution of scintillation detectors limits their usefulness, especially in closely spaced multi-energy spectroscopy. The energy required to produce one charge carrier (photoelectron) is of the order of 100 eV (Knoll, 1989), Therefore, a typical gamma photon produces a few thousand charge carriers. With such small number, the statistical fluctuations will place an inherent limitation on the energy

resolution that can be obtained under normal conditions. The only way to improve energy resolution is through reduction of the statistical fluctuations, which can only be achieved by increasing the number of charge carriers. The use of semiconductor detectors can achieve this objective, since the average energy required to produce one electron-hole pair is about 3 eV, and, therefore, 30 times more charge carriers are generated.

## 9.1 Process of sampling and preparation of samples for TENORM identification

For the sampling of soil and deposited materials a process based upon the strategy of the *judgemental sampling approach* was used. The practical work was made by Repinc et al. in 2004. Samples of soil and deposited materials were taken only from a specific spot in the research area, where increased levels of natural radiation were suspected, on the basis of historical information and the use of an instrument for measuring external gamma radiation. Such a sample is not representative of the actual concentration of pollutants in the entire research area, but it is representative of the specific sampling site and serves for the identification of pollutants from specific spots in the research area where their concentration level is the highest ("worst case conditions").

Preparation of samples of soil and deposited materials for gamma-ray spectrometry was based upon:

- drying at 60 ºC,
- grinding or pulverization (if necessary, as in the case of large furnace residues or tailings) and sieving through a 2 mm sieve,
- preparation of a geometrically-appropriate sample for gamma-ray spectrometric measurement.

## 9.2 Measurement of external gamma radiation

The following equipment for measuring external gamma radiation, used by Repinc et al. (2004), was mostly used:

- *Portable Meter Eberline ASP–1* with a scintillation detector (Ø "1×1" NaI crystal), intended principally for low levels of radiation. The instrument is equipped with a speaker and scale with the option of a readout in various ranges, which offers only a direct readout of the number of counts per minute (cpm) with a sensitivity of 4.9×10 μSv $h^{-1}$ for $^{137}Cs$ (with a 10 % margin of error). It provides identification of potentially increased gamma radiation, but does not provide data on the dose rate of external gamma radiation. The range from x10K to x100K (10,000 to 100,000 cpm) was used.
- *ADM–300SI Multi-function Survey Meter*, which is equipped with two built-in Geiger–Muller detectors for measuring dose rate of gamma radiation in the range of 0.01 μSv $h^{-1}$ – 100 Sv $h^{-1}$ with a ±15 % margin of error in the range up to 10 Sv and a response time of 2–5 seconds. The instrument provides the use of a scintillating detector (Ø"3x3" NaI crystals) that only provides information on the number of counts, much like the ASP–1 instrument.
- *FieldSPEC* instrument with a scintillation detector (Ø"1×2" NaI(Tl) crystal) for measuring dose rate of gamma radiation in the range from 10 nSv $h^{-1}$ to 250 nSv $h^{-1}$ and a G–M detector for measuring dose rate in the range from 250 nSv $h^{-1}$ to 1 Sv $h^{-1}$ with a sensitivity of >500 counts per second for μSv $h^{-1}$ $^{137}Cs$.

Measurements were taken at the standard height of 1 metre above ground.

## 9.3 Gamma-ray spectrometry

The gamma-ray spectrometry method is used for the analysis of gamma emitting radionuclides and in determining their concentration in soil and deposited materials.

The art of gamma ray spectrometry gained a great deal from the invention of semiconductor detectors. Lithium drifted silicon detectors have become the most common choice for low energy photon spectrometry (LEPS) systems, because of their excellent resolution at these energies and the fact that they are almost transparent to the high energy gamma ray photons. High Purity germanium detectors (HPGe) and Lithium drifted Germanium (GeLi) detectors are excellent choice for the high energy gamma rays, because of the high atomic number of germanium, and the greater depletion depth achievable in them. HPGe´s are perferred over GeLi detectors, because the latter requires cooling down to liquid nitrogen temperatures during storage and operation to suppress thermal generation of electron-hole pairs and to maintain the lithium profile (Knoll, 1989), while HPGe´s only require cooling during operation. The other characteristic of both are comparable (Knoll, 1989).

An HPGe detector with a relative efficiency of 25 % and a resolution of 1.9 keV was used in study made by Repinc et al. (2004). The dry, pulverised or sieved sample was weighed into a measuring vessel with a volume of 100 $cm^3$ and sealed airtight. Indicative levels were determined of $^{238}U$, $^{210}Pb$ and $^{40}K$ from brief gamma-ray spectrometric measurements carried out before the establishment of equilibrium. To conduct a complete gamma-ray spectrometric determination, it is necessary to wait at least four weeks, in order to let radioactive equilibrium established. $^{210}Pb$ was determined directly ($E\gamma$ = 46.5 keV), $^{238}U$ determined through its daughter product $^{234}Th$ ($E\gamma$ = 63.3 keV) and $^{226}Ra$ through the short-lived daughter products of radon $^{214}Pb$ ($E\gamma$ = 295.2 and 351.9 keV) and $^{214}Bi$ (609.3 keV). $^{228}Ra$ was likewise determined through its daughter product $^{228}Ac$ ($E\gamma$ = 338.5 and 911.1 and 968.9 keV) and $^{228}Th$ through its daughter products $^{212}Pb$ ($E\gamma$ = 238.6 keV) and $^{208}Tl$ ($E\gamma$ =583.1 keV). The activity of $^{40}K$ was measured at the energy of $E\gamma$ = 1460.8 keV and the activity of $^{137}Cs$ at $E\gamma$ = 661.6 keV. A correction of the results due to sample self-absorption was made, based upon additional measurements of the sample with external gamma-ray sources of $^{241}Am$, $^{226}Ra$ and $^{137}Cs$ according to the method of Cutshall (Cutshall et al, 1983). The certified reference materials IAEA-327 (soil) and IAEA-326 (soil) were used for efficiency calibration (Repinc et al., 2004).

# 10 TENORM IN SLOVENIA

TENORM have attracted much attention among professionals and the responsible authorities in recent years. Also in the new Act on radiation protection and nuclear safety, this issue is considered in detail. Researchers from the Jožef Stefan Institute collected a great deal of data on the radioactivity of technological and raw materials. This thesis, available reports on research projects, studies related to this field and historical written documents on former mining and industrial activities were useful tools for identification of relevant locations in the field. Namely, the data related to deposited materials from past industrial activities presented in this thesis include data on residues of processed mercury ore in Idrija, the phosphate industry at Hrastnik, coal mining in Zasavje region and at Kočevje and Kanižarica, uranium tailings at Žirovski vrh, red mud from bauxite processing at Kidričevo, slag from iron factories at Jesenice and Ravne, and tube scales from crude oil at Lendava. In addition, the present activities are also reported, such as coal ash production at the thermal power plants at Šoštanj, Trbovlje and in Ljubljana, and $TiO_2$ production at Celje. Within this set of present activities with materials containing enhanced natural radioactivity in the country, the use of zircon minerals (coatings in the ceramic industry and in production of dishes, coating of melting ovens) and the use of welding electrodes with the addition of thorium were identified. The identification process and the creation of an inventory of TENORM provided a precise delimitation of old burdens from the past activities and materials with technologically enhanced natural radioactivity still produced today. According to SNSA Annual Report 2004 on radiation and nuclear safety in the Republic of Slovenia (SNSA, 2005), most such deposited waste material consists of deposited coal ash (about 30 million tons), red mud (6.5 million tons) and iron slag and mercury ore residues (1.5 million tons and 1 million tons respectively), uranium mine waste from Žirovski vrh (3.5 million tons). The highest content of the radionuclide $^{226}Ra$ is in the uranium tailings (8,600 Bq $kg^{-1}$) and, in parts, in coal ash from Kočevje and Kanižarica (up to more than 2,000 Bq $kg^{-1}$), while other materials are much less radioactive (mostly about 400 Bq $kg^{-1}$ of $^{226}Ra$). Some TENORM are deposited in the controlled areas of the enterprise and others on areas accessible to the public. If we compare the radionuclide contents in our TENORM to the levels elsewhere in Europe or in the world, we find that radioactivity of our materials is mostly lower, with the possible exception of coal ash from the south of Slovenia and mercury ore residues at Idrija.
Now the biggest environmental and health problems in Slovenia are related to Pb in Zgornja Mežiška valley, Hg in the area of Idrija and Trieste Bay, Cd and Zn in Celje, toxic metals and other pollutants in vicinity of TPPs etc.

## 10.1 Survey of activities where TENORM are produced in Slovenia

In Slovenia two major source groups of TENORM exist:

a) past production:
   - coal ash: disposal, use in building structures
   - uranium ore mining and milling (in pre-NPP period)
   - phosphate processing (phosphoric acid production, fertilizers)
   - mercury ore mining and processing (lasting half a millennium)
   - iron and steel production (2 factories)
   - oil and gas production (1 ex-refinery)

b) current production or processing:
   - coal ash (electricity generation and disposal) from three Slovenian thermal power plants (TPPs)
   - $TiO_2$ pigment production in Cinkarna Celje
   - bauxite processing (1 factory- Talum)
   - phosphate processing (1 factory – TKI Hrastnik)
   - zircon minerals in ceramics, utensil enamel, melting furnace linings (e.g. EMO Kemija, Martex Volčja Draga, Gorenje – Keramika)
   - iron and steel production (1 factory)

While it is understood that the exposure of the public can be kept low under normal operational conditions for most industries, the absence or loss of institutional control over

contaminated lands on which large amounts of TENORM–containing residues have been deposited can result in redevelopment, intrusion and uncontrolled reuse of TENORM–containing materials.

## 10.2 Studies undertaken in the past

Despite the fact that measuring natural radioactivity is not yet required by law in Slovenia, numerous measurements of external radiation, natural radionuclides in the air, soil and water, and particularly radon in residential areas and in workplaces, have been carried out. Systematic research on radon begun in 1990 (Vaupotič et al, 1991). The main objective of these studies was to obtain an overview of the situation, discovering any potential higher concentrations and finding what causes them. Researchers also investigated if there are areas in Slovenia where higher concentrations of radon in the residential environment can be expected, due to the geological composition and structure of the ground. The results of the measurements carried out in schools and kindergartens so far are a rich database and will, together with measurement results in residential apartments, serve as a basis for determining intervention levels of radon for Slovenia (Vaupotič, 1994).

Measurements of natural radioactivity of Slovenian territory begun after radioactivity was discovered in the lower strate of the mercury mine in Idrija in year 1947. In 1990 the Slovene Geological Institute begun a programme to make the first chart of natural radioactivity in soil in Slovenia (Andjelov, 1993). Measurement of gamma radiation was made in a square sampling grid of 5 km × 5 km. The measurements showed that the potassium contents in soil in Slovenia range from 0.05 to 4.65 %, with an average of 1.23 % (385 Bq $kg^{-1}$), while the highest levels were measured in the area of Idrija – Škofja Loka and eastern part of the hills in the Posavje area and the eastern part of Pohorje (Andjelov, 1993).

As early as year 1953 radioactive prospecting in Slovenia showed increased levels of radioactivity in coal in Kočevje, Kanižarica and Vremski Britof. The same year experimental incineration of radioactive coal begun in three companies, which undertook to conserve the ash. The coalmine at Kočevje was researched systematically. In 1957 this research was terminated, because of the unresolved issue of processing uranium–containing coal into concentrate (Omaljev, 1971).

The western part of Posavske gube, which covers the central part of Slovenia from Idrija through Žirovski vrh, Škofja Loka, Trojane, Laško and Krško, to the Croatian border, was measured for several radioactive anomalies. The increased radioactivity of old scoria, accumulated from the smelter in Idrija thus supposedly originates from slate, which is 5–10 times more radioactive than other rock from the Hg mine in Idrija. Individual samples of slate from the mine in Idrija are supposed to contain up to 0.2 % of uranium. The total stock of slate in Idrija was estimated as several million tons, and while seeking and exploiting mercury ore, approximately 1 million tons were unearthed.

The results of prospecting in Žirovski vrh in 1960 demonstrated that the grey gröden sandstone and conglomerate in the north-east slope of Žirovski vrh in an over 10 km long zone were mineralized. In Karavanke, south of Ljubelj, radiometric analysis of compact lime showed a great amount of thorium next to a significant amount of uranium. In Pohorje and in the surroundings of Črna na Koroškem, the possibility of formation of primary locations of uranium ore can be deduced from the structures. The areas south-east of Črna na Koroškem are particularly interesting. In the Kočevlje Coal Mine increased radioactivity of the lignite was measured, where the uranium is probably bound to organic coal substances.

### 10.2.1 Žirovski vrh Uranium Mine

The uranium field was discovered in May 1960. Žirovski vrh Uranium Mine (RŽV) was founded in 1976, the excavation the uranium ore begun in 1981, and in 1984 the production of uranium yellow cake concentrate. The Žirovski Vrh Uranium Mine and Mill was in operation in the period from 1981 to 1990. Uranium concentrate was acquired in an acid

process. Its lifetime production was approximately 0.6 tons of uranium ore and approximately 3.5 million tons of tailings were excavated and 452 tons ($U_3O_8$ equivalent) of yellow cake were produced (Vokal et al., 2004). Both the mine and the mill are undergoing decommissioning and remediation of surface disposal of 1,548,000 tons of mine waste and red mud, and 593,000 tons of mill tailings.

Since the beginning of operation of the Boršt disposal site until June 1990, when production in the RŽV processing installation was terminated, 600,000 tons of hydrometallurgical tailings (HMJ) were deposited. HMJ is sandy, ground material, left-over from uranium ore processing. Its chemical structure is predominantly $SiO_2$, gypsum and sulphate salts. HMJ is a fine sand with grain size under 0.5 mm. On average it contains 0.9 kBq $kg^{-1}$ $^{238}U$, 3.7 kBq $kg^{-1}$ $^{230}Th$ and 8.6 kBq $kg^{-1}$ $^{226}Ra$, and it also contains soluble inorganic substances, particularly the ions $NH_4^+$ and $SO_4^{-2}$ (Repinc et al., 2004).

During operation of RŽV a disposal site formed in the deep gorge of the Jazbec brook was used for depositing mine waste material. Regular deposition of waste mine material at the Jazbec disposal site begun in 1983, and ended in 1990, along with the cessation of the regular production of uranium concentrate. Since then the mine waste material and contaminated materials, acquired by decommissioning and decontamination of some of the mine facilities and surfaces, have been deposited at the landfills. 1,500,000 tons of mine waste with an approximate concentration of 65–70 g $ton^{-1}$ $U_3O_8$ was deposited at the Jazbec disposal site (Logar, 1996). Next to that, 48,500 tons of red mud (60 kBq $kg^{-1}$ $^{230}Th$, 48 g $ton^{-1}$ $U_3O_8$ or 500 Bq $kg^{-1}$ $^{238}U$, 200 Bq $kg^{-1}$ $^{210}Pb$ and <200 Bq $kg^{-1}$ $^{210}Po$), a by-product of uranium ore production and some building construction materials were deposited here (Križman, 1996; Križman et al., 1995). At this mill waste tailings pile 3,000 tons of precipitated sediment from the mine water purification device were deposited. The dose rate of the external gamma radiation at the tailings pile and at its edge is 3–4 times higher than that of the natural background, (0.11 μSv $h^{-1}$ – 0.15 μSv $h^{-1}$ in nature, approximately 0.35 μSv $h^{-1}$ at the landfill) (Repinc et al., 2004). About 10 m away from the landfill the levels fall to the normal value in the natural environment, depending on the geology of the ground. Therefore, only the owners of surfaces very close to the landfill are and will be exposed to external radiation during the short period of carrying out agricultural activities (mowing, forestry).

An RŽV report (Benedik et al., 2004b) gives an evaluation of the influence of the RŽV on the environment and a comparison between operational and post-operational conditions. The results of the measurements show that additional external radiation, originating from the RŽV sources, is very low compared to the natural background. A measurable increase can only be noticed in direct proximity of mining installations and spoil tips, but not in the wider settlement area. The immersion contribution of short-lived radon progeny in the air, amounting to 2.5 μSv, is more relevant (Benedik et al., 2004b). The report indicates that enhanced radioactivity was measured up to a distance of 200 m from the Boršt disposal site. By covering with soil the upper part of the tailings pile, radiation in the surrounding area decreased. The owners of the surrounding land are only exposed to increased radiation in the case of substantial works on these lands. The estimated effective dose received is under 2 μSv, and the share of external gamma radiation from RŽV sources contributes 1.2 % (Benedik et al., 2004b). A comparison of the effective doses from RŽV sources received by the population living in nearby villages in the period 1991 to 2006 is demonstrated in Figure 10.1. It can be seen there is an increasing trend in the period 2001 – 2003.

According to Slovenian legislation and the above mentioned Council Directive No. 96/29/EURATOM, the dose limit, which may be received by a member of the population, is 1 mSv per year. The value of 0.34 mSv, which the population received in 2003, as the contribution from the mine, represents approximately one third of this value.

The monitoring programme of environmental radioactivity of the Žirovski Vrh Uranium Mine– the mine is currently in the closure phase – consists of measurements of the activities of long-lived radionuclides from uranium–radium decay chain in the environment, measurements of radon and its decay products in the air, and external radiation. Mainly the settled areas located in the valley, up to 3 km from the existing radiation sources, are

controlled. The impacts of the former mining and milling facilities have to be evaluated with regard to the reference measurements carried out at relevant locations outside the influence of the mine.

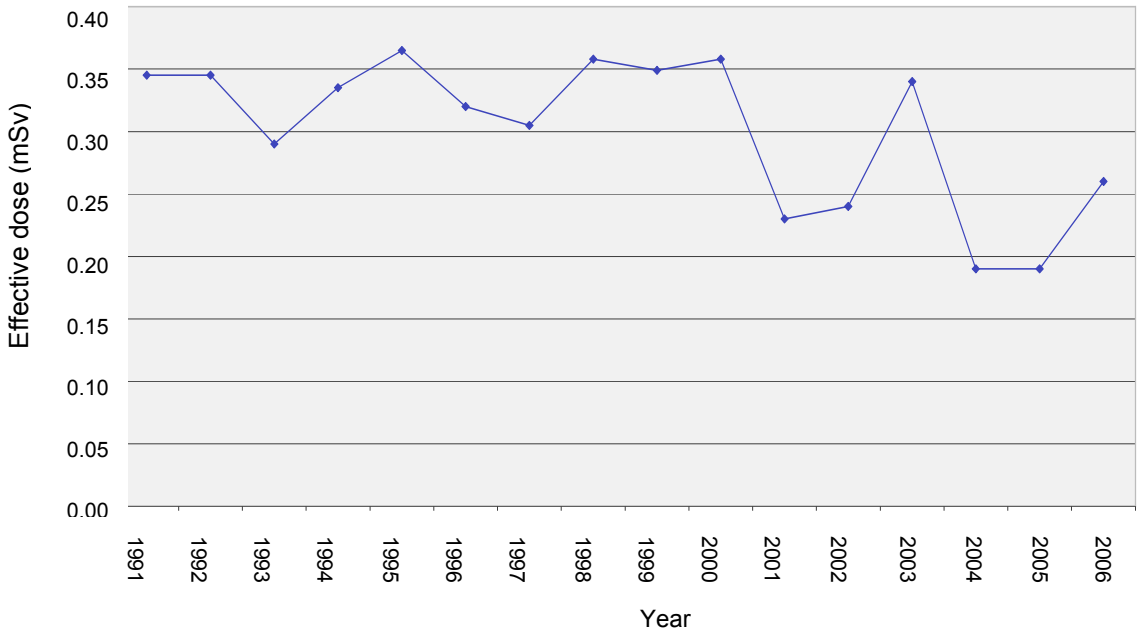


***Figure 10.1: Comparison of the effective doses in period 1991 – 2006 from RŽV sources.***

The calculation of an effective dose takes into account the following exposure pathways: inhalation of long-lived radionuclides, radon and its short-lived progeny, ingestion (intake with food and water) and external gamma radiation. The radiation exposure of the population living in the vicinity of the mine was estimated to be 340 μSv in the year 2003 (SNSA, 2004). This annual effective dose is considerably higher than in the previous two years (in 2001: 230 μSv and in 2002: 240 μSv) and the three following years (in 2004: 190 μSv, in 2005: 190 μSv and in 2006: 260 μSv) (Figure 10.1). The increase could be attributed to the lower measured value of the natural radon background. If we take into account long-term average concentrations at the reference point for radon background, the effective dose for 2003 would be essentially lower (about 200 μSv, which is similar to the last two years). The most important radioactive contaminant of the mine environment was still radon and its progeny, which contribute almost three quarters of the additional exposure (Table 10.1).

***Table 10.1: Effective doses in the period 2001 – 2006 received by the population in nearby villages due to radiation sources of the Žirovski Vrh Uranium Mine.***

| **Exposure pathway** | **Important radionuclides** | **Annual effective dose (μSv)** | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Year 2001** | **Year 2002** | **Year 2003** | **Year 2004** | **Year 2005** | **Year 2006** |
| Inhalation | - aerosols with long-lived radionuclides | 3 | 5 | 3 | 5 | 7 | 1 |
| | - only $^{222}$Rn | 4 | 4 | 6 | 4 | 5 | 6 |
| | - Rn and short-lived progeny | 164 | 174 | 270 | 160 | 130 | 208 |
| Ingestion | - U, $^{226}$Ra, $^{210}$Pb, $^{230}$Th in drinking water | 29 | 15 | 15 | 13 | 11 | 25 |
| | - fish ($^{226}$Ra, $^{210}$Pb) | 1 | 1 | 1 | 1 | 3 | 3 |
| | - agriculturl products, food ($^{226}$Ra, $^{210}$Pb) | <21 | <40 | <40 | <16 | <42 | <42 |

Continued …

***Table 10.1: Continuation***

| Exposure pathway | Important radionuclides | Annual effective dose (μSv) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Year 2001 | Year 2002 | Year 2003 | Year 2004 | Year 2005 | Year 2006 |
| External radiation | - γ radiation $^{222}$Rn and its decay products (deposition, immersion) | 2 | 2 | 2 | 1 | 1 | 2 |
| | - γ radiation of long-lived radionuclides | – | – | – | – | – | – |
| | - γ radiation in the area of uranium mill tailings | 2 | 2 | 2 | 2 | 2 | 2 |
| Total annual effective dose (rounded) | | 230 | 240 | 340 | 190 | 190 | 260 |

*Source: Annual Report 2001 on radiation and Nuclear Safety in the Republic of Slovenia (SNSA, 2002). Annual Report 2002 on radiation and Nuclear Safety in the Republic of Slovenia (SNSA, 2003). Annual Report 2003 on radiation and Nuclear Safety in the Republic of Slovenia (SNSA, 2004). Annual Report 2004 on radiation and Nuclear Safety in the Republic of Slovenia (SNSA, 2005). Annual Report 2005 on radiation and Nuclear Safety in the Republic of Slovenia (SNSA, 2006). Annual Report 2006 on radiation and Nuclear Safety in the Republic of Slovenia (SNSA, 2007).*

### 10.2.2 Idrija Mercury Mine

Mercury was discovered in Idrija in 1497, and mining was taken over by the government in 1580. Idrija is one of the few places in the world where mercury occurs in both its elemental liquid state and as cinnabar (mercury sulphide) ore. In Idrija, mercury ore has been excavated for 500 years. Ore was crushed and roasted, and the residues were disposed of during the whole of this period everywhere in the town and its surroundings. Later, on the some locations, houses and buildings were constructed. After World War II a quite high content of uranium was discovered in the cinnabarite, on average 100 grams of uranium per ton of ore (Križman and Stegnar, 1996). In the fifties more than one ton of radioactive ore was processed into yellow cake (Križman and Stegnar, 1996). At its peak, Idrija was the second largest mercury mine in the world, after Almaden, Spain, eventually yielding 13 % of all the mercury ever mined; 150,000 tons (Repinc et al., 2004).

The first reports on uranium in the mine are from the year 1947. After 1949 they discoverd that bituminous layers of ore, called “skonca” shales, contain uranium in substantial concentrations, which were almost 10 times higher than in other rock (Križman and Stegnar, 1996). In the period 1953–1957 1,657 tons of material with an average uranium content of 136 g ton$^{-1}$ were acquired in Idrija, which was partially processed into yellow cake in the so-called Viniči processing plant (Omaljev, 1971).

Measurements of radiation in Idrija area in the nineties confirmed increased external gamma radiation, as well as high levels of specific radioactivity in the soil of those parts of the city where the technological tailings were deposited. The measured dose rates of external gamma radiation ranged from 0.25–0.4 μGy h$^{-1}$, the higher values being measured on primary residues (Križman at al., 1996c). The results of the gamma dose-rate measurements are shown in Table 9.2. High concentrations of radon were found in buildings constructed on sites where waste materials had been deposited. The average radon concentration was 468 Bq m$^{-3}$, and in some of the older buildings it even reached 3 and 15 kBq m$^{-3}$ (Križman et al., 1996c).

The residue found around the former incineration plant is the primary incineration residue, while the secondary and tertiary residues are the ones that are mixed with the soil, sand or other materials. The level of uranium in the incineration residue is 4 to 20 times enhanced compared to background levels and is demonstrated in Table 10.2.

Incineration residues are deposited on approximately 25 % of the surface of the urbanized city centre, primary residues covering 7.25 ha, secondary residues 17 ha and tertiary residues approximately 5.5 ha (Drava, 2000).

***Table 10.2: Content of radionuclides and measured dose rates of gamma radiation on deposition facilities (wastes from Idrija) (Križman et al., 1996c).***

| Sample | Dose rate (μGy $h^{-1}$) | Specific activity (Bq $kg^{-1}$) | | | |
|---|---|---|---|---|---|
| | | $^{238}U$ | $^{226}Ra$ | $^{232}Th$ | $^{40}K$ |
| Primary incineration residues | 0.25 – 0.4 | 996 – 1,090 | 1,020 – 1,140 | 52 – 64 | 345 – 635 |
| Secondary incineration residues | 0.16 – 0.24 | 214 – 870 | 110 – 845 | 30 – 48 | 295 – 920 |
| Tertiary incineration residues | 0.12 – 0.14 | 167 | 161 | 49 | 530 |
| Soil (background) | 0.08 – 0.11 | 60 | 60 | 60 | 450 |

A subsequent sampling of furnace residues was carried out in year 2004 (Repinc et al., 2004) in cooperation with workers of the Idrija Mercury Mine Company at the time of excavation works in the town centre for purposes of the local infrastructure. This made work easier and enabled sampling at greater depths. The results of measurements are displayed in Table 10.3. At sampling site 1 there is increased specfic activity of radionuclides from the $^{238}U$ decay series. Increased valuse indicate that radionuclides from the $^{238}U$ series are concentrated in furnace residues which are deposited on the Kolektor disposal site and also on Prejnuta.

***Table 10.3: Measurements of radionuclide content in soil samples from area of the town centre in Idrija (Repinc et al., 2004).***

| Samples | Specific activity (Bq $kg^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}Pb$ | $^{238}U$ | $^{226}Ra$ | $^{228}Ra$ | $^{228}Th$ | $^{40}K$ | $^{137}Cs$ |
| Sample site 1 – tailing disposal site Kolektor, sampling at depth of 1 m | | | | | | | |
| Coarse furnace residues | 83 ± 4 | 88 ± 9 | 87 ± 3 | 29 ± 1 | 29 ± 2 | 243 ± 9 | < 10 |
| Fine residues | 236 ± 28 | 384 ± 33 | 422 ± 13 | 33 ± 3 | 30 ± 3 | 211 ± 14 | < 10 |
| Furnace residues | 1,089 ± 72 | 1,404 ± 126 | 1,364 ± 65 | 75 ± 10 | 74 ± 15 | 450 ± 13 | < 10 |
| Sample site 2 – Prejnuta tailing disposal site, sampling at depth of 3 m | | | | | | | |
| Furnace residues | 479 ± 57 | 866 ± 28 | 683 ± 19 | 44 ± 3 | 40 ± 1 | 311 ± 11 | < 10 |
| Sample site 3 – Mercator tailing disposal site, sampling at depth of 1 m | | | | | | | |
| Coarse furnace residues | 45 ± 4 | 65 ± 6 | 60 ± 4 | 22 ± 3 | 22 ± 2 | 199 ± 7 | < 10 |
| Mixed furnace residues | 93 ± 14 | 124 ± 11 | 100 ± 4 | 17 ± 9 | 25 ± 3 | 214 ±7 | < 10 |
| Sample site 4 – Bašerija, sampling on excavation | | | | | | | |
| Mixed furnace residues | 51 ± 3 | 59 ± 10 | 41 ± 1 | 10 ± 4 | 11 ± 1 | 122 ± 9 | 65 ± 4 |

### 10.2.3 Kočevje Coal Mine

In Kočevje, the coal mine was in operation from 1803 and ceased production in 1972. In parallel to an average annual production of about 100,000 tons in this century, huge amounts of coal mining wastes and coal ash were freely disposed of on an area of 1.25 $km^2$ between the town of Kočevje and the nearby village of Šalka vas. As an example map with marked disposal area of mining is presented in Figure 10.2. Self-ignition of coal residues often occurred, leading to a smoky atmosphere in the valley. Excavated underground shafts collapsed and a lake with an area of 0.25 $km^2$ appeared in the vicinity of the town.

After World War II it was recognized that brown coal from the Lower Carniola region (coal mines in Kočevje, Kanižarica, Vremski Britof) contain quite high amounts of uranium, up to ten times more than other coals in Slovenia (Križman et al., 1996b). Radiation measurements were performed in the last decade in the mining and disposal area.

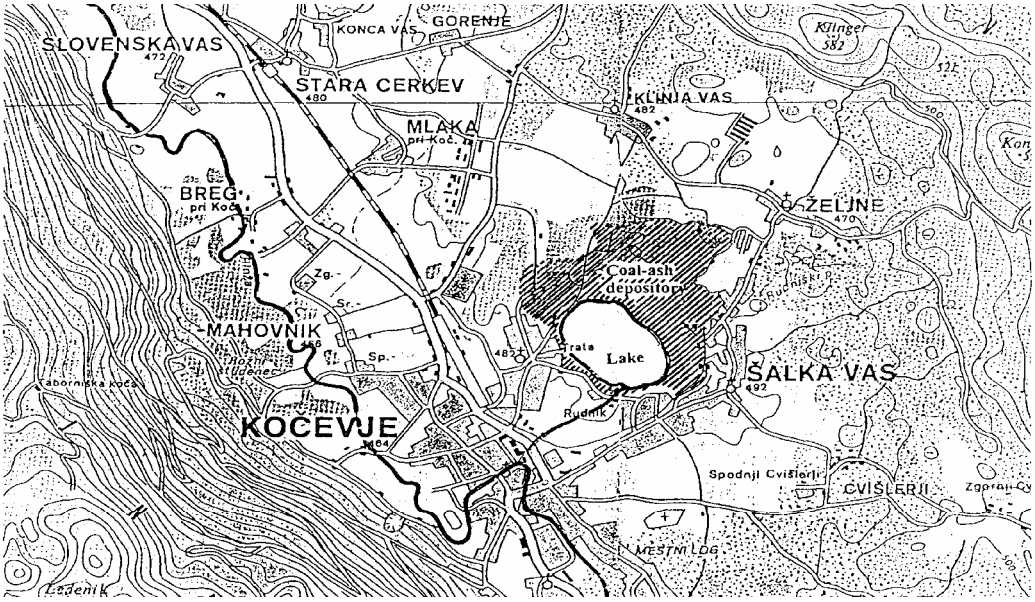


***Figure 10.2: Map with marked disposal area and lake in the area of the Kočevje Coal Mine (Križman et al, 1996b).***

Measurements were performed by the Kočevje Secondary School and by the Jožef Stefan Institute. Measurements covered the following items: measurements of gamma dose-rate levels on the coal and ash tailings of the disposal area, analysis of radionuclide content in disposed materials, radon measurements in houses located in the ex-mining area, measurements of radon and radon daughter concentrations outdoors, and radioactivity measurements of the lake and seepage water and sediments. Results showed that radioactivity in the disposal terrain is not uniformly distributed and that radioactivity was enhanced in the central parts of the depository. Gamma dose-rates were up to 300 – 400 nSv $h^{-1}$, while values of 150 – 250 nSv $h^{-1}$ were found in most parts of the whole area (Table 10.4) (Konda, 1995). The highest radiation levels (up to 400 nSv $h^{-1}$) were found on the eastern sie of the lake, the open pit mine, old coal-tailings depository and on hot spots with coal-ash. All coal samples and their mixtures with ash or soil contained considerable quantities of uranium and radium – mainly in the range of 400 – 1,200 Bq $kg^{-1}$, but in some places (at Šalka vas: on coal tailings, in the courtyard) even more than 4 kBq $kg^{-1}$, while contents of thorium and potassium in most samples were in the normal range (50 – 70 Bq $kg^{-1}$ for $^{232}$Th, 250 – 350 Bq $kg^{-}$1 for $^{40}$K) (Križman et al., 1996b).

***Table 10.4: Radionuclide content and gamma dose-rate levels in the area of the Kočevje Coal Mine (Križman et al., 1996b).***

| Location – sample | Dose rate (nSv $h^{-1}$) | Specific activity (Bq $kg^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | $^{238}$U | $^{226}$Ra | $^{210}$Pb | $^{232}$Th | $^{40}$K |
| East lake side, open-pit mine – coal, ash, slag | 150 – 300 | 2,168 | 2,315 | 1,393 | 56.1 | 228 |
| North-west lakeside – ash, coal | 100 – 200 | 328 | 313 | 248 | 52.2 | 337 |
| South-west lakeside –coal, ash | – | 1,236 | 1,258 | 1,475 | 46 | 358 |
| West lakeside – coal, ash | 100 – 200 | 1,794 | 1,793 | 1,374 | 60.9 | 296 |
| Šalka vas, Trdnjava – soil, ash, coal | 200 – 400 | 4,130 | 4,519 | 3,229 | 50 | 160 |
| Mine – coal | – | 1,146 | 1,861 | 1,667 | 59 | 168 |
| Šalka vas, Mlaka – soil | 100 | 75 | 80.6 | 73.4 | 61.5 | 374 |

Investigation showed that the uranium content in soil in the Kočevje region considerably exceeds the national average level. In the toron of Kočevje the highest outdoor radon concentrations in Slovenia were found (in the winter time, in a period of stable weather, daily average radon concentrations were about 80 Bq $m^{-3}$, with early morning maxima even up to 150 Bq $m^{-3}$) (Križman et al., 1996b). These are surprisingly high figures when compared to simultaneously measured values in the area of the uranium mine at Žirovski vrh (maximum values of 50 – 55 Bq $m^{-3}$ (Križman et al., 1996b) were observed at a moderate distance from the area of radon sources). This feature, together with the climatic characteristics and the deposition of millions of tonnes of waste coal tailings and ash are obviously together the main reasons for the occurrence of the highest levels of outdoor radon.

Measurements were taken in year 2004 (Repinc et al., 2004) of eight soil samples, which had been sampled in the toron of Kočevje by pupils of the Kočevje High School based on measurements of external gamma radiation. The results of these measurements are displayed in Table 10.5. At two locations the specific activity of the $^{238}U$ decay series radionuclides was increased (Recinko and At museum locations).

***Table 10.5: Content of radionuclides in soil samples from Kočevje, time period 10. October – 15. October 2004 (Repinc et al., 2004).***

| **Sample location** | **Dose rate (μSv $h^{-1}$)** | **Specific activity (Bq $kg^{-1}$)** | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $^{210}Pb$ | $^{238}U$ | $^{226}Ra$ | $^{228}Ra$ | $^{228}Th$ | $^{40}K$ | $^{137}Cs$ |
| Recinko, Roška 64 | 0.63 | 782±73 | 1,487 ± 110 | 1,559 ± 31 | 41±9 | 33±5 | 190±16 | 81±5 |
| At museum locomotive | 0.45 | 819±86 | 1,920 ± 165 | 2,543 ± 65 | 40±3 | 36±9 | 158±32 | 109±14 |
| Meadow by Mlakarjevo | 0.14 | 122±13 | 125±15 | 156±2 | 60±2 | 58±2 | 478±14 | 41±3 |
| Field by cemetery | 0.15 | 155±19 | 151±12 | 250±9 | 65±5 | 66±4 | 372±12 | 21±2 |
| Forest at power plant | 0.10 | 175±15 | 77±8 | 121±4 | 65±2 | 61±2 | 454±12 | 163±4 |
| House at power plant | 0.31 | 424±39 | 392±37 | 736±22 | 46±4 | 43±1 | 314±14 | 69±4 |
| Meadow at cemetery | 0.18 | 305±34 | 229±21 | 746±22 | 44±4 | 43±2 | 280±14 | 38±4 |
| Meadow Trata, Trata XIV | 0.08 | 83±10 | 93±8 | 96±3 | 67±3 | 66±2 | 470±13 | 20±2 |

### 10.2.4 Senovo Coal Mine

The intention of this study carried out by the Jožef Stefan Institute (IJS) in the year 1999 was to determine the state of radioactive radiation at the tailings landfill and in its vicinity, as well as to estimate any influence might have on the environment. Mine separation tailings were deposited at the soil tip while the mine was in operation (marl, lime, certain amounts of coal, that had burnt in the past due to inadequate technology of deposition). The area of the landfill, where self–ignition of coal occurred, is reddish, while in the north-eastern part, the tailings were deposited using a different technology and self-ignition did not occur (Repinc et al., 2004). Measurements of external gamma radiation were carried out over the whole area of the landfill and its surroundings, together with measurements of the levels of natural radionuclides of the uranium–radium decay chain in mine tailings and surrounding soil, measurements of uranium levels and $^{226}Ra$ in the water of revisionary shafts and water draining from the tip, as well as measurements of radionuclide levels of uranium in the sediments of Dovški potok and measurements of radon concentrations in air.

The uranium level in coal from Senovo is low (around 200 Bq $kg^{-1}$) and is one of the less radioactive coals in Slovenia (Križman et al., 1989). The specific activity of radioniuclides in ash from combustion of coal from the Senovo Coal Mine is shown in Table 10.6.

***Table 10.6: Specific activity of radionuclides in coal ash from Senovo (Križman et al., 1989).***

| Type of coal | Specific activity (Bq $kg^{-1}$) | | |
|---|---|---|---|
| | $^{238}U$, $^{226}Ra$ | $^{232}Th$ | $^{40}K$ |
| Senovo, in form of dust | 227 | 71 | 616 |
| Senovo, granulated coal | 193 | 77 | 681 |

The results of specific activity measurements of natural radionuclides in tailings and in soil in a nearby pasture are presented in Table 10.7. It may be seen that the specific activity of $^{238}U$ and $^{226}Ra$ are little enhanced compared to the specific activity of soil from the pasture near the mine.

***Table 10.7: Specific activity of radionuclides in samples of tailings and soil (Jeran et al., 1999).***

| Sample | Specific activity (Bq $kg^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $^{238}U$ | $^{226}Ra$ | $^{210}Pb$ | $^{232}Th$ | $^{40}K$ |
| Mine tailings | 41 − 70 | 46 − 81 | 46 − 66 | 28 − 58 | 351 − 622 |
| Soil – pasture | 47 | 51 | 60 | 60 | 605 |

Jeran et al. (1999) summed up the following findings:

- the content of natural radionuclides in the tailings are a little elevated compared to the surrounding soil. Due to the manner of deposition of the coal tailings, some of the ground is less compact and more permeable for radon and supposedly, in the case of higher concentrations of both radionuclides in the material, less suitable for the construction of residential and other closed buildings;
- radon concentrations in the soil air in the area do not exceed natural concentrations and the external gamma radiation in the landfill is within the range of values found for external radiation in the surroundings;
- mine tailings in Senovo do not represent a threat to the surroundings and eventually can be built on.

### 10.2.5 Thermal Power Plants

The Ljubljana and Trbovlje thermal power plants that consume sub-bituminous coal and the Šoštanj thermal power plant where lignite has been used, all present sources of increased natural radioactivity. The latter two are located in narrow and densety-populated valleys, near coal mines. Filter ash is deposited onto wet and dry landfills in the vicinity of the thermal power plants (Brajnik et al., 1988).

Coal, like most terrestiral materials, contains low concentrations of $^{238}U$ and $^{232}Th$ and their radioactive progeny. Burning of coal and other fossil fuels is a source of radiation exposure from naturally occurring radioactive materials (NORM) wastes. Table 10.8 indicates the amounts of coal combusted in 2005 in all three Slovenian thermal power plants. TPP Šoštanj, as Slovenia´s largest TPP and the biggest producer of electricity, consumed more than 4 million tons of coal. Radioactive elements are released to the environment during fuel extraction and burning, and may represent a source of increased exposure to the public living near TPP.

***Table 10.8: Mass of coal combusted in three TPPs in Slovenia in year 2005 (Kukovičič Lakić D., 2007; TET, 2005; TEŠ, 2005)***

| Sample | Annual consumed mass of coal (ton) | | |
|---|---|---|---|
| | Trbovlje TPP | Šoštanj TPP | Ljubljana TPP |
| Coal | 523,495 | 4,014,000 | 473,294 |

### *10.2.5.1 Trbovlje Thermal Power Plant*

A study from 1982 included measurements of levels of natural radioactive elements in samples of fly ash from the landfill of Trbovlje thermal power plant. Table 10.9 indicates that annual production of fly ash exceed a mass of 110,000 tons in the last three years and production of slag exceeds mass of 38,500 tons in the last three years. Surface samples of ash from the areas of increased gamma radiation contain 10–15 μg $g^{-1}$ of uranium, which is three to five times more than surrounding soil. $^{226}$Ra is present in somewhat larger concentrations than would correspond to radioactive equilibrium with uranium. Specific activities of 150−300 Bq $kg^{-1}$ $^{226}$Ra are five to ten times greater than concentrations of $^{226}$Ra in typical soil. Specific activities of $^{232}$Th are three times greater than concentrations in soil (Brajnik et al., 1982).

***Table 10.9: Produced mass of fly ash and slag in years 2003 – 2005 (TET, 2005).***

| Year | Mass of produced by-products (ton) | |
|---|---|---|
| | Fly ash | Slag |
| 2003 | 157,771 | 46,564 |
| 2004 | 142,635 | 38,566 |
| 2005 | 117,464 | 46,805 |

Representative coal samples normally contain 4 μg $g^{-1}$ of uranium, which within the margin of error is usually in radioactive equilibrium with $^{226}$Ra, or there is a littel less radium, and approximately 10 μg $g^{-1}$ of thorium[1] (Brajnik et al., 1982). Ash from the surface of the landfill therefore contains 2.5 to 3 times more uranium and 3 times more radium and thorium than coal (Brajnik et al., 1982).

A study of the effect of radioactive emissions from thermal power plants included evaluation of gamma radiation (gamma-ray spectrometric measurements of coal, ash and/or deposited ash), of depositions of ash onto soil and grass, of exhalation of radon from landfills, and of long-lived radionuclides in the environment. Concentrations of $^{222}$Rn from the tailings disposal site near Trbovlje ranged from 20–200 Bq $m^{-3}$, as opposed to air from crevices which contained 4–8 kBq $m^{-3}$ (Brajnik et al, 1988).

Specific activities of natural radionuclides in coal and filter ash are given in Table 10.10. Coal from Trbovlje is the least radioactive coal in Slovenia.

***Table 10.10: Content of radionuclides in coal and in ash (Brajnik et al., 1988) from different TPP´s.***

| Thermo power plant | Coal | Filter ash | | | |
|---|---|---|---|---|---|
| | Specific activity (Bq $kg^{-1}$) | | | | |
| | $^{238}$U | $^{238}$U | $^{226}$Ra | $^{210}$Pb | $^{232}$Th |
| Trbovlje TPP | 50 – 60 | 120 – 240 | 150 – 300 | 200 – 500 | 80 |
| Ljubljana TPP | 50 – 80 | 120 – 260 | 150 – 300 | 200 – 500 | 80 |
| Šoštanj TPP | 100 | 250 | 250 | 300 | – |

Measurements of soil around the Trbovlje thermal power plant were carried out within a study from 2002 on three locations and in two layers at Dobovec, Retje and Prapretno sampling site, and indicate noticeably increased radioactivity in the top layer of soil on account of wet or dry deposition of $^{210}$Pb (Benedik et al., 2002).

### *10.2.5.2 Šoštanj Thermal Power Plant*

The Šoštanj TPP is the largest power plant in Slovenia, since it has an installed capacity of 750 MW of electrical power. It annually consumes some four million tons of lignite, which belongs to the class of medium-radioactive coals in Slovenia, and this production in turn

[1] Note: 1 μg $g^{-1}$ U = 12.33 Bq $kg^{-1}$ $^{238}$U, 1 μg $g^{-1}$ Th = 4.11 Bq $kg^{-1}$ $^{232}$Th

causes the formation of up to 800,000 tons of fly ash (TEŠ, 2005). The ash contains about the same amount of uranium and radium (300–350 Bq $kg^{-1}$), and compared to the radioactivity of soil around the landfill, which contains 40–50 Bq $kg^{-1}$ $^{238}U$ and $^{226}Ra$ on the average, the concentrations of radionuclides from the U–Ra decay chain in the ash are six to nine times greater (Repinc et al. 2004). The ash landfill on which ash is deposited, covers some 50 ha of land. The landfill is located right next to a subsidence lake that was a product of coal mining, between Velenje and Družmirje lakes. Slag has also been deposited onto the landfill in addition to fly ash (Mljač, 1994).

Ash from the Šoštanj TPP is deposited onto a landfill of 0.5 $km^2$. The consequences these non-covered areas are transportation routes with inhalation of dust particles containing long-lived decay products and inhalation of radon and its short-lived products. The concentrations of radon and its products are similar to those in the surrounding area, due to the low exhalation rate of radon from the ash landfill (5–14 mBq $m^{-2}$ $s^{-1}$ on the landfill compared to 20–60 mBq $m^{-2}$ $s^{-1}$ in soil) (Kotnik et al., 1999). Leaching of radionuclides with lake water and rain, and drainage water all constitute an important source of radioactive contamination of Velenje Lake, water and sediments. The high alkalinity of the lake due to the presence of ash (which had a pH value of 11–12) affected the factor of solubility and as a corollary the concentration of radionuclides in lake water – low concentration of uranium (0.02 mg $m^{-3}$), while $^{226}Ra$ occurs in concentrations up to 70 Bq $m^{-3}$ (Kotnik et al., 1999). River waters and sediments show increased levels of radioactivity up to a distance of 10 km (Mljač and Križman, 1995).

Research on the effect of the ash disposal site on the surrounding area have been carried out. A programme of measurements included measurements of radioactivity of airborne particles, atmospheric precipitation, surface waters, and radioactivity of deposited materials and polluted filtered waters and drainage waters from the landfill. Previously measured concentrations of radon on the ash landfill were reasonably low (average annual level of 14–18 Bq $m^{-3}$) and comparable to concentrations around the landfill, where 12–17 Bq $m^{-3}$ have been measured. The ash most strongly affects waters that accumulate in the very area of remediated subsidence. These are closed system waters, transport waters and leachate waters that discharge into Družmirje Lake through a canal. Deposited ash also considerably affects the radioactivity of the depression of Družmirje Lake and its effluent, and to a lesser extent the River Paka. Gamma radiation dose rate in the range of 0.22–0.26 μSv $h^{-1}$ has been measured on the ash landfill, while a level ranging from 0.09 to 0.14 μSv $h^{-1}$ has been measured in the natural environment around the landfill. Scattering of soil (in a layer 20 cm thick) over the settling tanks has reduced gamma radiation to the level of the natural environment (Mljač, 1994).There was an initial attempt to measure the radioactivity of input and output materials from blocks 4 and 5 of the Šoštanj TPP. Results of analyses of by-products indicated that most of the uranium, $^{226}Ra$ and $^{232}Th$ remained in ash and slag, while expectedly most of $^{210}Pb$ was found in dust particles. Measurements of levels of $^{238}U$, $^{226}Ra$, $^{232}Th$, $^{210}Pb$ and $^{40}K$ radionuclides in materials from blocks 4 and 5 have been carried out (Kotnik et al., 1999) and are presented in Table 10.11.

***Table 10.11: Content of natural radionuclides in different samples from block 4 and block 5 of Šoštanj TPP (Kotnik et al., 1999).***

| Sample type | Specific activity (Bq $kg^{-1}$) / activity (Bq $m^{-3}$) | | | | |
|---|---|---|---|---|---|
| | $^{238}U$ | $^{226}Ra$ | $^{210}Pb$ | $^{232}Th$ | $^{40}K$ |
| Coal from block 4 | 105 | 92 | 100 | 10 | 145 |
| Coal from block 5 | 78 | 85 | 85 | 16 | 150 |
| Slag from block 4 | 340 | 250 | 140 | 33 | 330 |
| Slag from block 5 | 230 | 390 | 60 | 63 | 410 |
| Ash from block 4 | 410 | 420 | 420 | 44 | 570 |
| Ash from block 5 | 320 | 280 | 490 | 72 | 680 |
| Aerosols from block 4 | – | – | 1,750 Bq $m^{-3}$ | – | – |
| Aerosols from block 5 | – | – | 2,610 Bq $m^{-3}$ | – | – |

The results of analyses indicated that the radioactive elements from coal concentrate mostly in ash, while a volatile $^{210}$Pb also absorbs onto dust particles of flue gases. The research furthermore demonstrated that the desulfurisation facility substantially contributes to the reduction of $^{210}$Pb in dust particles. The activity of $^{210}$Pb in the air after the purification of flue gases ranges from 1.1 to 2.7 Bq m$^{-3}$ in block 4 and from 1.1 to 1.7 Bq m$^{-3}$ per volume of pumped air (Kotnik et al., 1999). The evaluated air emission of $^{210}$Pb ranges from 4.6 to 13 GBq per year, which constitutes 1.3 – 9 % of the input activity study (Kotnik et al., 1999). Measurements of soil around the TPP Šoštanj have been carried out on locations of Veliki Vrh, Zavodnje and Šoštanj in three layers and indicate notably increased radioactivity in the top layer of soil on account of wet or dry deposition of $^{210}$Pb (Kotnik et al., 2002).

Due to the enormous quantities of ash – 800,000 tons of fly ash (TEŠ, 2005) – that forms during coal combustion in the thermal power plant, a factory of building materials (EFE) has been constructed in Šoštanj, which from 1960 to 1986 had been producing among other things building blocks out of fly ash for the construction of apartments. Some ten thousand Slovenian apartments are estimated to have been built with EFE blocks, which contain more than 75 % of ash (Mljač, 1993). Table 10.12 summarizes the specific activity of radionuclides in different building materials.

***Table 10.12: Specific activity of natural radionuclides in building materials in Slovenia (Repinc et al., 2004).***

| Type of building material | Specific activity (Bq kg$^{-1}$) | | |
|---|---|---|---|
| | $^{226}$Ra | $^{232}$Th | $^{40}$K |
| EFE brick | 309 | 40 | 406 |
| EFE plaster | 190 | 33 | 360 |
| Normal brick (Novo mesto) | 69 | 72 | 454 |
| Cement block (Ljubljana) | 20 | 11 | 105 |
| Aerated concrete (Siporex) | 22 | 10 | 143 |

Measurements of radioactivity in building materials made out of fly ash indicated that the level of radioactivity exceeds the prescribed permissible level; therefore building materials made out of fly ash are no longer used. A consequence of the increased levels of radionuclides is the increased external gamma radiation received by those living in buildings constructed of EFE blocks (where a person receives an annual dose of 0.60 mSv, compared to 0.39 mSv received from normal bricks) and the emission of radon from such building materials (the highest measured concentration of $^{222}$Rn in a building of EFE blocks was 67.7 Bq m$^{-3}$, compared to 41.5 Bq m$^{-3}$ in buildings of normal bricks) (Repinc et al., 2004). The greatest burden to the population with ionizing radiation is thus caused not by deposited ash on landfills, but by ash in building materials, where residents are more exposed to ionizing radiation.

### *10.2.5.3 Ljubljana Thermal Power Plant – Heating Station*

Fly ash and slag that form during coal combustion in the Ljubljana TPP – heating station had in the past been transported to landfills near Ljubljana (Zajčja Dobrava, Litijska cesta, Tacen, southern bypass) and is now being deposited onto the Barje landfill on Cesta dveh cesarjev since the beginning of the 1970s. Table 10.13 shows the mass of fly ash and slag produced in the period 2003 – 2006. Measurements of levels of natural radionuclides in ash samples of coals from the Trbovlje, Velenje, Zagorje, Kanižarica and Kreka mines have been carried out within the study of 1989 (Table 10.14). This study included measurements of external gamma radiation dose rates on the surface of ash the landfill on the Barje, which indicated increased background radiation (0.17 μSv h$^{-1}$ on average, 0.20 μSv h$^{-1}$ maximum) that was 2 to 3 times greater than the natural background, while the contribution could no longer be measured as the distance increased (Križman et al., 1989). The intensity of radiation is also lower in the sand cover, where the dose rate of external gamma radiation measured was from 0.10 μSv h$^{-1}$ to 0.135 μSv h$^{-1}$, with the maximum level of 0.20 μSv h$^{-1}$ (Križman et al., 1989). It was discovered that if the deposited ash is covered with a layer of soil or sand, the

additional radiation due to radioactive ash is completely eliminated because of the absorption of gamma radiation in this material.

***Table 10.13: Mass of fly ash and slag produced in period 2003 – 2006 (Kukovičič Lakić, 2007).***

| Year | Mass of produced by-products (ton) | |
|---|---|---|
| | Fly ash | Slag |
| 2003 | 20,455 | 3,560 |
| 2004 | 27,983 | 3,170 |
| 2005 | 30,263 | 3,416 |
| 2006 | 23,250 | 2,620 |

***Table 10.14: Specific activity of natural radionuclides in coal ash (Križman et al., 1989).***

| Coal type and/or aggregation | Specific activity (Bq kg$^{-1}$) | | |
|---|---|---|---|
| | $^{238}$U, $^{226}$Ra | $^{232}$Th | $^{40}$K |
| Kanižarica, dust | 1,420 | 98 | 479 |
| Kanižarica, pea | 1,909 | 69 | 369 |
| Kreka, lignite | 300 | 74 | 493 |
| Zagorje, dry sowing ash | 264 | 86 | 682 |
| Velenje, ash | 264 | 74 | 561 |
| Trbovlje, bottom ash | 183 | 93 | 623 |
| Trbovlje, dust | 148 | 92 | 577 |
| Zagorje, dust | 283 | 100 | 450 |

Composite ash samples displayed increased levels in May and June on account of an increased share of coal from Kanižarica (Table 10.15).

***Table 10.15: Specific radioactivity of natural radionuclides in a combined ash sample made up of 3 months combined samples of ash from Kanižarica coal (source: Križman et al., 1989).***

| Sample type | Specific activity (Bq kg$^{-1}$) | | |
|---|---|---|---|
| | $^{226}$Ra, $^{238}$U | $^{232}$Th | $^{40}$K |
| Composite ash sample, Kanižarica | 234 − 460 | 85 − 93 | 493 − 666 |

The use of areas covered with ash in the construction of residential buildings is not objectionable in the opinion of experts from the Jožef Stefan Institute. Ash from the Ljubljana TPP – heating station has been used in this way for remediation of an airport plateau in Ruardij. The slope of Ruardij had been used a permanent disposal site for mining tailings that were being deposited in the near and far vicinity of Zagorje during the mining period. A study of measurements of radiation in the area of Ruardij included analyses of soil samples from the surroundings, of mining tailings on the slope of Ruardij, and of deposited ash that had already been brought to the airstrip (Table 10.16). Mining tailings deposited in Ruardij, which were being deposited in the areas around the Zagorje Coal Mine in 200 years of mining activity, contain 2 to 3 times higher specific activities of $^{238}$U and $^{226}$Ra than surrounding soil, since it contains up to 100 Bq kg$^{-1}$ $^{226}$Ra, in addition to the ground strew with tailings being less compact and more permeable to radon (Križman and Konda, 1994).

***Table 10.16: Specific activity of natural radionuclides in materials deposited on Ruardij disposal site (Križman and Konda, 1994).***

| Sample type | Specific activity (Bq kg$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $^{238}$U | $^{226}$Ra | $^{210}$Pb | $^{232}$Th | $^{40}$K |
| Tailings | 55 – 94 | 55 – 95 | 67 – 91 | 30 – 54 | 268 – 553 |
| Soil | 31– 52 | 42 – 52 | 30 – 51 | 34 – 47 | 438 – 659 |
| Fly ash | 145 – 453 | 160 – 429 | 140 – 472 | 57 – 77 | 305 – 575 |

External gamma radiation, measured directly on the deposited ash, depends on the types of coals used (Table 10.17). The lowest levels were measured in ash of coal from Zasavje and in Indonesian coal (0.10–0.15 μSv $h^{-1}$) (Križman and Konda, 1994). External radiation in the surrounding area above the landfill is lower. Approximately 0.10 μSv $h^{-1}$ has been measured on the slope of Ruardij, where the ground is mostly composed of tailings (Križman and Konda, 1994).

***Table 10.17: Measured dose rates on disposal site of Ruardij and in near area (Križman and Konda, 1994).***

| Location of measurement | Dose rate (μSv $h^{-1}$) |
|---|---|
| Ruardij disposal site | |
| Ash (September 1993) | 0.2 |
| Ash (January 1994) | 0.15 |
| Tailings | 0.1 |
| Covering over ash | 0.1 |
| Reference locations | |
| Above tailings | 0.09 |
| Kotredež | 0.12 |

The Ljubljana combined thermal power plant – heating station meets 90 % of the thermal energy needs in the district heating system of Ljubljana, 48.1 % of thermal energy needs in the district heating system of Slovenia (Slovenian national share in 2002) and 3 % of Slovenian electricity needs within the Slovenian energy system (Kukovičič Lalič, 2007). Combustion of coal causes the formation of ash and slag as waste products, which constitute the largest share of wastes from the Ljubljana thermal power plant – heating station. Imported coals of better quality were tested as early as in 1992 and since 1993 domestic coal (ash content of more than 20 %, sulphur content of 2–5 %) has gradually been replaced with imported coals (ash content of 1–3 % and sulphur content of under 0.2 %) (TE-TOL, 2005). In 2001 the combustion of domestic coal was stopped and only imported ones used (Indonesian coal), which notably decreased emissions of sulphur dioxide and landfill burdening (TE-TOL, 2005). Table 10.18 shows the specific activity of natural radionuclides in Indonesian coal and in the ash produced.

***Table 10.18: Specific activity of natural radionuclides in coal from Indonesia and in ash (Repinc et al., 2004).***

| Sample | Specific activity (Bq $kg^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $^{238}U$ | $^{226}Ra$ | $^{210}Pb$ | $^{232}Th$ | $^{40}K$ |
| Coal –1 | < 9 | 7 ± 3 | < 9 | 12 ± 1 | 28 ± 15 |
| Coal–2 | < 10 | < 5 | < 10 | 11 ± 1 | < 17 |
| Ash–1 | 54 ± 33 | 98 ± 7 | 102 ± 44 | 82 ± 3 | 587 ± 66 |
| Ash–2 | 31 ± 31 | 58 ± 5 | < 20 | 42 ± 2 | 102 ± 43 |

Ash and slag are being deposited onto the municipal landfill of Ljubljana, where they use this waste material for the stabilization of the tips and wastes themselves. The Ljubljana TPP – heating station Plc annually consumes less than 500,000 tons of coal, which produces some 25,000 tons of waste ash and slag per year.

### 10.2.6 Phosphate Industry – TKI Hrastnik

The company was built in 1860, when Jurij Gosleth from Trieste started processing chrome ore. TKI Hrastnik is a joint stock company engaged in the development, production and processing of basic industrial chemicals, special chemicals, fine chemicals, and the manufacture of products for the retail trade. There are two main production lines, namely basic chemical production including a chlor – alkali electrolysis plant with annual production of chlorine and caustic soda of about 15,000 tons each, and a phosphate plant with an annual capacity of 20,000 tons of sodium tripolyphosphate and 5,000 tons of other phosphates (Vizler, 2007). They are the sole producer of sodium hydroxide, hydrochloric

acid, hypochlorite and chlorine in Slovenia. Their general consumer goods programme includes household cleaners, laundry detergents, food additives, personal care products and fine chemicals.

An area of a few square miles in Zasavje holds a complex of coal mines, a thermal power plant with an ash landfill and the phosphate industry named TKI Hrastnik. TKI Hrastnik phosphate industry processed phosphate ore until 1994. The Unično landfill was used for the disposal of phosphogypsum and phosphate sludge. Approximately 80,000 tons of phosphogypsum were deposited during the regular operating process per annum, while the entire quantity from operating period is estimated to contain some 200,000 tons of phosphogypsum, deposited over an area of 5,000 $m^2$, with a layer that is 30 metres thick (Vizler, 2007)

The Institute of Occupational Safety has measured the specific activity of radionuclides in the rivulet Ničnica and outdoor concentrations of radon. Outdoor radon concentrations were in the range 15 – 30 Bq $m^{-3}$, while is higher than the usual values in environment (5–15 Bq$m^{-3}$) (Kanduč et al., 1992). Kanduč et al. (1990) conducted that specific activity of radionuclides in Ničnica show no impact from the disposal site to the environment, and, that radon emanation, due to dilution in the air also has no impact on the environment (the near surroundings are not populated).

The Hrastnik Municipal and Housing Company Plc was the manager of the landfill, but refused to take part in the study "The Effect of Technologically Enhanced Naturally Occurring Radiative Material on the Radioactivity Level of Groundwater and Surface Waters in Slovenia" in 2003 and there was no foreseeable cooperation in the future, too (Repinc et al., 2004). The Unično landfill is no longer used as a landfill for industrial wastes that are otherwise still occasionally being transported from TKI Hrastnik in a form of sulphate sludge, but serves now as a landfill for municipal and industrial wastes and could be used in the long-term period as the regional landfill of Hrastnik, Trbovlje, Zagorje, Radeče and partly Laško municipalities. Leachate from the disposal is being collected, appears only in small quantities and is then discharged back to the landfill, using the closed system principle.

Research on the effect of discharges of wastewaters from coal mines (Zasavje and Trbovlje), of the Trbovlje thermal power plant (TET), and of the TKI Hrastnik ash landfill on the radioactivity of the River Sava have been carried out in 1990 in Zasavje (Kobal et al, 1990). During the measurement process, the phosphate industry was releasing phosphogypsum into the Boben rivulet that joins the River Sava after a couple of hundred metres.

Measurements of $^{226}Ra$ and total beta activity in composite water samples from the River Sava and Boben rivulet were taken, along with measurements of $^{226}Ra$ in suspended particles. The results indicated that no effect in increasing radioactivity levels of the River Sava water system due to coal mines, TET and ash landfill could be detected. However, the phosphate industry had indeed increased the radioactivity level of the Boben rivulet, which was a recipient of releases of phosphogypsum and waste water. A consequence of this is an increased radioactivity level of the River Sava, which, however, is not critical.

In 1989 the Jožef Stefan Institute measured a level of 508 Bq $kg^{-1}$ $^{226}Ra$ in phosphate ore (Križman et al., 1989). Later measurements of radioactivity were carried out by the Institute of Occupational Safety in 1992 and 1994. Levels of radionuclides in phosphogypsum of the uranium decay chain radionuclides (263 Bq $kg^{-1}$ $^{238}U$, 520 Bq $kg^{-1}$ $^{226}Ra$, 482 Bq $kg^{-1}$ $^{210}Pb$) were found to be increased, with lower levels of other natural radionuclides (7.9 Bq $kg^{-1}$ $^{232}Th$, 4.6 Bq $kg^{-1}$ $^{40}K$) (Vizler, 2007). Measurements of radioactivity of leachates and of the Ničnica rivulet indicated that no effect of the landfill on these waters could be detected due to the low solubility of phosphogypsum, while leachate from the landfill contained only 30 Bq $m^{-3}$ $^{226}Ra$ (Benedik et al., 2004a). A dose rate of external gamma radiation varying from 0.12 to 0.16 mSv $h^{-1}$ (0.06–0.09 mSv $h^{-1}$ in the surrounding terrain) was measured on the surface of the open phosphogypsum landfill (Vizler, 2007).

### 10.2.7 Processing of Titanium Minerals – Cinkarna Celje

Cinkarna Celje was established 134 years ago, in the year 1873 as a zinc foundry. From a mainly metallurgical company it has now grown into a chemical - processing business. Cinkarna Celje started titanium dioxide ($TiO_2$) production in the year 1973.

Cinkarna's main product pigment titanium dioxide accounts for more than 60 % of the total sales, followed by the second most profitable business activity of titanium-zinc sheet metal production, which accounts for 15 % (Company – strategy and history, 2005). In 1973 they successfully rounded off the production of white pigments by starting a sulphate method of production. Titanium dioxide pigment is indispensable in the production of paints, rubber and plastics, and in the paper, cosmetics and food industry. $TiO_2$ supplied in 25 kg paper bags and 1-ton container bags and other packaging is available on request, for instance silo-trucks and railway wagons used for transporting powdered materials. The most important raw material in $TiO_2$ production is sulphuric acid, which is produced by Cinkarna for its own needs and the surplus is marketed at home and overseas. Cinkarna is accredited to 9002 quality standards.

Cinkarna Celje has a production capacity of 44,000 tons of titanium dioxide per year, with an expected increase to 56,000 tons per year (Company – strategy and history, 2005). Before technological modifications in 2000, Cinkarna Celje was depositing solid wastes from the production of titanium dioxide onto its own Bukovžlak solid waste landfill, waste phosphogypsum to the Bukovžlak monofill (wet stacking) prior to 1991 and after 1991 to the Za Travnikom monofill (wet stacking) (Drava, 2000). All three landfills are located a few kilometres east of the industrial complex.

There was a change in the ratio of input raw materials in 1994 (increased proportion of purer and more highly concentrated titanium slag instead of natural ilmenite with a lower level of $TiO_2$). Due to lower levels of iron compounds, green vitriol ($FeSO_4 \times 7H_2O$) no longer forms as a separate waste in the production process, which required special treatment in the past. There was also a reduction in the use of sulfuric (IV) acid ($H_2SO_4$). The technological process is based upon the comminution of ores that contain $TiO_2$ (approximately 60 % in ilmenite and 80 % in titanium slag) into a soluble form. The sulphate solution is then purified and hydrolysed, and the precipitated hydrolysate calcinated. The purified titanium dioxide calx is finally surface-treated for various end uses. The acid effluent that forms during the production of $TiO_2$ is neutralized in two stages, first with limestone meal ($CaCO_3$) and then with lime milk ($Ca(OH)_2$), which results in formation of a gypsum slurry ($CaSO_4 \times 2H_2O$) that is pumped away to the Za Travnikom landfill, where the suspension of gypsum and of other insoluble oxides and hydroxides subsides. The overflow, which is a diluted solution of saturated gypsum water, drains off to a water course (Dobje rivulet). Neutralized liquid wastes from the production of titanium dioxide, i.e. the filtrate or decantate after the neutralization of strongly and weakly acidic liquid wastes, are drained off into the River Hudinja.

The volume of the Za Travnikom landfill equals 6.6 million $m^3$, while the area of its lake constitutes 38.5 ha (Drava, 2000). A shift in the disposal method from current wet stacking to dry stacking of gypsum is planned for the oncoming years, with simultaneous remediation of the existing wet landfill.

Based upon an evaluation of waste conducted by the responsible institution, gypsum qualifies as an inert waste. A solid phase of a suspension of gypsum and other insoluble oxides, hydroxides etc subsides on the wet landfill, while the overflow, which is a diluted solution of saturated gypsum water, drains off to the water course. In 1999 Cinkarna Celje removed 224,000 kg of solid wastes with a classification number 061199 and 197,000,000 kg of wastes with a classification number 061101 (gypsum suspension) (Company – strategy and history, 2005). 198,000,000 kg of gypsum from the production of titanium dioxide were removed in 2000 (Repinc et al., 2004). On account of the modification of technology from 2000 onward, solid wastes from the production of titanium dioxide are no longer deposited onto the Bukovžlak solid wastes landfill. Insoluble ore residues, after a counter-current wash in the clarifier, are directed towards neutralization along with strongly acidic effluents.

Ilmenite is the input raw material in the production of $TiO_2$, while waste gypsum and acid are its by-products. Average specific activities of $^{226}Ra$ in ilmenite are estimated to be around 200 Bq $kg^{-1}$ (Repinc et al., 2004). The processing industry could potentially cause extensive contamination with $^{226}Ra$ and $^{228}Ra$, daughter products of $^{238}U$ and $^{232}Th$. Table 10.19 presents the specific activity of natural radionuclides in ilmenite and residues from $TiO_2$ production.

***Table 10.19: Specific activity of radionuclides in ilmenite and waste plaster from Cinkarna Celje (Repinc et al., 2004; Benedik et al., 2004a).***

| Sample | Specific activity (Bq $kg^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}Pb$ | $^{238}U$ | $^{226}Ra$ | $^{228}Ra$ | $^{228}Th$ | $^{40}K$ | $^{137}Cs$ |
| Ilmenite | – | 80 – 170 | 150 – 260 | 50 – 260 | – | – | – |
| Waste plasters | 79 ± 4 | 21 ± 2 | < 4 | 15 ± 2 | 66 ± 5 | < 12 | < 10 |
| Deposit formed on pipes and on filters | 51,700 | 160,000 | 52,000 | 550,000 | 490,000 | – | – |

The calcite deposits formed on filter pipes during the technological process where radionuclides concentrate constitute TENORM with the highest specific activity of radionuclides in Slovenia. The Institute of Occupational Safety has measured the following activities in a such sample: $^{210}Pb$ 51,700 ± 3,000 Bq $kg^{-1}$; $^{238}U$ 160,000 ± 16,000 Bq $kg^{-1}$; $^{228}Th$ 490,000 ± 20,000 Bq $kg^{-1}$; $^{226}Ra$ 52,000 ± 25,000 Bq $kg^{-1}$; $^{228}Ra$ 550,000 ± 30,000 Bq $kg^{-1}$ (SNSA , 2000).

### 10.2.8 Aluminium Production – Talum Plc, Kidričevo

In 1942, during World War II, the Germans started building an alumina refinery in Kidričevo. They then suspended construction during wartime. The interrupted construction was resumed after the war, so that the alumina refinery was completed in 1954, which had annual production capacity of 45,000 tons of alumina, and an electrolysis plant with a production capacity of 15,000 tons of aluminium (Company Talum, 2006). The production output of the refinery further increased towards 1974 to 110,000 tons of alumina and 45,000 tons of aluminium per year (Company Talum, 2006). From the very beginning the refinery – with its production of alumina and aluminium – significantly influenced the way and quality of life in the surroundings and wider regions. It also affected the environment with a heavy pollution burden, since it lacked adequate technology to prevent such effects. A technological and planned ecological remediation of the refinery began in 1985 with the construction of a new electrolysis plant with modern technology and modernization of the existing electrolysis process, while the production of aluminium increased to 75,000 tons per year. The final termination of aluminium production by electrolysis in May 1991 and termination of alumina production in September 1991 were two important landmarks in the process of ecological remediation of the refinery.

The production of alumina required large quantities of energy in the form of steam. Steam boilers were heated with coal and great quantities of ash and sulphur dioxide have been released into the environment through the smokestack; up to 25,000 tons of ash and 7,500 tons of $SO_2$ per year, during the most extensive period of alumina production (Repinc et al., 2004). The need for steam greatly decreased after the termination of alumina production. Accordingly, the operation of the coal-fed boiler room was stopped in 1995. The termination of metallurgical alumina production in September 1991 represented the elimination of the main pollution sources from this production, as well as cessation of red mud and ash disposal. New, ecologically clean production programmes have been introduced to existing devices, such as zeolites, calcium silicate, water glass, special aluminas. A continuous supply of alumina has been thereafter fully organised, with the cooperation of Hydra International Inc. A 20,000 tons silo was erected for this purpose in the Port of Koper, from where alumina is regularly transported to Kidričevo in special tank wagons.

Alumina production and the coal-fed boiler room heavily polluted the local air and soil. Red mud residues amounted to from 140,000 to 170,000 tons per year and ash contributed from

60,000 to 70,000 tons per year, where a distinction has been made between fly ash and wet ash (Benedik et al., 2004b). Deposited red mud and ash resulted in pollution of groundwater (alkali input), while $SO_2$ and fly ash (ash from the smokestack) polluted the atmosphere. Red mud is the gangue from bauxite ore from which aluminium has been eluted and was being deposited onto a tailings disposal site until 1991, when the production of alumina was stopped. Red mud was deposited as a water suspension onto a disposal site that covers some 42 hectares (Drava, 2000). Inclusive up to the year 1991 6.5 million tons of red mud were deposited there (Benedik et al., 2004b). Wet ash was deposited onto a disposal site of 8 hectares, where 1.5 million tons of ash were deposited (Benedik et al., 2004b). Levels of natural radionuclides in red mud and ash are presented in Table10.20.

***Table 10.20: Specific activity of natural radionuclides in red mud and in soil on the Kidričevo ash landfill (Benedik et al., 2004a).***

| Sample | Specific activity (Bq $kg^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}Pb$ | $^{238}U$ | $^{226}Ra$ | $^{228}Ra$ | $^{228}Th$ | $^{40}K$ | $^{137}Cs$ |
| Red mud | 82 ± 3 | 125 ± 12 | 175 ± 5 | 347 ± 3 | 340 ± 10 | 84 ± 8 | < 10 |
| Ash | 217 ± 11 | 456 ± 15 | 341 ±19 | 75 ± 2 | 64 ± 1 | 465 ± 19 | < 10 |

The aluminium factory ordered a study on the effect of red mud on groundwater from the Geological Survey of Ljubljana in 1986. The results of this study revealed that a layer of red mud that came into contact with sandy ground had penetrated half a metre deep and silted the aquifer. This caused the formation of a layer with conductivity in the range of asphalt concrete under the disposal site. A programme of revitalization was designed in 1991 by a group of development experts. Their basic objective was to prevent any further adverse effects on the environment – powdering and percolation of rainwater through a layer of red mud into the groundwater. They ascertained that the area could be revegetated by the introduction of organic substances, soil or ash onto the surface of the red mud. The red mud disposal site is now covered with a layer of soil. There is no activities in the red mud disposal site due to Talum (site manager), and the site is classified as a landfill of non-hazardous wastes. As stated above, the production of alumina required large quantities of energy in the form of steam. Steam boilers were heated with coal and the residue – wet ash – was deposited onto a disposal site of 8 hectares (Benedik et al., 2004b). 1.5 million tons of ash have been deposited there (Benedik et al., 2004b). The ash landfill that is located south-east of the former red mud disposal site is today half-covered with grass and was the site where soil samples had been taken. The ash landfill is labelled as an important environmental problem; therefore a series of activities within the framework of legislative requirements have been planned for the coming years. The ash landfill is classified as a landfill of inert wastes (Company Talum, 2006).

Abandoned disposal sites of red mud and ash in the industrial zone around Kidričevo affect the quality of underground waters on account of percolation of rainwater and leakage of accumulated water from both disposal sites. Most notably polluted is a proportionally narrow strip of groundwater that is 500 m wide at most and that extends from the eastern boundary of the disposal site through the southern part of the industrial zone and then eastward from the industrial zone towards a poultry farm. Substances measured in underground waters are characteristic of red mud and ash eluates and partially of some residues from the former production, such as increased alkalinity, aluminium, iron, cyanides, fluorides, vanadium and mineral oils. Due to very favourable hydrological characteristics of the underground water in the relevant area, particularly because of copious quantity of water, rapid dilution of these pollutants is taking place. The equally favourable geological structure of the aquifer furthermore prevents the spread of pollution over the entire area (ARSO, 2002).

### 10.2.9 Iron and Steel Industry in Jesenice – Slovenian Steelworks Acroni Ltd

On account of the mineral deposits (mines of Sava) and available water power, foundry activity expanded as early as the Middle Ages in villages on the southern slopes of the Karavanke mountain range. There is mention of a foundry order from 1381, while the

beginnings of iron smelting activities reach back to Antiquity. The valley gained importance in the 16th century, which prompted the appearance of several blast furnaces along the River Sava Dolinka. The iron industry was mainly in the hands of the Bucellini, Garconi, Ruard and Zois families. In 1869 the foundries became the property of the Carniolan Industrial Company (Gestrin and Melik, 1966). At the end of the 19th century, when foundries throughout the Julian Alps ended in failure because of competition from the iron industry, Jesenice took over their installations and drew in redundant workers. This brought about the development of the largest Slovenian centre of iron industry that also provided employment for the wider region.

Acroni Jesenice is one of the companies of the Slovenian Steelworks trust. 1,400 workers are employed there. They manufacture hot rolled and cold rolled strips, sheets and plates from different steel grades and products from steel plates (Production programme, 2006). Production is carried out in the following plants: PC Hot processing, PC Cold processing and PC Plate processing (Production programme, 2006).

Slag is a by-product of the steel-manufacturing process. Its formation is unavoidable from both the technological and economic point of view. The types of slag that form during the technological process are:

- blast furnace slag, which forms during the smelting process in an electric arc furnace during the production of non-alloy steels; 110 kg of slag per ton of steel is formed (Purkat, 2007),
- steel slag, which forms after the steal-treatment process, after the processes of secondary metallurgy and in an electric arc furnace during the production of stainless materials; 45–90 kg of slag per ton of steel is formed (Purkat, 2007).

The technological path of slag formation begins in the steelworks and depends on the nature of the steel, its physical, chemical and other properties. Scrap iron from processing industries and useless old equipment is used as the basic raw material in the manufacture of steel. This process allows economical recycling of precious alloys of the steel industry. The Javornik internal landfill has been operating since 1987. The landfill is located in a town called Slovenski Javorniki that lies on the left bank of the Sava south-east of the centre of Jesenice. Total area of the landfill equals 2.2 ha (Drava, 2000). Wastes from the production of steel were deposited on the landfill in the period between 1987 and 2003 (Table 10.21). It is estimated that 126,000 $m^3$ of wastes have been dumped on the landfill in this period (Purkat, 2007).

***Table 10.21: Type and annual quantity of wastes deposited on the Javornik landfill in the period 1987 – 2003 (Purkat, 2007).***

| **Wastes** | **Quantity (ton)** |
|---|---|
| Unprocessed slag | 209,030 |
| Solid wastes from gas treatment containing dangerous substances | 74,800 |
| Solid wastes from gas treatment other than those mentioned in 10 02 07* (oxide from regeneration) | 145 |
| Other wastes from cooling-water treatment | 780 |
| Other ferrous metals particles (waste sediments made in cutting at the chopper) | 572 |
| Waste blasting material other than those mentioned in 12 01 16* | 24 |
| Metal sludge (grinding, honing and lapping sludge) containing oil | 24 |
| Other linings and refractories from metallurgical processes other than those mentioned in 16 11 03* | 31,671 |
| **Total mass of deposited wastes** | **317,046** |

Blast furnace slag and steel slag, dust from dust abatement equipment and refractory materials were quantitatively prevalent among the deposited wastes. It is assessed that the

relevant landfill could store another 177,000 $m^3$ or 424,800 tons of wastes, which should be sufficient until 2011 (Purkat, 2007). If we disregard disposals in 2005 we can say that in the period 2003 – 2006, there was an increase in the mass of disposed wastes (Table 10.22).

Dust from dust abatement equipment that forms during the production of regular materials (so far only the dust from the production of stainless materials is being deposited) is transported for processing to Germany, to the company B.U.S. 4,160 tons of dust were transported for processing in 2003.

***Table 10.22: Type and annual quantity of wastes deposited on the Javornik landfill in period 2003 – 2006 (Purkat, 2007).***

| **Wastes** | **Quantity (ton)** | | | |
|---|---|---|---|---|
| | **Year 2003** | **Year 2004** | **Year 2005** | **Year 2006** |
| Unprocessed slag 10 02 02 | 8,200 | 14,243 | 9300 | 22,106 |
| Solid wastes from gas treatment containing dangerous substances | 2,400 | – | – | – |
| Solid wastes from gas treatment other than those mentioned in 10 02 07* (oxide from regeneration) | 269 | – | – | – |
| Other ferrous metals particles (waste sediments made in cutting at the chopper) | 76 | – | – | – |
| Waste blasting material other than those mentioned in 12 01 16* | 91 | – | – | – |
| Other linings and refractories from metallurgical processes other than those mentioned in 16 11 03* | 950 | 1,506 | – | – |
| **Total mass of deposited wastes** | **11,986** | **15,749** | **9,300** | **22,106** |

Measurements of external gamma radiation were performed in the year 2004 (Repinc et al., 2004) on the new and still active part of the Javornik tailings disposal site, where waste products of the steel industry are being deposited. Results of these measurement are presented in Figure 10.3.

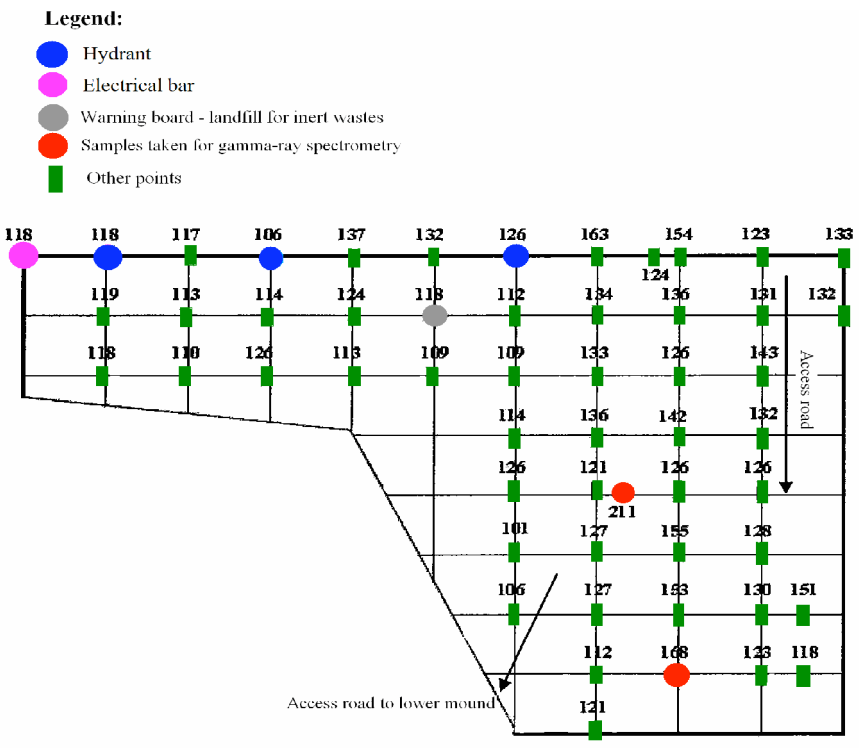


***Figure 10.3: Measurements of external gamma radiation on Javornik tailings disposal site (results are shown in nSv $h^{-1}$, measuring grid 10 m × 10 m) (Repinc et al., 2004).***

A slag sample (sample 3) from the tip of the Javornik tailings disposal site next to the Jesenice–Ljubljana road was taken, approximately 20 metres from the Slovenski Javornik traffic sign. The tip is covered with overburden, with the slag still visible in some places. Measurements of dose rate taken at the surface level varied from 0.1 to 0.2 μSv $h^{-1}$. Results of measurements are displayed in Table 10.23.

A sample of fine ash was analysed. Fine ash is not disposed of onto the disposal site, but is instead forwarded to Germany for processing.

***Table 10.23: Content of radionuclides in samples taken on Javornik tailings disposal near Jesenice (Repinc et al., 2004).***

| Sample | | Slag | Slag | Mound, tailings | Fine ash |
|---|---|---|---|---|---|
| Dose rate (nSv $h^{-1}$) | | 211 | 168 | | – |
| Specific activity (Bq $kg^{-1}$) | $^{210}$Pb | 219 ± 19 | 93 ± 12 | 101 ± 8 | 50 ± 8 |
| | $^{238}$U | 486 ± 50 | 52 ± 6 | 121 ± 10 | < 5 |
| | $^{226}$Ra | 634 ± 16 | 56 ± 1 | 130 ± 5 | 15 ± 1 |
| | $^{228}$Ra | 42 ± 1 | 18 ± 2 | 53 ± 2 | < 10 |
| | $^{232}$Th | 39 ± 4 | 18 ± 1 | 52 ± 5 | < 10 |
| | $^{40}$K | 195 ± 14 | 137 ± 9 | 358 ± 10 | 427 ± 9 |
| | $^{137}$Cs | 212 ± 7 | 55 ± 4 | 51 ± 3 | 11 ± 2 |

### 10.2.10 Iron Industry – Metal Ravne

Ravne ironworks enjoy a lengthy metallurgical tradition that extends over 370 years, with Metal Ravne being established after the division of the ironworks into several smaller companies in 1992 (Metal Ravne − Company, 2006).

Metal Ravne manufactures high-alloy steels, stainless steels and other high-quality steels out of scrap iron. Scrap iron is the chief raw material in the production process and is ranked on according to quality into standard classes with the limited presence of certain unwanted impurities such as wood, concrete, soil, plastic and oils, and the prohibited presence of PCBs and radioactive materials. Each consignment of scrap iron is inspected and there is an examination for the possible presence of radioactive materials. Other raw materials include fluxes such as lime or dolomite, carbon, ferroalloys, deoxidizers and materials for the insulation of furnaces. Scrap iron is usually stored outside on leak-proof surfaces; other raw materials are usually kept in closed depots.

Wastes have been deposited in these areas throughout all of the iron industry years and Metal Ravne presumes that large-scale depositions in the present area of the Ravne tailings disposal site took place after World War II. Within this study we carried out sampling in the lower (newer) part of the Ravne landfill, where brown slag is heaped in a relatively homogeneous way, and also in the upper (older) and already built-up tip of the Ravne tailings disposal site.

Data from inventorying the quantity of wastes produced are monitored with regard to manufactured steel and not the input raw materials. The efficiency ratio between input material and liquid steel equals approximately 88 %, which implies that more raw materials are used than steel is manufactured.

The Ravne tailings disposal site is a landfill with inhomogeneous distribution of inert wastes, which are created during the processes of manufacture and processing of steel by companies located in the area of the Ravne Ironworks (slag, oxide coating, waste bricks, foundry sands, rubble). It is located in the immediate vicinity of the Metal Ravne company, in the industrial zone of Ravne. It is estimated that the area measures 100,000 $m^2$ and the total quantity of deposited material equals 1,500,000 $m^3$ (Repinc et al., 2004). The disposal site is operational, with some 20,000 tons deposited per year (Repinc et al., 2004). Wastes are deposited in heaps and then levelled with a bulldozer. The top part of the disposal site is

thus converted into a plateau, which can be used for various purposes (storage depot). Waste disposal is scheduled until 2050 (Drava, 2000). The disposal site is included in the list of industrial landfills as a disposal site of inert wastes.

Measurements taken from the lower part of the Ravne tailing disposal site are given in Figure 10.4. An average external gamma radiation dose rate of 0.17 ± 0.06 μSv $h^{-1}$ on the lower part of the disposal site has been measured (Repinc et al., 2004). Slag is being deposited there, which is piled into heaps. Since the measurement of external gamma radiation did not indicate significant deviation from the value of the surrounding reference location, a representative sample of deposited material from the lower part of the Ravne tailings disposal site was taken for the purpose of gamma-ray spectrometric measurement.

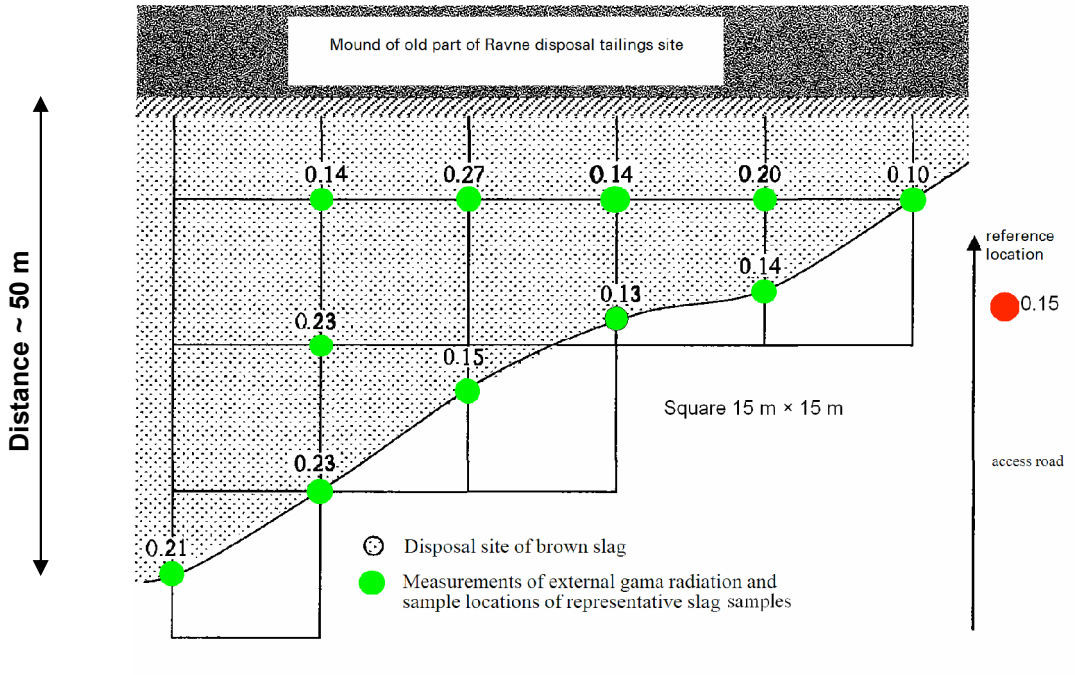


***Figure 10.4: Sampling scheme and results of measurements from the lower part of the Ravne tailings disposal (Repinc et al., 2004).***

The top part of the disposal site is flat and covered with gravel; escarpments are covered with grass. This is at the same time an overburden, since the materials used are inert. On the upper part of the disposal site measurements were taken only from the mound, which then descends into the lower part of the Ravne tailings disposal site. The results of the measurements are presented in Figure 10.5 and Table 10.24. Two samples of deposited material (oxide coating) were taken.

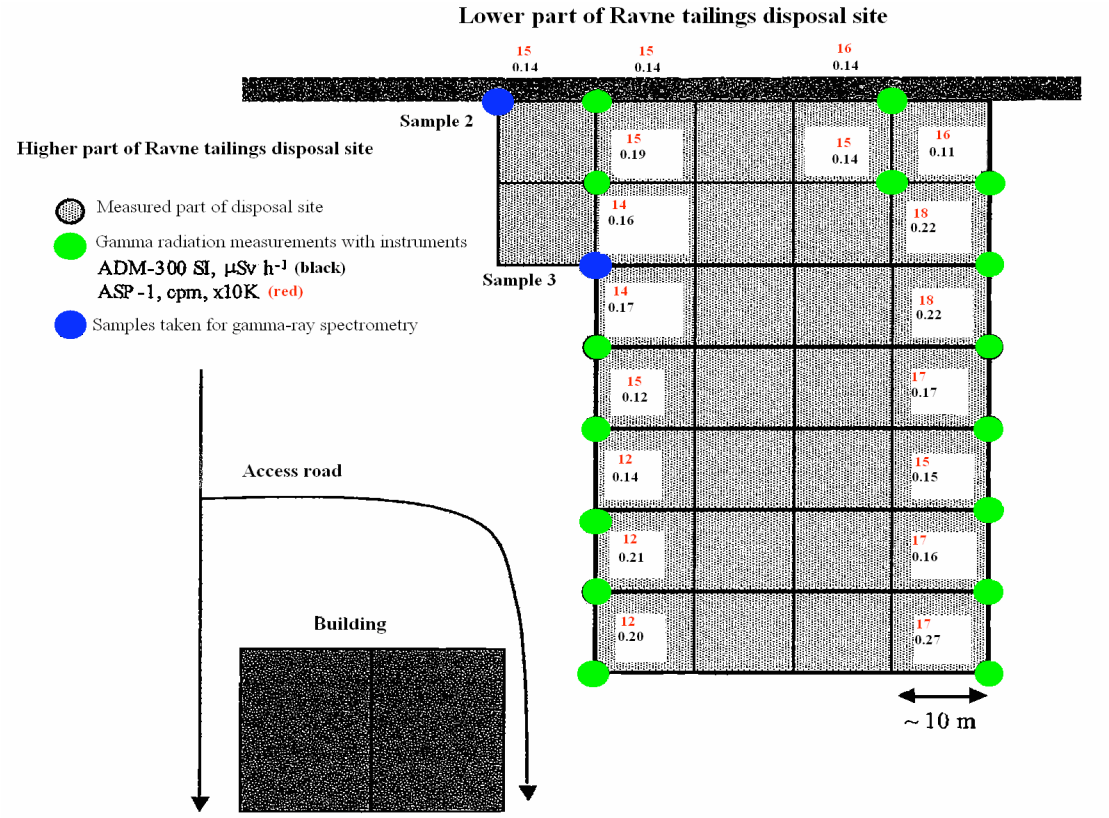


***Figure 10.5: Sampling scheme and results of measurements of upper part of the mound of the Ravne tailings disposal site (Repinc et al., 2004).***

***Table 10.24: Content of radionuclides in samples taken on Ravne tailings disposal (Repinc et al., 2004).***

| Sample | Specific activity (Bq kg$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}$Pb | $^{238}$U | $^{226}$Ra | $^{228}$Ra | $^{232}$Th | $^{40}$K | $^{137}$Cs |
| Lower mound of Ravne tailings disposal site | | | | | | | |
| Sample 1, slag | < 10 | 30 ± 3 | 41 ± 4 | 10 ± 2 | 11 ± 2 | 25 ± 2 | < 10 |
| Upper part of mound of Ravne tailings disposal site | | | | | | | |
| Sample 2, oxide coating | 53 ± 8 | 35 ± 6 | 48 ± 2 | 12 ± 2 | 12 ± 2 | 51 ± 3 | < 10 |
| Sample 3, oxide coating | 47 ± 8 | 20 ± 2 | 39 ± 2 | 10 ± 2 | 10 ± 2 | 41 ± 4 | < 10 |

## 10.2.11 Vremski Britof Bituminous Coal Mine

These coal deposits that lie on the Cretaceous-Tertiary boundary in Istria and the neighbouring Karst region belong to completely unique coal seams. Istrian coal is a bituminous coal that does not colorize potassium hydroxide, can be converted into coke, is of a deep-black colour but leaves a brown stain. It is reasonably hard, has a very high calorific value but also a high concentration of sulphur.

Mining activity in Vremski Britof has its beginnings in 18$^{th}$ century. Systematic mining was carried out only by the Italians between 1920 and 1931 and on the eve of World War II. After 1945 mining activity was confined to the Zavrhek mine/shaft, which held a 108-metre deep shaft that had been depleted and flooded in the autumn of 1955. Accordingly, work started with a revival of the Jadran IV shaft and also of old French excavations on the left side of the river. Coal from Vremski Britof is supposed to have been used in the Cinkarna Celje zinc

plant and Salonit Anhovo (Mohorič, 1978b). During radiometric prospecting in 1953 an increased level of coal radioactivity was discovered, with Austrians also showing interest in this coal, mainly on account of its high concentration of uranium, which they were extracting from ash.

There was formerly a large mound of mining tailings in the area of the Zavrhek shaft. The residents of this region levelled the mound and built-up the area after the purchase of the mining estate. Several residential houses are located in this area and there is a large residential house and a transformer station in the immediate vicinity of the shaft that is now filled with concrete.

Locals claim that a shaft in Vremski Britof remained in operation after the closing of Zavrhek shaft and until 1964, which had a depth of 68 metres and the first drift 36 metres deep. Mining structures, a forge, residues from separation and a nearby small mound of tailings are still present in the area of Vremski Britof. Today outcrops of coal seams can no longer be found on the surface virtually everywhere as formerly.

Measurements of external gamma radiation were taken in year 2004 (Repinc et al., 2004) in an approximately 100 metres wide area around the Zavrhek mine shaft and on the mining tailings landfill in Vremski Britof. Two soil samples were taken from hot-spots in Zavrhek with a measured higher dose rate of external gamma radiation when compared to other measurements from this area, and one sample from Vremski Britof.

Measurements of external gamma radiation made in year 2004 in Zavrhek were taken from the area surrounding the former 108-metre deep shaft of the coal mine, which had been operational until 1956 (Repinc et al., 2004). In the immediate vicinity of the mining shaft, which is filled with concrete, stands a residential building of moderate-size, whose owners had bought the former mining estate and levelled a mound of tailings that was located in this area. Measured dose rates of external gamma radiation from this area were between 0.15 and 0.20 μSv $h^{-1}$ (Repinc et al., 2004).

Increased radioactivity, measured by the IJS (Repinc et al., 2004), was detected at two locations (Figure 10.6), namely:

- On the sampling site of sample 1, where dose rates of external gamma radiation were between 0.35 and 0.40 μSv $h^{-1}$. Sample 1 consists mainly of humus-covered rock.
- On the sampling site of sample 2, where dose rate of external radiation equalled ~ 0.5 μSv $h^{-1}$. Sample 2 consists of soil beneath a layer of grass.

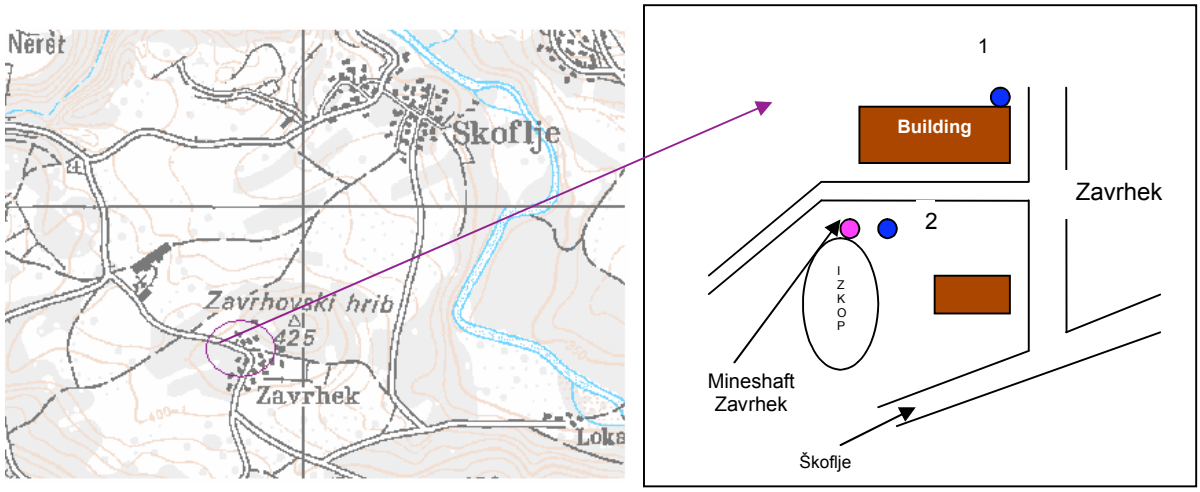


***Figure 10.6: Map and scheme of sample locations in Zavrhek (Repinc et al., 2004).***

A small mound of mining tailings can be found on the location of the former mine in Vremski Britof, next to the separation plant and the forge, which covers ~ 30 m × 30 m and where measurements of the dose rate of external gamma radiation were taken. A spot with an increased dose rate was found by the path next to the forge, where a sample of soil was

taken (sample 3; soil mixed with rock) for the purpose of gamma-ray spectrometry. The results of the measurements are presented in Table 10.25. It may be seen that the increased specific activity of sample 2 is due the higher content of $^{238}U$, $^{226}Ra$, $^{210}Pb$ and $^{40}K$ in soil.

***Table 10.25: Content of radionuclides in samples – taken near the Vremski Britof Coal Mine (Repinc et al., 2004).***

| Sample | Specific activity (Bq kg$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}Pb$ | $^{238}U$ | $^{226}Ra$ | $^{228}Ra$ | $^{232}Th$ | $^{40}K$ | $^{137}Cs$ |
| Zavrhek, humus covered rock (sample 1) | 28 ± 4 | 38 ± 3 | 50 ± 4 | < 10 | < 10 | 11± 1 | < 10 |
| Zavrhek, layer of grass (sample 2) | 3,590±312 | 4,942 ± 395 | 6,138 ± 119 | 22 ± 4 | 15 ± 5 | 153 ± 30 | 111 ± 12 |
| Vremski Britof, mound, soil mixed with rock (sample 3) | 690 ± 52 | 943 ± 75 | 1,457 ± 56 | 15 ± 9 | 8 ± 2 | 71 ± 10 | 37 ± 3 |

## 10.2.12 Kanižarica Coal Mine

The coal mine lies within the Črnomelj municipality and is located 3.5 km from the railway station. Coal deposits were already being exploited in the second half of 19th century, when the mine supplied coal to the foundry that had been built in Gradac at Črnomelj in 1850. Regular excavation of coal probably began in 1857, therefore we consider this to be the year of establishment of the Kanižarica Coal Mine. There are no data on its production at that time. 3,975,783 tons of sub-bituminous coal have been excavated from the Kanižarica Coal Mine in the period after World War II and 4,300,000 tons (rounded up) in total, from the beginning to the end of this mine. Coal production increased from 10,660 tons in the year 1946 to 143,000 tons in year 1969 on account of mine renewal and modernization, which was the highest annual production achieved in the history of this mine (Kanižarica Coal Mine, 2005).

Sub-bituminous coal was the principal source of energy in Slovenia after Word War II and coal mining was considered to be an activity of particular social significance. However, the structure of energy sources in the energy system changed considerably in the 1990s. Demands for ecologically-cleaner energy sources gained importance and the use of coal started to decline. The development strategy of the Slovenian energy system altered and sub-bituminous coal production naturally had to adapt. After Slovenian independence the Government adopted a decision to close small-scale coal mines, the Kanižarica sub-bituminous coal mine among them. Accordingly, coal excavation was scheduled to decrease and the last 20,000 tons left the pit in 1996. The year 1997 is the historical end of the Kanižarica Coal Mine (Kanižarica Coal Mine, 2005).

Several heaps of mining tailings were created on the site above the coal deposit during the operation of the mine. The area of the tailings site is 22,000 m$^2$ without escarpments and the volume of the deposited material some 71,000 m$^3$ (Kanižarica Coal Mine, 2005). The tailings site was located east of the mouth of the pit entrance. There was no extensive felling of trees in this area in the past.

Mining ended in this region after passage of the act on closing the Kanižarica mine in 1995. The closing programme adopted by the Government included, among other things, remediation of areas in the exploitative region of the mine such as the management of degraded areas, rehabilitation of the municipal infrastructure and remediation of the damage that had been caused through mining. Surface reclamation works also began with the closing process, mainly the remediation of the tailings site and other degraded areas resulting from mining. An industrial-commercial zone of 25 ha will be set up in the reclaimed area of the mine (Kanižarica Coal Mine, 2005).

Measurements and sampling were conducted in year 2004 (Repinc et al., 2004) in the area of still active deposition and remediation of mining tailings, where three samples of tailings and soil were taken. Tailings and soil are still being deposited into heaps on research area 1 that measures an estimated ~ 200 m × 200 m. The highest level was measured at site 1. The samples consisted of mining tailings mixed with coal and soil.

A former mining tailings disposal site is located in the rehabilitated area below the managerial building of the mine, which has been covered with overburden and grassed during the process of remediation. The research area 2 is covered with overburden and we took a sample of the reddish soil was used as overburden. A building has already been erected on part of the excavation area (Figure 10.7), with an excavation for the next building beside it. A sample of mining tailings was taken from the spot where the highest of external gamma radiation dose rate (sample 4) was measured. Sampling sites are indicated in Figure 10.7 and results of measurements in Table 10.26.

***Table 10.26: Specific activity of radionuclides in samples taken at locations of the Kanižarica Coal Mine (Repinc et al., 2004).***

| **Sample** | **Specific activity (Bq kg$^{-1}$)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}$Pb | $^{238}$U | $^{226}$Ra | $^{228}$Ra | $^{232}$Th | $^{40}$K | $^{137}$Cs |
| Sample 1, mixture of coal and soil | 552±68 | 749±64 | 612± 13 | 12±2 | 12±2 | 61± 16 | <10 |
| Sample 2, mixture of coal and soil | 279 ± 20 | 480 ± 56 | 300 ± 11 | 35 ± 2 | 36 ± 3 | 221 ± 12 | 15 ± 11 |
| Sample 3, reddish soil | 208 ± 27 | 371 ± 29 | 325 ± 10 | 19 ± 2 | 17 ± 2 | 98 ± 8 | <10 |
| Sample 4, reddish soil | 271 ± 31 | 427 ± 39 | 437 ± 10 | 23 ± 2 | 22 ± 2 | 125 ± 13 | <10 |
| Sample 5, reddish soil | 112 ± 13 | 126 ± 12 | 111 ± 2 | 91 ± 3 | 93 ± 2 | 562 ± 19 | <10 |

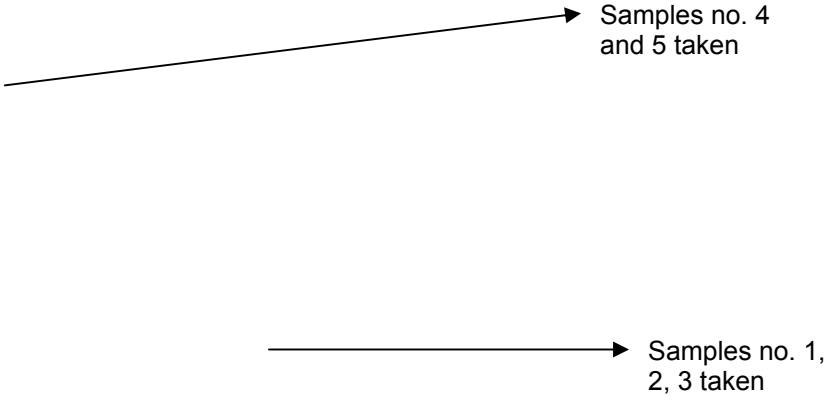


***Figure 10.7: Picture of the mining area of the Kanižarica Coal Mine (prepared after Kanižarica Coal Mine, 2005 and Repinc et al., 2004).***

### 10.2.13 Natural Gas and Oil Extraction (Nafta Lendava, 2005)

In 2003 Nafta Lendava was engaged in activities for the comprehensive rehabilitation of the company, which were outlined and initiated in 2002. Six subsidiary companies were established that are fully owned by the Nafta Lendava Company. The companies function as the group of Nafta Lendava enterprises. The Nafta Lendava Group thus comprises the following subsidiary companies in addition to the umbrella company:

- Nafta Petrochem, engaged in the production of methanol-based glues and resins.
- Nafta Strojna, engaged in the production of specialized machines and devices used in the chemical, petroleum and wood industries.
- Nafta Geoterm, engaged in the extraction of crude oil and natural gas, as well as ecological remediation of oil wells.
- Eko Nafta, which despite close-down of the refinery, plans to manufacture and market ecologically sound fuels with the emphasis on biofuels, in accordance with the guidelines of the European Union.
- Nafta Inženiring, which is an engineering company specialized in planning, supervision and management of investments, and in the conduct of work from all stages of the investment processes.
- Nafta Informatika, engaged in the maintenance and development of software for the business informational system of the Nafta Lendava Group.

Processes that are relevant within the framework of these tasks are foremost the extraction of natural gas and oil, and the management of waste produced, which falls under the domain of two subsidiary companies, Nafta Geoterm and Nafta Petrochem.

The most important mission of Nafta Petrochem is the ecologically sound production of organic chemicals and their derivatives. They operate a waste water treatment plant with an inflow of so-called “produced” water, which is extracted along with oil and natural gas. Development and setting up of the waste water treatment plant reaches back to 1980. The water treatment plant with its inflow of various waters utilizes mechanical, chemical and biological purification. Water is removed from the silt produced through centrifugation, and the silt is then solidified by adding quicklime. A temporary industrial landfill is used only for solidification cooling, while the waste is later deposited onto the Dolga Vas municipal landfill.

The Central Gas Station (CPP) of Nafta Lendava in Petišovci contains six reservoirs in which produced water and silt that are removed from extracted oil accumulate. Sampling of this silt was carried out in reservoir R4. The results of specific activity of radionuclides are presented in Table 10.27.

Sampling (Repinc et al., 2004) was carried out from drill pipe jackets and tubing pipe jackets of Nafta Lendava in the area of the Museum of the Petroleum Industry, and from drill pipe jackets from Moravske Toplice.

Measurements of external gamma radiation dose rate from the area of the Central Gas Station indicated no perceptible increase near reservoirs and around oil and natural gas pipelines. Measured dose rates ranged between 0.11 μSv $h^{-1}$ and 0.24 μSv $h^{-1}$ (Repinc et al., 2004). Measurements of external gamma radiation dose rates from the surface of drill pipes of Nafta Lendava showed no increased activity and did not deviate significantly from the measurements of background.

***Table 10.27: Content of radionuclides in samples taken at the location of Nafta Lendava (Repinc et al., 2004).***

| Sample | Specific activity (Bq $kg^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}$Pb | $^{238}$U | $^{226}$Ra | $^{228}$Ra | $^{232}$Th | $^{40}$K | $^{137}$Cs |
| Reservoir R4, silt | 40 ± 6 | 17 ± 3 | 154 ± 5 | 187±4 | 129 ± 2 | 212 ± 8 | <10 |
| Nafta Lendava, drill pipe jacket | 39 ± 11 | 71 ± 8 | 29 ± 10 | 20 ± 10 | 16 ± 10 | 124 ± 13 | <10 |

Continued …

***Table 10.27: Continuation***

| Sample | Specific activity (Bq kg$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{210}$Pb | $^{238}$U | $^{226}$Ra | $^{228}$Ra | $^{232}$Th | $^{40}$K | $^{137}$Cs |
| Nafta Lendava, tubing pipe jacket | 56 ± 9 | 30 ± 6 | 173 ± 34 | 26 ± 10 | 38 ± 10 | 54 ± 7 | <10 |
| Pipe jacket (Moravske Toplice) | 15 ± 11 | <10 | 270 ± 30 | 620 ± 41 | 245 ± 25 | 77 ± 11 | <10 |

## 10.2.14 Zirconium Minerals in Industry

A health inspector carried out three inspections on the Sežana (Slovenia – Italy) border crossing in 2000 regarding transportation. During the last inspection, rejection of the cargo was proposed because of excessive radioactivity. A driver by the name of G. Fekete (Black Family, Hungary) had been transporting ore containing zirconium silicate, which is rich in natural radioactive isotopes like uranium, radium and thorium. It has been ascertained after the acquisition of appropriate data on the activity that the concentration level did not exceed 70 kBq kg$^{-1}$ and that no special permit was necessary. However, this substance can pose a threat to workers in industry as a source of ionizing radiation. It is used in the production of ceramic glazes. Deposits of zirconium silicate can be found in Australia and South Africa, and the substance reaches Slovenia in the form of fine sand that is intended for instant use. The manufacturers of this product usually provide no data in the accompanying import documentation on the level of radionuclides. A representative of the Impol Company from Slovenska Bistrica on the 29$^{th}$ March 2000 discovered using of a manual radiation dose detector that a truck with a cargo bound for EMO Kemija Ltd contained material with an increased level of radioactivity. Analysis carried out by the Jožef Stefan Institute indicated the presence of $^{40}$K, while at the same time it was ascertained that zirconium silicate was deposited in Emo Kemija Ltd, which the company has been importing from Italy (SNSA, 2000).

Emo Kemija Ltd from Celje belongs to a group of smaller, yet (on account of product quality) reputable European manufacturers of frit and enamel. Priority activities of the factory are those of development, production and marketing of frits and enamels for the enamelling industry, frits and glazes for the ceramic industry, etc (EMO − company, 2005).

Martex Ltd from Volčja Draga is the leading Slovenian manufacturer of enamelled ceramic floor tiles with a hundred-year-old pottery tradition and a thirty-year-old tradition of production of ceramic tiles (Martex, 2005).

In Gorenje–Keramika from Šmartno ob Paki various ceramic mixtures are used in the production of ceramic products. Gamma-ray spectrometric analyses conducted in Italy indicated that the zirconium silicates contain 2,130–3,900 Bq kg$^{-1}$ $^{238}$U and 680–880 Bq kg$^{-1}$ $^{232}$Th (Repinc et al., 2004). Zirconium sand of Australian origin contains 2,460 Bq kg$^{-1}$ $^{238}$U; the level in sand is higher from Brazil (11,138 Bq kg$^{-1}$ $^{238}$U) and Malaysia (14,650 Bq kg$^{-1}$ $^{238}$U) (Repinc et al., 2004).

Tungsten electrodes with the addition of thorium are used in the industry for smelting, since they are resistant to high temperatures and have minimum solubility and corrosiveness. They contain 1.8 – 2.2 % of $ThO_2$ (72 Bq kg$^{-1}$ $^{232}$Th), as well as smaller quantities of metal oxides of zirconium, lanthanum, yttrium and cerium. The rods contain from 70 to 180 Bq $^{232}$Th per piece, which exceeds the thresholds under both criteria from the Decree on Radiation Practices when ten pieces are packed together (Table 3.1). Tungsten electrodes contribute only insignificantly to the external exposure to gamma radiation, as well as to the internal exposure on account of ingestion and inhalation during the smelting process, since there is virtually no release of radioactive substances from the electrodes. However, the whetting of electrodes does present a significant contribution to the exposure of workers, since a fine dust is formed during this process. The electrodes are used in the Impol Plc company, the industry of metal intermediate products from Slovenska Bistrica, where

products from aluminium and its alloys are manufactured by casting, rolling, extruding, and drawing, and in the Slovenian Steelworks Acroni Ltd from Jesenice.

## 10.3 Studies of TENORM impact on the radioactivity of underground and surface waters in Slovenia

In Slovenia most of the activities involving TENORM have been identified by various research studies. Processing of some raw materials creates by-products that have enhanced contents of some radionuclides. These products are usually disposed on sites where they are exposed to leaching of radioactive material into surface water and/or underground water, thus having a certain impact on the environment. Well-known are the disposal sites of coal ash and coal tailings (at Velenje, Trbovlje, Kočevje), the areas of the former disposal of roasted residues of mercury ore in Idrija and the disposal site of red mud from processing of bauxite (Kidričevo). Less known is technologically enhanced radioactivity due to titanium dioxide production (Celje) and phosphate processing (phosphogypsum from the Hrastnik chemical factory which was deposited for a relatively short period at the Unično site).

Benedik et al. (2004a) made a research study to examine the impacts of TENORM on the radioactivity of surface waters and underground water. Four locations were examined, namely Idrija (Hg ore), Velenje (lignite), Celje (ilmenite) and Kidričevo (bauxite, coal). The roasted residues of mercury ore and of lignite contain radioactivity of the uranium–radium chain, while phosphogypsum, waste acid from ilmenite processing and red mud contain mostly elements from the thorium decay series. Only key radionuclides of the U–Ra decay series in water were determined, while potassium (which is specific for waters in contact with coal ash) and radionuclides of the thorium series were not analysed. Seepage water from the disposal landfill at Unično, with deposited phosphogypsum totalling 0.2 million tons, was not measured due to the non-cooperative attitude of the management (Repinc et al., 2004).

In underground water at Velenje no enhanced radioactivity was detected but it can be seen from the report of the ERICo Institute that water from the same borehole contained as much as 56 Bq $m^{-3}$ $^{226}$Ra, 37 Bq $m^{-3}$ $^{210}$Pb and 232 Bq $m^{-3}$ $^{40}$K (Mljač, 2003). The quoted values of $^{210}$Pb at Idrija and Kidričevo exceed the derived limit value (200 Bq $m^{-3}$) based on the EC directive on the quality of water intended for human consumption 98/83/EC. These measurements should be repeated and appropriate measures should be carried out if necessary. The concentrations of $^{226}$Ra reach about one tenth of the limit value (500 Bq $m^{-3}$), derived from the same regulation.

Research studies already made on the topic of TENORM in Slovenia show that in future more attention has to be paid to radioactivity caused by TENORM. Future regulations, foreseen by the Act on radiation protection and nuclear safety, are being prepared to cover this subject appropriately.

Deposition on soil of material released from disposal sites/tips may also lead to enhanced downwind radiation fields. The deposited material may be re-suspended and give rise to inhalation exposure or enhanced concentrations in surface water when the material lands on water.

# 11 ESTIMATIONS OF EFFECTIVE DOSE

In the National control programme of radioactivity in Slovenia doses of external radioactivity are measured using 50 thermoluminescent dosimeters (TLDs). Dosimeters measure natural gamma emitters, the gamma component of cosmic rays and the ionizing component of cosmic rays. TLDs do not measure the neutron component of cosmic rays, which contributes about 12 % to the total effective dose of external radioactivity (UNSCEAR, 2000). The results of TLDs measurements in the year 2005 showed an average annual dose of 0.82 ± 0.14 mSv (SNSA, 2006). The Republic of Slovenia lies between latitude 45°25`N and 46°52`N. The UNSCEAR report (UNSCEAR, 2000) states that the annual dose from neutron flux at latitudes 40°N–50°N at sea level is 0.080 mSv. Applying a shielding factor of 0.8, an indoor occupancy factor of 0.8 and an outdoor occupancy factor of 0.2, the annual effective dose $E_n$ from cosmic ray neutrons to the Slovenian population is:

$$E_n = (0.080 \cdot 0.2 + 0.080 \cdot 0.8 \cdot 0.8) = 0.070 \text{ mSv} \quad (1)$$

In Table 11.1 are summarised annual effective doses of external radiation to residents of Slovenia. These annual doses are estimated based on the natural radioactivity component and radioactivity that is result of global contamination of the environment. The range of the natural contribution in the period 2002 – 2006 was between 0.86 and 0.89 mSv. The increase in 2005 is due to increased gamma radiation (ionizing component of cosmic rays) which was 0.82 mSv. In the period 2002 – 2004, gamma radiation was 0.79 mSv and in the year 2006 it was 0.8 mSv.

***Table 11.1: Annual effective doses received by the population in Slovenia due to natural radioactivity and global contamination of the environment (period 2002 − 2006).***

| Source of radioactivity | Annual effective dose in year 2002 (mSv) | Annual effective dose in year 2003 (mSv) | Annual effective dose in year 2004 (mSv) | Annual effective dose in year 2005 (mSv) | Annual effective dose in year 2006 (mSv) |
|---|---|---|---|---|---|
| Gamma radiation, ionizing component of cosmic rays | 0.79 (92 %) (SNSA, 2003) | 0.79 (92 %) (SNSA, 2004) | 0.79 (92 %) (SNSA, 2005) | 0.82 (92 %) (SNSA, 2006) | 0.80 (92 %) (SNSA, 2007) |
| Neutron component of cosmic rays | 0.07 (8 %) Ref. (1) | 0.07 (8 %) Ref. (1) | 0.07 (8 %) Ref. (1) | 0.07 (8 %) Ref. (1) | 0.07 (8 %) Ref. (1) |
| **Total (natural radioactivity)** | **0.86 (100 %)** | **0.86 (100 %)** | **0.86 (100 %)** | **0.89 (100 %)** | **0.87 (100 %)** |
| Contribution from global contamination as the consequence of past atmospheric bomb tests and the nuclear accident in Chernobyl | < 0.007 (SNSA, 2003) | < 0.007 (SNSA, 2004) | < 0.007 (SNSA, 2005) | < 0.007 (SNSA, 2006) | < 0.007 (SNSA, 2005) |
| **Total** | **0.86** | **0.86** | **0.86** | **0.89** | **0.87** |

The average Slovenian annual effective dose from natural sources to a single individual is about 2.5 to 2.8 mSv per year (SNSA, 2006), which is slightly higher than the world average, which is 2.4 mSv, ranging from 1 to 10 mSv (UNSCEAR, 2000). The contribution to natural radioactivity from natural gamma emitters, the ionizing component of cosmic rays and cosmic gamma emitters in Slovenia was 0.86 mSv in the period 2002 – 2004, 0.89 mSv in the year 2005 and 0.87 mSv in the year 2006. From Table 11.2 it can be seen that annual effective doses are below the Slovenian average natural radioactivity.

The purpose of the estimation presented in Table 11.2 is to consider what annual effective doses are received by people who are continuously exposed to external gamma radiation from TENORM at specific locations. The estimation of annual effective doses is conservative, because they are based on the assumption that people spend one fifth of their time outdoors (UNSCEAR, 2000). In previous sections are presented results of external gamma radiation measurements and measurements of concentrations of specific radionuclides in soil. These results were the basis for estimation of annual effective doses for

specific locations. It is true that some locations (e.g. Cinkarna Celje − Lake dam Za travnikom, RŽV) are not populated or there are no residents within a minimum radius of 1 km. The intention was to see what would the estimated annual doses be at those locations so a comparison between the numbers could be made.

In such estimations it should be remembered the comparability of calculated effective doses may be questioned because of:

- use of different measurement instruments/methods for measuring dose rates,
- reliability of the measurement comparison,
- uncertainty about the instrument calibration,
- detection limit of the instrument used.

The annual effective doses in Table 11.2 were calculated with the assumption that:

- people are exposed to measured doses all year at all locations; on that account a conversion coefficient of 0.7 Gy $Sv^{-1}$ was used for estimation of annual effective doses and an outdoor occupancy factor of 0.2 (Annex B, UNSCEAR, 2000).

$$E = H_T \cdot t \cdot 0.2 \cdot 0.7 \quad (2)$$

*E* *annual effective dose (Sv)*
$H_T$ *dose rate (Gy $h^{-1}$)*
*t* *time (1 year or 8760 h)*
*0.2* *outdoor occupancy factor*
*0.7* *conversion coefficient (Sv $Gy^{-1}$)*

To determine measured dose rates, Table 11.2 presents calculated dose rates based on radionuclide concentrations in the soil at the specific locations where the dose rates were measured. Applying the dose coefficients (UNSCEAR, 2000) relating to soil concentrations and applying the conversion coefficient of 0.7 (UNSCEAR, 2000), the absorbed dose rate $H_T$ is:

$$H_T = \sum c \cdot h_T \cdot C_c \quad (3)$$

$H_T$ *absorbed dose rate (Sv $h^{-1}$)*
$h_T$ *dose coefficient (nGy $h^{-1}$ per Bq $kg^{-1}$)*
*c* *concentration of radionuclide in soil (Bq $kg^{-1}$)*
$C_c$ *conversion coefficient (0.7 Sv $Gy^{-1}$)*

The dose coefficient for $^{40}K$ is 0.0417 nGy $h^{-1}$ (Bq $kg^{-1})^{-1}$, for radionuclides from the $^{238}U$ decay chain 0.426 nGy $h^{-1}$ (Bq $kg^{-1})^{-1}$, and for radionuclides from the $^{232}Th$ decay chain 0.604 nGy $h^{-1}$ (Bq $kg^{-1})^{-1}$ (UNSCEAR, 2000).

***Table 11.2: Comparison of measured and calculated dose rates at specific locations and estimation of annual effective doses.***

| **Location** | **Measured dose rate (nSv $h^{-1}$)** | **Calculated dose rate (nSv $h^{-1}$)** | **Calculated annual effective dose (mSv $a^{-1}$)** |
|---|---|---|---|
| NAFTA LENDAVA | 110 – 240 | – | 0.13 – 0.29 |
| VREMSKI BRITOF | | | |
| Zavrhek (average measurement) | 150 – 200 | – | 0.18 – 0.25 |
| Zavrhek (humus cover rock) | 350 – 400 | 39 | 0.43 – 0.49 |
| Zavrhek (soil beneath layer of grass) | 500 | 4385 | 0.61 |
| METAL RAVNE | 170 | 31 | 0.21 |
| ACRONI JESENICE | | | |
| average dose rate at disposal site | 127 | – | 0.16 |
| sampling location 1 (hot spot) | 211 | 211 | 0.26 |
| sampling location 2 (hot spot) | 168 | 77 | 0.21 |

Continued ….

***Table 11.2: Continuation.***

| Location | Measured dose rate (nSv $h^{-1}$) | Calculated dose rate (nSv $h^{-1}$) | Calculated annual effective dose (mSv $a^{-1}$) |
|---|---|---|---|
| KOČEVJE | | | |
| Recinko | 630 | 484 | 0.77 |
| At museum locomotive | 450 | 592 | 0.55 |
| Meadow by Mlakarjevo | 140 | 140 | 0.17 |
| Field by cemetery | 150 | 158 | 0.18 |
| Forest at power plant | 100 | 118 | 0.12 |
| House at power plant | 310 | 364 | 0.38 |
| Meadow at cemetery | 180 | 249 | 0.22 |
| Meadow Trata, Trata XIV | 80 | 90 | 0.1 |
| East lake side | 150 – 300 | 721 | 0.18 – 0.37 |
| North-west lake side | 100 – 200 | 130 | 0.12 – 0.25 |
| Šalka vsa (soil) | 100 | 105 | 0.123 |
| West lake side | 100 – 200 | 444 | 0.12 – 0.25 |
| Šalka vas (soil, sah, coal) | 200 – 400 | 989 | 0.25 – 0.49 |
| CINKARNA CELJE | | | |
| Lake dam Za travnikom | 70 | – | 0.09 |
| Lake | 38 | – | 0.05 |
| TKI HRASTNIK | | | |
| Disposal site Unično | 120 – 160 | – | 0.15 – 0.2 |
| Surrounding terrain | 60 – 90 | – | 0.07 – 0.11 |
| TE–TOL | | | |
| Ash (September 1993) | 200 | – | 0.25 |
| Ash (January 1994) | 150 | – | 0.18 |
| Tailings | 100 | – | 0.12 |
| Covering over ash | 100 | – | 0.12 |
| Above tailings | 90 | – | 0.11 |
| Kotredež | 120 | – | 0.15 |
| Surrounding area above the Ruardij landfill | 100 | – | 0.12 |
| BARJE | | | |
| Sand cover | 100 – 135 | – | 0.12 – 0.17 |
| Surface of ash landfill (average value) | 170 | – | 0.21 |
| IDRIJA | | | |
| Primary incineration residues | 250 – 400 | 336 – 386 | 0.31 – 0.49 |
| Secondary incineration residues | 160 – 240 | 118 – 307 | 0.2 – 0.3 |
| Tertiary incineration residues | 120– 140 | 134 | 0.15 – 0.17 |
| Soil (background) | 80 – 110 | 74 | 0.1 – 0.13 |
| Slovenia | 99 | – | 0.12 |

Table 11.2 shows the measured and calculated dose rates. Calculated dose rates, which are underlined (Table 11.2), are higher or lower than measured dose rates. Other calculated dose rates are comparable to measured dose rates. This calculation based on the radioactive contents was in agreement with the on-site measured radiation dose rate. The activity of $^{40}K$ in soil is an order of magnitude higher than that of $^{238}U$ or $^{232}Th$ (UNSCEAR, 2000).

In the assessment UNSCEAR (2000) suggests the representative concentrations of $^{40}K$, $^{238}U$, $^{226}Ra$ and $^{232}Th$ in soil. The median values for *in situ* concentrations of $^{40}K$, $^{238}U$, $^{226}Ra$ and $^{232}Th$ in the World are 400, 35, 35 and 30 Bq $kg^{-1}$, and the population weighted values are 420, 33, 32 and 45 Bq $kg^{-1}$, respectively (UNSCEAR, 2000). For Slovenia median values are 370 Bq $kg^{-1}$, 41 Bq $kg^{-1}$ and 35 Bq $kg^{-1}$ for $^{40}K$, $^{226}Ra$ and $^{232}Th$, respectively (UNSCEAR, 2000). On measured sites in Kočevje, specific activities of radionuclides from uranium decay series were higher and this contributed to higher calculated effective dose. In Idrija the highest specific activities of $^{40}K$ were measured (up to 920 Bq $kg^{-1}$). Median concentration of $^{40}K$ in Slovenia is 370 Bq $kg^{-1}$ (UNSCEAR, 2000). Measured specific activities of $^{40}K$ were

also higher in Idrija, Ruardij at Zagorje ob Savi and Kočevje. Specific activities of $^{232}$Th were higher than 35 Bq kg$^{-1}$ on all sites with the exception of Ravne and Vremski Britof. In Kočevje the highest specific activities of $^{232}$Th were measured (up to 66 Bq kg$^{-1}$). Specific activities of $^{226}$Ra were higher than 41 Bq kg$^{-1}$ on all sites. In Vremski Britof the highest specific activities of $^{226}$Ra were measured (up to 6,138 Bq kg$^{-1}$). High values were measured in Kočevje (up to 4,519 Bq kg$^{-1}$) and in Idrija (up to 1,140 Bq kg$^{-1}$). Specific activities of $^{238}$U were higher than 35 Bq kg$^{-1}$ on all sites. In Vremski Britof the highest specific activities of $^{238}$U were measured (up to 6,138 Bq kg$^{-1}$). High values were measured in Kočevje (up to 4,130 Bq kg$^{-1}$) and in Idrija (up to 1,090 Bq kg$^{-1}$).

For the radionuclide $^{226}$Ra in the $^{238}$U decay chain it is known that it may have a slightly different concentration than $^{238}$U, because separation may occur between its parent $^{230}$Th and uranium, and because radium has greater mobility in the environment, and that the decay products of $^{226}$Ra include the gaseous element radon, which diffuses out of the soil, reducing the exposure rate from the $^{238}$U series (UNSCEAR, 2000).

The cause of higher measured dose rates (dose rates higher than 100 nSv) is in the most cases a high concentration of $^{226}$Ra and $^{238}$U in soil and high concentration of $^{40}$K in soil. The difference in the measured dose rate and the calculated dose rate is also a result of anthropogenic pollution with artificial radionuclides and the result of a cosmic contribution.

To prove the estimations it is necessary to make consideration of all relevant radionuclides, chemical and physical processes of concern, pathways and exposure scenarios so as to provide the basis for:

- comparison with dose and risk constraints and environmental protection criteria;
- consideration of events, including their probabilities, that could lead to a release of radionuclides or other contaminants, or that could affect their rates of release or their rates of transport through the environment;
- estimation of radiation doses likely to be received by workers during operations;
- estimation of radiation doses and risks to members of the public, and specifically to the critical group, by different pathways, and estimation of environmental impacts;
- analysis of uncertainties and sensitivities, as appropriate, in order to determine the potential origins of the greatest risks.

For people living near disposal sites or on ex-disposal sites (e.g., Kočevje, Vremski Britof, Idrija) the risk of exposure to TENORM is higher than for people who do not live so near disposal sites of TENORM (e.g., Celje, Zagorje ob Savi, Hrastnik-Unično, Jesenice, Lendava). From the results presented in Table 11.2 it may be concluded that the annual effective doses are lower than the average natural background in Slovenia, doses do not indicate any reason of concern and show that TENORM do not represent harmful exposure for human health.

# 12 CONCLUSIONS

Based upon previous research studies that have been carried out by various research organizations in the past twenty years, upon historical data from the period between the 18th and 20th century and upon measurements of external gamma radiation and gamma-ray spectrometric analyses of the collected samples, identification of the most notable activities in Slovenia resulting in the occurrence of TENORM was made. The results presented indicate that materials deposited in the locations studied in Idrija, Kočevje, Vremski Britof and Kanižarica contain higher levels of natural radionuclides than those normally found in soil of the territory of Slovenia. The reason lies in the increased levels of uranium in ore and coal, which has been further intensified in waste products (furnace waste, ash) through the processes of production and exploitation.

In addition to the identification of specific radionuclides, an inventorying of TENORM that occur during particular activities was conducted. This includes identification of input raw materials and wastes, assessment of quantities, specific activities of key natural radionuclides and the scope of disposal sites where these wastes are being deposited.

The collected data, which are presented in forms that were available in study reports (e.g. as specific activity, dose rate, concentration), suggest that a minor quantity of TENORM occurs in Slovenia during industrial activities, which is mainly deposited onto secure disposal sites that are inaccessible to the general population, therefore likely causing only low exposure of particular individuals. The quantities of materials that are regularly produced in industry on a yearly basis are well recorded; old burdens remain a problem, since they are more difficult to identify and record on account of insufficient historical data. More than 90 % of TENORM occur during coal combustion in thermal power plants and in the steel industry, and they do not contain appreciable activities of natural radionuclides and are being deposited onto secure disposal sites (Repinc et al., 2004). The most critical from the viewpoint of radionuclide content, accessibility to the population and the quantity of these materials remain TENORM from former activities, particularly residues from mercury ore mining and residues from burnt coal in Kočevje and Vremski Britof, which have been deposited without supervision in town centres in the past. They are often the main contributor to the increased burden of residents with ionizing radiation in these areas, due to their use for construction purposes. In this areas private building constructions should be the subject of strict regulations.

In spite of the fact that increased sources of natural radioactivity can be found in Slovenia, the specific activities of radionuclides in wastes nevertheless seldom exceed prescribed exemption thresholds specified in the Decree on Activities involving Radiation (Off. Gaz. RS, No. 48/04). A comparison of the specific activities of TENORM in Slovenia with levels from around the world reveals that specific activities of significant radionuclides are typically lower, with the exception of coal ash and mining residues from regions with naturally increased radioactivity (Kanižarica, Kočevje, Vremski Britof, Idrija). The case of Vremski Britof is a good indicator that such studies, especially very specifically oriented ones, require special attention. Based upon generic evaluations of identified activities, TENORM occurring in such activities predominately represent only a small risk to individuals arising from exposure to ionizing radiation. On locations in Idrija, Ruardij at Zagorje ob Savi, Kanižarica, Senovo and Kočevje specific activities of $^{40}K$, are higher than 370 Bq $kg^{-1}$ (UNSCEAR, 2000).

Data from presented studies indicate that sites, where specific activities of radionuclides from U-series ($^{238}U$, $^{226}Ra$ and $^{210}Pb$) are higher, are sites with higher annual effective dose rates (e.g., Vremski Britof, Kočevje, Idrija). Calculated annual effective doses on all sites (Lendava, Vremski Britof, Ravne na Koroškem, Jesenice, Kočevje, Celje, Hrastnik, Ljubljana-Barje, Kotredež, Ruardija and Idrija) are lower than the average natural background in Slovenia. Doses do not indicate any reason of concern. Many of these sites are already “marked” as environmental and pollution control problem in Slovenia, but not due to TENORM. On Ravne na Koroškem and in whole area of the Zgornja Mežiška valley environmental and health problems are related to Pb mining and milling activities. In Idrija major environmental and health problem is related to Hg in environment. In Celje

environmental pollution with toxic metals (e.g. Cd, Zn) rises health issues. All information that are presented in the thesis show that every pollutant (e.g. TENORM, toxic metals) may be environmental concern. To define possible adverse effects on environment and on human health, systematic approach or holistic environmental and health studies are needed. TENORM studies showed that specific activities of radionuclides on investigated sites are lower than average natural background and due to that, they do not present harmful influence on environment or on human health.

When we are investigating human environment we must also include another important phase of work. This is public awareness. People should be informed about research studies that are running, about results of studies and provisional prognoses of future influence on human health. Public awareness in not just communication it is conversation between relevant stakeholders, education and awareness of envionmental issueses.

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# ANNEX 1

***Table A1.1: Survey of TENORM in Slovenia.***

| Activity | Location of production | Reference |
|---|---|---|
| **URANIUM MINING AND MILLING** | | |
| | Žirovski vrh Uranium Mine (mine operated in the period 1981-1990) | |
| **PHOSPHATE INDUSTRY** | | |
| | Phosphate industry TKI Hrastnik – from year 1994 (Hrastnik; disposal area Unično near town Marno) | TKI, 2005 |
| **TITANIUM OXIDE INDUSTRY** | | |
| | Cinkarna Celje (titanium dioxide production launched in the year 1973) | Company – strategy and history, 2005 |
| **OIL DRILLING** | | |
| | Nafta Lendava | |
| **ZIRCONIUM AND CERAMICS INDUSTRY** | | |
| | EMO Kemija Celje (Celje), Gorenje – Keramika (Šmartno ob Paki), Martex Volčja Draga (Volčja Draga | Češmiga, 1959 |
| **METAL MINING AND SMELTING** | | |
| MINING AND MILLING OF IRON ORE | | |
| 1. Iron mining | Preska at Polšnik, Fužina (1808; mine was near town of Planina pri Sevnici), Kopitov grič (1873; mine was near town of Zabočevo at Borovnica), Mokronog (from year 1913), Pilštanj (from year 1872), Savske jame in Lapajna (from year 1847; mine was near towns of Planina and Begunje under Golica), Studence (from year 1859; mine was near town of Studence near Žalec), Šentvid pri Planini (from year 1868; mine was near town of Šentvid at Planina, which is near Planina pri Sevnici), Vače (from year 1792). | Češmiga, 1959<br><br>Gestrin and Melik, 1966 |
| 2. Ironworks | Upper Carniola: Jesenice, Bohinjska Bistrica, Tržič, Kamna gorica, Spodnja Kropa, Zgornja Kropa, Spodnji Železniki, Zgornji Železniki, Kamnik | |
| | Lower Carniola: Gradac v Beli krajini (from year 1857), Zagradec ob Krki, Dvor pri Žužemberku, smelter Pasjek pri Savi – **smelter** was built in 1792 (right bank of river Save between Sava and Zagorje ob Savi; ore from Vače, Preska, Zagorje, Sitarjevec at Litija, Šmartno pri Litiji, Dobovec under Kum, Jelovec at Radeče), **smelter** Zavrstnik pri Litiji | |
| | Styria: Planina pri Sevnici, Mislinje, Lovrenc and Primož na Pohorju, Oplotnica, at Hudinji under Vitanje, Muta ob Dravi, Troblje at Slovenj Gradec, Štore (from year 1851) | |
| | Carinthia: Ravne na Koroškem | |
| | **Iron and steel industry still operating:** Acroni Jesenice, Metal Ravne, Štore Steel | |
| LEAD MINING AND MILLING | | |
| 1. Lead mining | Zavrstnik in Sitarjevec near Litija, Mežica Lead Mine (Main ore was formed of galenite (PbS) and sphalerite (ZnS). As a second transformation there were also ores the smithsonite ($ZnCO_3$), hydrozincite ($ZnCO_3 \cdot Zn[OH]_2$), cerussite ($PbCO_3$) and wulfenite ($PbMoO_4$)), Marija Reka (mine was in the Mrzlica hill near Trbovlje by the road Trbovlje-Prebold). | Češmiga, 1959<br><br>Gestrin and Melik, 1966 |

Continued …

***Table A1.1: Continuation***

| Activity | Location of production | Reference |
|---|---|---|
| **METAL MINING AND SMELTING** | | |
| LEAD MINING AND MILLING | | |
| 1. Lead mining | Knapovže at Medvode (from year 1853; mine was 14 km NW of Ljubljana, near the town of Topol), Bohor (from year 1874; mine was near the towns of Stranje and Golobinjek near Senovo), Log pri Vrhovem (from year 1882; mine was near town of Kompolje on right river bank of Sava, near Radeče), Srednik (from year 1889; mine was near town of Cerovec, 6 km NW of Sevnica), Šmarje pri Grosupljem, Lead Mine at Litija and Jablanica on right bank of river Sava (Lead was found in villages Gozd-Reka, Štangarske poljane, Zavrstnik, Sitarjevec at Litija, Zagorica, Na jezeh, Maljak, Pasjek, Jablanica, Liberga, dolina Preska, dolina Reka, Pusti malen, Lipoglav and Pleše east of Škofljica. The richest was the triangular area Sitarjevec-Jablanica-Meljak). | Češmiga, 1959<br><br>Gestrin and Melik, 1966 |
| 2. Lead milling | Lead plating workshop in Zagorje ob Savi (Toplice – from year 1843)– ore was from Litija area, Šoštanj (**smelter** was built in year 1877 on left bank of river Paka), Mežica, Žerjav (from year 1896), Pečnik (village between Mežica and Dolgo Brdo, **smelter** operated to year 1914) | Češmiga, 1959<br><br>Gestrin and Melik, 1966 |
| ZINC MINING AND MILLING | | |
| 1. Zinc mining | Litija Zinc Mine (lead was found in towns of Sitarjevec pri Litiji, Zagorica, Na jezeh, Sv.Agata, Jesenje, Tolsti vrh at Konjski potok), Trebelno (from year 1874; mine was between towns of Tržišče and Mokronog, east of Trebnje), Šoštanj (from year 1845; mine was in the region of the Šoštanj commune, on both sides of river Paka, near Šoštanj and near Velenje coal mine). | Češmiga, 1959 |
| 2. Zinc milling | **Smelter** in Zagorje ob Savi (Toplice – from year 1843) and **smelter** in Loke at Kisovec, Cinkarna Celje (beginnings in year 1875), Šoštanj (**smelter** was built in 1877 on right bank of river Paka) | Gestrin and Melik, 1966<br><br>Češmiga, 1959 |
| ALUMINIUM MILLING | | |
| | Talum Kidričevo (from year 1954) | |
| MERCURY MINING AND MILLING | | |
| 1. Mercury mining | Zavrstnik, Sitarjevec pri Litiji, Na jezeh, Marija Reka (mine lay near Mrzlica hill not far away from Trbovlje-Prebold road), Idrija (from year 1490), Sv.Ana (mine was found in year 1760; it lay in Sv. Ana commune on the Tržič-Ljubelj-Celovec road) | Češmiga, 1959<br><br>Šlebinger, 1949 |
| 2. Mercury milling | Idrija, Sv. Ana, Sitarjevec pri Litiji | |
| COPPER MINING | | |
| | Škofje (from year 1851; mine lay in Škofje pri Planini commune, N and NW from Idrija), Zlatenik (mine lied Blagovica commune), Ržiše, Cirkuše (in the area of Zagorja ob Savi). | Češmiga, 1959 |
| ANTIMONY MINING AND MILLING | | |
| 1. Antimony mining | Lepa njiva (from year 1874; mine lay near town Lepa njiva, which is 4,5 km N from Mozirje in Savinjska dolina), Trojane (from year 1907; mine lay near villages of Trojane, Brezje, Ržiše and Čemšenik) | Češmiga, 1959 |

Continued …

***Table A1.1: Continuation.***

| Activity | Location of production | Reference |
|---|---|---|
| **METAL MINING AND SMELTING** | | |
| ANTIMONY MINING AND MILLING | | |
| 2. Antimony milling | Trojane (production of metallic antimony was in operation for a short time) | |
| MANGANESE MINING | | |
| | Begunjščica (mine lay on south side of Begunjščice hill, at 1400 m altitude; mine was in operation between years 1847 - 1915), Mirna (from year 1917; mine lay near village of Brezovica and was 1.5 km from town of Mirna, by Trebnje-Sevnica railway). | Češmiga, 1959 |
| **COAL MINING AND POWER GENERATION FROM COAL** | | |
| 1. Coal mining | Kočevje Coal Mine, Šentjanž Coal Mine, Zagorje Coal Mine (mine lay in ex-municipalities of Ržiše, Loke, Zagorje, Potoška vas, Kotredež; valley is surrounded by the hills Mali vrh, Jablana, Partizanski vrh, Čemšeniška planina, Moravsko hribovje with Sv.Gora), Trbovlje Coal Mine (mine lay in tertiary valley, which extended over the area between Zagorja ob Savi, Trbovlje, Hrastnik and Laško), Hrastnik Coal Mine (mine lay in ex-municipalities of Dol pri Hrastniku, Marno, Sv.Lenart and Ojstro, N from river Sava in direction W-E), Govce (village W of Laško), Liboje Coal Mine (mine was in towns of Liboje and Zabukovica), Zabukovica Coal Mine (mine was south of river Savinja in villages of Griže pri Celju, Zabukovica and Sv. Pongrac), Pečovnik Coal Mine (mine lay SE from Celje castle), Senovo Coal Mine, Hrastovec (from year 1846; mine was near village Hrastovec, which is near the town of Poljčane in Styria region). | Gestrin and Melik, 1966<br><br>Češmiga, 1959 |
| 1. Coal mining | Zgornje Zreče (from year 1868), Stari trg pri Slovenj Gradcu (from year 1835), Leše at Prevalje (the most important Slovenian mine in the thirthies of the 19th century), Laško Coal Mine (mine lay W of river Savinja in villagesof Brezno, Huda jama, Sv.Krištof, Sedraž and Marno), Bituminous Cola Mine Zavrhek, Rodik (by Ljubljana-Koper railway) – Timav Bituminous Coal Mine (operated in 19$^{th}$ century and to year 1913), Vremski Britof Bituminous Coal Mine – in Primorska region (beginnings in 18$^{th}$ century, systematic excavation in years 1920-1931), Kanižarica Coal Mine (mine lay in Črnomelj commune in town of Kanižarica, beginnings in year 1857), Velenje Lignite Mine, Makole Hard Cola Mine, Ilirska Bistrica Lignite Mine, Globoko Lignite Mine (mine lay W of river Sotla near Croatian border), Orle (operation period from 1878 to 1948; mine was near the town of Ljubljana - Rudnik), Babna gora (from year 1877; mine was near the village of Babna gora, which is near the town of Loka pri Žusmu), Bela, Motnik (from year 1855; mine was near the town of Ločica pri Vranskem, in villages of Bela and Motnik), Brezovica at Mirna (from year 1857), Briše and Pleše (from year 1852; mine was near the town of Loka pri Zidanem Mostu), Danijel (from year 1860; mine was near the town of Loke pri Zagorju, near Kisovec), Hrastovec at Škale (from year 1852; mine was in village of Škale, which is near the town of Šoštanj), Dobovec pri Rogatcu (1877), Konjiška vas (from year 1869; mine was near the village of Konjiška vas which is near the town of Slovenske Konjice). | Gestrin and Melik, 1966<br><br>Češmiga, 1959 |

Continued …

***Table A1.11: Continuation.***

| Activity | Location of production | Reference |
|---|---|---|
| **COAL MINING AND POWER GENERATION FROM COAL** | | |
| 1. Coal mining | Mežica (from year 1869; mine was near Mežice), Podsreda (from year 1864; mine was near the town of Podsreda), Stranice (from year 1873), Šemnik (from year 1845; mine was near the town of Šemnik at Izlake), Vrh pri Boštanju (1893), Zbelovo (1873; mine is near the town of Zbelovska Gora near Poljčane). | Gestrin and Melik, 1966<br><br>Češmiga, 1959 |
| 2. Thermal power plants | Trbovlje TPP, Šoštanj TPP, Ljubljana TPP | |