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Variation of natural radionuclides in non-ferrous fayalite slags during a one-month production period

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Highlights

- Natural radionuclides monitored in non-ferrous slag during 1 month production.
- Large activity concentration fluctuations of natural occurring radionuclides.
- Disequilibrium in the ^{238}U decay series and equilibrium in the ^{232}Th decay series.
- Extensive comparison between different types of metallurgical slags.
- Continuous monitoring of the produced slag is advised to assure safe application.

Abstract

The European Basic Safety Standards (EU-BSS) describes a set of NORM (Naturally Occurring Radioactive Materials)-processing industries which produce residues known to be possibly enriched in NORs (Naturally Occurring Radionuclides). These residues can be used as a component in building materials aimed for public usage. The industrial processes, in which the residues are produced, are often complex and total monitoring can be challenging especially when the origin of the used raw materials varies. In this study the NORs present in non-ferrous fayalite slags of a secondary smelter facility, a NORM-processing industry according to the EU-BSS, were monitored daily during a one-month production period. In addition flue dust samples and feedstock samples, known to contain elevated levels of NORs, of the same period were measured. The survey involved the gamma-ray spectrometric analysis of the decay products from the ^{238}U and ^{232}Th decay chains,

^{235}U and ^{40}K using HPGe detectors. Secular equilibrium was observed for the slags, flue dust and feedstock samples in the ^{232}Th decay chain, in contrast to the ^{238}U decay chain. During the month in question the ratios of maximum over minimum activity concentration were 3.1 ± 0.5 for ^{40}K, 4 ± 1 for ^{238}U, 6 ± 1 for ^{226}Ra, 13 ± 7 for ^{210}Pb, 4.5 ± 0.6 for ^{228}Ra and 4.7 ± 0.7 for ^{228}Th for the slags. Even with the activity concentration of the feedstock material ranging up to 2.1 ± 0.3 kBq/kg for ^{238}U, 1.6 ± 0.2 kBq for ^{226}Ra, 22 ± 7 kBq/kg for ^{210}Pb, 2.1 ± 0.2 kBq/kg for ^{228}Ra and 2.0 ± 0.4 kBq/kg for ^{228}Th, none of the slag samples exceeded the exemption/clearance levels of the EU-BSS and RP-122 part II, which can respectively provide guidance under equilibrium and in absence of equilibrium. As each NORM-processing industry has its own complexity and variability, the observed variations point out that one should approach one-time measurements or low frequency monitoring methods cautiously. Low frequency measurements should be optimised depending on the discharge of the batches. A follow up of the industrial process and its output can provide important insights to assure a limited public exposure upon application of these industrial residues.

Finally a comparison is made with reported data on other metallurgical slags and the use of the slags in building materials is evaluated using the Activity Concentration Index (ACI) proposed by the EU-BSS.

1. Introduction

Each year over 400 million tons of metallurgical slags, a by-product from metal producing industries, are produced world-wide (van Oss, 2013). Due to the presence of Naturally Occurring Radionuclides (NORs) in the raw materials used by the metallurgical industries the produced metallurgical slag can contain enhanced concentrations of NORs. In Table 1 an overview is given on the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for different types of metallurgical slags reported in the literature. These activity concentrations are found in the intervals 2-69 kBq/kg, 2-130 kBq/kg and 2-23 kBq/kg for ^{226}Ra, ^{232}Th and ^{40}K, respectively. It must be noted that this list is not exhaustive and some data originate from samples of the 1980's. In several cases the number of measured samples is not specified and not all considered NORs (^{226}Ra, ^{232}Th and ^{40}K) are reported. The data and nomenclature are shown as mentioned in the corresponding reference. Data on other radionuclides mentioned in the corresponding reference is not shown in Table 1. The two main classes of metallurgical slags are non-ferrous and ferrous slags (Piatak et al., 2015a). Especially for non-ferrous slags such as Sn, Nb and Cu slags, higher activity concentrations can be found reaching up to (Table 1):

- 69 kBq/kg ^{226}Ra, 130 kBq/kg ^{232}Th and 23 kBq/kg ^{40}K for Sn slag,
- 5 kBq/kg ^{226}Ra and 118 kBq/kg ^{232}Th for Nb slag
- 2.1 kBq/kg ^{226}Ra, 0.1 kBq/kg ^{232}Th and 1.3 kBq/kg ^{40}K for Cu slag.

Non-ferrous slags typically consist mainly out of Fe and Si whereas the ferrous slags are typically rich in Ca and Si (Piatak et al., 2015a). The production of non-ferrous slag is limited to approximately 12% of the total worldwide slag production (National Slag Association, 2013). Non-ferrous industries that process niobium ores or work on tin, lead or copper smelting and therefore produce Nb, Sn, Pb and Cu slags are specifically considered in Council directive 2013/59/Euratom, known as the European Basic Safety Standards (EU-BSS), as practices involving naturally-occurring radioactive materials (NORM). In addition residues of steel production are regulated by the EU-BSS for use in building materials. In Table 1, it is also demonstrated that a large range of activity concentrations can be found for a given type of metallurgical slag. For example for Sn slag, the activity concentrations range from 0.5 - 69 kBq/kg for ^{226}Ra, 0.2 - 130 kBq/kg for ^{232}Th and 0.3 - 23 kBq/kg for ^{40}K. The measured activity concentrations for different non-ferrous slags are in several cases higher than the activity concentrations for exemption or clearance of NORs in solid materials in secular equilibrium with their progeny, proposed by the EU-BSS (European Commission, 2014). The EU-BSS exemption/clearance levels were chosen in accordance with the exemption/clearance levels of the IAEA "Application of the concepts of exclusion, exemption and clearance". A global level benefits the industries processing and transporting these materials from an administrative and legislative point of view. These EU-BSS | IAEA levels are 1 kBq/kg for natural radionuclides from the ^{238}U and ^{232}Th decay series and 10 kBq/kg for ^{40}K (Table 2) however these levels are only applicable if secular equilibrium in the decay series is obtained. The EU-BSS allows higher values in case of disequilibrium but does not specify which levels are recommended. RP (Radiation Protection)-122 specifies these values and applies of a summation rule for the radiological evaluation (Table 2) (European Commission, 2002).

Before use of non-ferrous slag can be allowed, the EU-BSS requires that the value of the activity concentration relative to the exemption/clearance levels is determined. In addition the EU-BSS specifies a screening index called the Activity Concentration Index (ACI) applicable for building materials containing these residues (Equation 1).

$$ACI = \frac{Ac_{Ra226}}{300\ Bq/kg} + \frac{Ac_{Th232}}{200\ Bq/kg} + \frac{Ac_{K40}}{3000\ Bq/kg} \qquad (1)$$

With Ac as activity concentration of the mentioned radionuclide expressed in Bq/kg.

According to the EU-BSS this index allows estimating the requirement that upon application of these building materials the public exposure is below the effective dose limit of 1 mSv a year. An ACI value below 1 assumes that the dose limit of 1 mSv a year is not exceeded. The application of metallurgical slags in building materials is gaining interest and the applications depend on the chemical composition, cooling path, availability, price, etc. (Piatak et al., 2015a). Usage of metallurgical slags in tiles, in railway ballast, in roofing materials, in coloured glass and in cementitious materials are reported (Piatak et al., 2015b). The main usage is as a raw material in asphalt and concrete mixtures for road construction – mainly for ferrous slag (Piatak et al., 2015b). Recently the application of non-ferrous slag as a binder to produce inorganic polymers building materials was reported (Pontikes et al., 2013). Inorganic polymers (IPs) are novel types of building materials with lower CO_2 emissions in comparison to concrete (Provis, 2014). IPs can be used in similar applications as conventional concrete (Provis and Van Deventer, 2014). In addition, other reuse and recycle options are reported, like usage as sand blasting material, as reprocessing material for secondary metal recovery and for environmental remediation (Al-jabri et al., 2011; Piatak et al., 2015b). Despite these applications, still large fractions of slags currently ends up on landfills (Piatak et al., 2015a).

A common feature of the listed studies on metallurgical slags in Table 1, is that the measurements represent a one-time sampling and that none of the considered studies follow the output of the process over a period of time. Therefore no information is available to verify to which extent variations in the industrial process or in the origin of the incoming raw materials over time can impact the activity concentration of the produced non-ferrous slag. The current study, which focuses on non-ferrous fayalite slags produced in a secondary smelter for production of different types of non-ferrous metals, aims to address this aspect. The production during a one-month production period was monitored. Within this framework the activity concentrations of NORs are evaluated against the exemption/clearance levels of annex VII of the EU-BSS. The variation in activity concentration of the long-living natural radionuclides is discussed, as well as the (dis)equilibria which are present. Finally the ACI is discussed since these slags are used for the production of IP building materials.

2. Methods and materials

2.1 Samples

The samples in this study originate from a secondary smelting plant aimed at the production of different types of non-ferrous metals. The factory handles a broad range of primary and secondary raw materials from industries listed in annex VI of the EU-BSS as industries with naturally occurring radioactive materials (European Council, 2014). The smelter facility is sorted under the category tin/lead/copper smelting in annex VI of the new EU-BSS. Non-ferrous fayalite slags are produced as by-product.

2.1.1 Non-ferrous fayalite slag samples

Every day, several smelting cycles are performed and with each cycle a different amount of slag is produced. These residues are the remaining after the recovery of non-ferrous metals from the feedstock by pyrometallurgical processes.

Representative samples of slags from each smelting cycle were taken during a one-month period. The samples were collected directly from the liquid bath situated in the furnace. This implies that the sample is representative of the batch and that it is homogeneous. The produced fayalite slags were cooled by water quenching. In order to limit the number of samples for analysis and because the slags are discharged daily, one sample for each day was produced based on samples from several smelting cycles of that particular day. The relative contribution of each smelting cycle sample to the daily sample was proportional to the slag production quantity of each smelting cycle (Equation 2).

$$Composition\ daily\ sample = \sum_{i=1}^{n} \frac{Quantity\ production\ batch\ i}{Quantity\ day\ production} * 100\% \qquad (2)$$

All cycle samples were dry and milled to powders by disk milling. In total 31 slag mixtures were produced corresponding to 31 consecutive days of slag production. Each slag mixture dry mass varied between 80 g and 140 g. The samples of a first batch of slag samples were measured after a period of approximately 470 days after sample collection. Samples from a second batch (indicated as second batch), in total two fayalite slags samples, were sampled at a later date, prepared in the exact same way as the first batch and measured after a period of approximately 180 days after sample collection.

The slag samples are rich in aluminium oxides (typically 6% (by mass)), iron oxides (typically 55% (by mass)) and silicon oxides (typically 23% (by mass)).

2.1.2 Flue dust samples

The flue dust is recovered by leading the off-gasses through fabric filter units. These are cleaned at regular time intervals by which the dust is transferred to dust silos for temporary storage. By the cleaning action and the subsequent fluidization of the dust for transport purposes, the dust is already mixed in the silos. Trucks are loaded directly from those silos. At several places of the truckload, grab samples are collected and mixed to form a homogeneous sample for measurements. Nine different batches of dust samples were monitored during the one month production period, containing mainly Zn, and minor amounts of other non-ferrous metals. The dry mass of the collected samples ranged from 42 g to 76 g. The samples were measured after a period of approximately 470 days after sample collection.

2.1.3 Feedstock samples

All feedstock materials are monitored upon arrival via a detection portal. As a result of this screening one type of feedstock material with elevated activities is selected for further investigations in the framework of this study. The considered feedstock material is mainly a metallic by-product of a primary non-ferrous metal producer, containing iron (> 70%), and minor amounts of other metals. The radioactivity is primarily resulting from slag inclusions, which are difficult to separate from the metal phase. The considered feedstock material is a minor fraction of the total feedstock materials used in the production process. Samples for measurement were produced by mixing delivered lots (size from 25 to 50 ton) homogeneously by mobile cranes, and subsequently performing several “coning & quartering” actions until a homogeneous and representative sample of about 500 kg is reached. This sample is further downsized by the same techniques using manual actions until a sample of circa 50 kg remains. Grab samples of this final sample were used for measurements. Five different batches of feedstock materials were monitored during the one month production period. The dry mass of these samples ranged between 260 g and 570 g. The samples were measured after a period of approximately 470 days after sample collection.

2.2 Radiological analysis

Measurements were performed on different HPGe-detectors of the Radionuclide Metrology Laboratory of JRC-Geel in Belgium. All detectors are located in the 225 m deep underground laboratory Hades located on the premises of the Belgian Nuclear Centre SCK•CEN in Mol, Belgium except for Ge T-5 which is located above ground. The detector details are listed in Table 3. The low background count rates of the underground detectors were in the order of 200 to 400 counts per day in the energy interval 40 to 2700 keV. The background count rate of individual peaks was mostly below 1 count per day. This low background is particularly important when measuring NORs that are known to be present in all detector systems. All samples for gamma-ray spectrometric analysis were transferred to radon tight Teflon containers and stored for at least 21 days to reach secular equilibrium between ^{226}Ra and daughters. The slag and flue dust samples were positioned 2 mm above the endcap of each HPGe-detector except for detector Ge-8 where the samples were placed directly on the endcap. The feedstock samples were positioned 11 mm above the endcap of the HPGe-detector. The measurement times ranged from 2 to 7 days and the dead time was always below 1%.

Canberra's Genie 2000 software was used for data acquisition and spectrum analysis. The EGSnrc (electron gamma shower National Research Council Canada) (Kawrakow et al., 2009). Monte Carlo code was used to calculate the full energy peak (FEP) efficiencies and the coincidence summing corrections. The Monte Carlo code input consists of the sample’s measured dimensions, composition and density, and the detector set-up. Isotropic and uncorrelated emission of the gamma-rays was assumed in the simulations. A homogeneous distribution of radionuclides in the sample and of the sample material in the sample container were two other assumptions that were adopted in all the calculations.

The radionuclides occurring in natural decay series of ^{238}U and ^{232}Th, as well as ^{235}U and ^{40}K were investigated by their emitted gamma rays. An overview of the used gamma lines is found in Croymans et al. 2016 (Croymans et al., 2016).

A weighted mean of the activity was calculated for radionuclides with multiple gamma-rays. The activity of the different gamma-rays was taken into account. The Decay Data Evaluation Project (DDEP) website was used for the nuclear decay data (Laboratoire national Henri Becquerel, 2016).

The 186 keV peak is a doublet with contributions from ^{235}U (185.7 keV) and ^{226}Ra (186.2 keV). By subtracting the contribution from ^{226}Ra, which activity was determined from its daughters ^{214}Pb and ^{214}Bi, from the 186 keV doublet peak, the activity of ^{235}U is calculated. In addition this result was confirmed by the other three main gamma lines of ^{235}U i.e. 143.8 keV, 163.4 keV and 205.3 keV. As natural isotopic abundance is expected for ^{235}U in these "non-nuclear" samples, one can see the measured ^{238}U/^{235}U activity ratio as a quality control of the measurement.

The activity concentration (in this paper meaning the activity per unit of mass) was determined by dividing the final activity determined for each radionuclide by the measured dry mass of the sample. All the activity concentrations are determined on the measurement date, mentioned in section 2.1 for each sample. Thus, no decay correction to the sampling date was made. The time of measurement between the first slag sample and the last slag sample was 42 days.

The uncertainties of the obtained activity concentrations are the combined standard uncertainties calculated according to the GUM (Guide to the expression of uncertainty in measurement) (JCGM WG1, 2008). When combining several gamma-rays to one activity-value for one radionuclide and when combining activity-values from several daughters to one mother radionuclide using weighted means, the correlated parameters were excluded from the calculation of the uncertainty of the weighted mean and added separately afterwards in quadrature in order not to obtain unrealistic and far too low final uncertainties.

The ACI was calculated for slag 1 to 31 using the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K (Equation 1). The EU-BSS assumes equilibrium between ^{232}Th and ^{228}Ac, and therefore the activity concentration of ^{228}Ac is used. The ACI calculation performed here assumes that the building material is constructed solely of the non-ferrous slag. Novel developments in IP production allow developing building materials solely out of non-ferrous fayalite slag (Kriskova et al., 2015).

Uncertainty of the ACI is calculated like in Equation 3

$$u(I) = \sqrt{\left(\frac{1}{300}\right)^2 \; u^2\,(Ac_{226Ra}) + \;\left(\frac{1}{200}\right)^2 \; u^2\,(Ac_{232Th}) + \;\left(\frac{1}{3000}\right)^2 \; u^2\,(Ac_{40K})} \quad (3)$$

Where I is the activity concentration index, u(Ac) is the uncertainty of the activity concentration of the mentioned radionuclide.

3. Results & Discussion

Figures 1 and 2 show the measured activity concentrations of radionuclides from the ^{232}Th and ^{238}U decay series in the slag mixtures. Table 4 shows the minimum and maximum activity concentrations, the ratio of the maximum over the minimum activity concentration and the ratio of different long living radionuclides over each other for feedstock material, flue dust and slag samples.

3.1 Assessment of radiological equilibrium in samples

3.1.1 The ^{232}Th decay series

The activity concentrations of the relatively short-lived ^{224}Ra, ^{212}Pb, ^{212}Bi and ^{208}Tl (corrected for its branching) were equal within the measurement uncertainties. Their weighted mean value gave the activity concentration for ^{228}Th ($t_{1/2}$= 1.9126 years). The activity concentration of the short-lived ^{228}Ac was in equilibrium with its mother ^{228}Ra ($t_{1/2}$= 5.75 years). Looking at Table 4 the ratio of ^{228}Ra over ^{228}Th equals 1 in the feedstock material samples, flue dust samples and slag samples. For the slags, this equilibrium is not likely to have been established in the relatively short time (~470 days, two-thirds of the $t_{1/2}$ of ^{228}Th, and ~180 days, a quarter of the $t_{1/2}$ of ^{228}Th; respectively for Batch 1 and 2) between the production and the measurement. This means that Ra is not separated from Th during the industrial process of non-ferrous metal production. Th and Ra are both lithophilic and will therefore end up in the slag phase (Bourdon et al., 2003; White, 2013). The affinity for silicates of both radionuclides confirms the unaffected equilibrium during the industrial process. Often in literature, equilibrium is assumed between ^{232}Th and ^{228}Ra, here the activity of ^{228}Ra is shown since this one is actually measured.

3.1.2 The ^{238}U decay series

For the ^{238}U series (Figure 2), the activity concentrations of ^{234}Th and ^{234m}Pa represent the activity concentration of ^{238}U, secular equilibrium is assumed in case of the slags since measurements of the slags took place 470 days after the production. The activity concentrations of ^{214}Pb and ^{214}Bi were equal within the measurement uncertainties so their mean value was taken as the activity for ^{226}Ra. The ^{226}Ra activity concentrations are for the slags a factor 1.7 ± 0.4 to 7 ± 2 lower than the activity concentration of ^{238}U (Table 4). This indicates an absence of equilibrium between ^{238}U and ^{226}Ra in the slags. This absence is surprising since U, Th and Ra, all are part of the first section of the ^{238}U decay series (^{238}U to ^{226}Ra) and are lithophilic elements (Bourdon et al., 2003; White, 2013). So these elements have a high affinity for silicates and are expected to mainly end up in the slag phase.

This disequilibria is also present in the investigated feedstock material but less distinct, with a minimum and maximum ratio ^{238}U/^{226}Ra of 1.2 ± 0.2 and 1.9 ± 0.3 respectively (table 4). Looking at another output material of the industrial process, the flue dust demonstrates an even more outspoken absence of equilibria with a minimum and maximum ^{238}U/^{226}Ra ratio of respectively 10 ± 3 and 30 ± 10. It must be noted that the ^{238}U (maximum 50 ± 10 Bq/kg) and ^{226}Ra (maximum 3.3 ± 0.2 Bq/kg) activity concentrations of the flue dust samples are low in comparison with ^{238}U (minimum 42 ± 4 Bq/kg) and ^{226}Ra (minimum 14 ± 2 Bq/kg) activity concentrations of the slag samples (Table 4). In addition, per ton slag approximately 25 kg of flue dust is produced. This means transport of ^{238}U and ^{226}Ra to the flue gasses is limited. The activity concentrations of ^{238}U and ^{226}Ra in the metallic fractions are low - this is confirmed by the company, however no data can be made publicly available. Regarding the lithophile properties of U and Ra and their limited absolute transport, it is believed that other sources of NORs which have a higher degree of disequilibrium than the measured feedstock material are present and consequently explain the relatively high level of disequilibria in the slag samples.

The activity concentrations ratios of ^{210}Pb over ^{226}Ra in the non-ferrous slags range between 0.14 ± 0.09 and 1.4 ± 0.5 (Table 4). In nine cases an absence of equilibrium is observed and the activity concentration of ^{210}Pb is lower than the activity concentration of ^{226}Ra. However in slags 6 to 11, slags 17 to 23, slag 25 and slags 27 to 29 equal activity concentrations are measured (Figure 2). It is important to note that the observed equal activity concentrations of ^{226}Ra and ^{210}Pb cannot originate from the instalment of equilibrium of ^{210}Pb with ^{226}Ra during or after processing, since the half-life of ^{210}Pb is 22.23 years. Table 4 shows that for the flue dust the minimum and maximum ratios ^{210}Pb/^{226}Ra are 110 ± 30 and 900 ± 300 respectively and for the feedstock material they are 8 ± 3 and 20 ± 7 respectively. So the absence of equilibrium is already present in the feedstock material but is less pronounced for the slag samples and more pronounced for the flue dust samples. An enrichment in Pb concentration and enhanced ratios ^{210}Pb/^{226}Ra in dust samples were also observed by Khater and Bakr which studied the transport of ^{210}Pb transport in metallurgical industries (Khater and Bakr, 2011). The transport of Pb towards flue dust and fumes can be subscribed to the volatile nature of Pb. In addition the ratio ^{210}Pb over ^{226}Ra in the slags samples is influenced by the transport of Pb towards the metallic phase i.e. the produced metal alloy. This transport is depending on the reduction potential in the furnace of the investigated smelter facility. Strong reducing conditions favor the transport of Pb towards the metal phase.

No ^{210}Pb was measured in slags 1 to 5 and the Minimum Detectable Activity (MDA) with a confidence limit of 95% was below 20 Bq/kg for slags 1 to 4 and 160 Bq/kg for slag 5. The MDA of slag 5 is higher due to the thicker dead layer of detector Ge-3, which impacts the FEP for the low-energy gamma-ray of ^{210}Pb.

The ratio of activity concentrations ^{238}U/^{235}U of all slags agreed within the uncertainties (except for slag 19) with the expected value of 21.6. The measured ^{238}U/^{235}U ratios (Figure 3) indicate therefore the expected natural isotopic composition. This is an important quality control measure, which indicates that the gamma-spectrometric measurements were robust.

3.1.3 ^{40}K

Potassium-40 is not a part of a decay series and has lithophilic properties (White, 2013). The ^{40}K activity concentrations in the slags vary between 26 ± 8 Bq/kg and 80 ± 10 Bq/kg (Figure 4 and Table 4).

3.2 Temporal variation in the activity concentrations

The ratios of the maximum measured activity concentration over the minimum activity concentration for each long living radionuclide in the different materials (Table 4) indicate significant fluctuations. For the slags, the lowest ratio was 3.1 ± 0.5 for ^{40}K and the highest ratio was 13 ± 7 for ^{210}Pb whereas for the flue dust samples the lowest ratio was 2.0 ± 0.3 for ^{228}Ra and the highest ratios was 4.3 ± 0.7 for ^{40}K. The variations in the non-ferrous slag and flue dust samples can be explained as the smelter facility uses a mixture of primary and secondary raw materials. The radiological content of the input materials is strongly depending on the origin and as the data of the investigated feedstock material (Table 4 and Figure 4) suggests also variations occur even when the origin of the input material is the same (IAEA, 2003). For the feedstock materials the lowest observed maximal/minimal ratio was 2.2 ± 0.6 for ^{228}Th and the highest observed ratio was 9 ± 7 for ^{40}K.

The selection of the input material is driven by economical factors and optimised in function of the produced metals in order to obtain a stable elemental composition in the slags and metals (Nakamura and Halada, 2015). In addition the company states that the amount of metals present in the input stream influences the quantity of slags and metals produced. Both quantities are also influenced by the process parameters. Therefore differences occur between the production batches and as a result a large variation in activity concentration is observed even in the studied one-month period. It is clear that conclusions based on the radiological characterisation of one day production can be very misleading.

These measures will only bear information on a specific time and not on the variation of the activity concentrations. Drawing conclusions based on a one-time sampling or low frequency sampling in order to ensure radiation protection of general public and workers should be performed cautiously. The authors recommend performing radiological measurements depending on the frequency of the discharge of the residues taking into account the complexity and variability of the facility/industry.

3.3 Comparison of activity concentrations with the literature.

As discussed in the introduction and shown in Table 1 metallurgical slags can contain various amounts of NORs. Overall the activity concentrations of the measured fayalite slags of this study are low compared with the metallurgical slags of Table 1. The quantity of slag per produced quantity of metal can vary depending on the production process. Gorai et al. estimated that for every ton of copper 2.2 ton of slag is produced whereas Proctor et al. estimated that 220-370 kg blast furnace slag is produced per ton of produced iron (Gorai and Jana, 2003; Proctor et al., 2000). This in combination with the chemical characteristics of the slags and metals produced influences the transport of radionuclides and gives rise to enrichments or depletions in comparison with the input materials. Here the slags originate from a secondary smelter facility, with a tonnage ratio of produced slags over metal above 1 and with scrap being the main input material for the recycling of metals. Since not all the feedstock contains enhanced concentrations of NORs, the result is that the activity concentration of the resulting slag is lower than the most active components in the feedstock.

3.4 Evaluation in function of legislative criteria

3.4.1 Evaluation considering the exemption and clearance levels

Except for ^{210}Pb in the flue dust samples, all activity concentrations of the long living radionuclides in the slag and flue dust samples are below the EU-BSS | IAEA and RP-122 exemption/clearance levels (Table 2 and 4). This is in contrast with the feedstock materials for which all radionuclides – except for ^{235}U and ^{40}K - are above the exemption/clearance levels.

RP-122 part II specifies the exemption/clearance levels even when the secular equilibrium is absent via a summation rule. For slag 18 – having the highest observed activity concentrations - the result of this summation rule is 0.52 ± 0.03, well below the exemption/clearance level of 1.

3.4.2 Evaluation for use as building material considering the ACI

Figure 5 shows the variation of the ACI when the fayalite slag is solely used (100%) to construct a building material. No day production batch exceeded the index value of 1, therefore every day production batch can be used as an building material. It must be noted that the highest observed activity concentrations (slag 18) are approximately a factor 12, 10 and 120 below the exemption/clearance levels of the EU-BSS for respectively ^{226}Ra, ^{232}Th and ^{40}K, however the index has a value of approximately 0.8. So being well below the exemption/clearance levels does not necessarily imply that is in accordance with the limits applying to building materials.

Finally, it was observed that when only minor amounts of feedstock material, containing activity concentrations well above the EU-BSS exemption/clearance levels are used, the activity concentrations of the slags are below the exemption/clearance levels and the ACI value of 1 is not exceeded.

Portal monitoring provides valuable information on the input materials that could be of concern. Nevertheless setting up holistic balances containing information on the activity concentration of all input materials per produced batch of output material can be difficult and cumbersome due to the complexity of industrial processes and large number of different input materials used. Therefore one cannot exactly determine the impact of “elevated” feedstock materials so output monitoring in function of discharges provides the necessary information whether the residues are exempted or if they can be used in building materials considering the EU-BSS.

4. Conclusion

The current study monitored different materials processed in a non-ferrous smelter facility, which fits within the framework of the EU-BSS. Equilibria are discussed for the ^{232}Th and ^{238}U decay series. The ^{232}Th decay series was found to be in equilibrium for all the slags, measured feedstock material and flue dust. This was not the case for ^{238}U decay series due to lack of equilibrium in the feedstock material and the impact of the industrial process. The activity concentrations of the slags were all below the provided exemption/clearance levels of the EU-BSS and RP-122 part II, and are also low in comparison to slags reported in literature. The activity concentrations of the flue dust samples were all except for ^{210}Pb below the exemption/clearance levels. For the feedstock material only ^{40}K and ^{235}U were below the exemption/clearance levels. In addition the ACI is not a restriction regarding the use of these non-ferrous slags to produce building materials.

Comparing the minimum and maximum observed activity concentrations for different radionuclides, differences up to a factor 13, 4.3 and 9 are registered for respectively slag, flue dust and feedstock samples. These variations occur due to heterogeneity within the same input materials, and variation in input materials, input and output quantity and in the process parameters. The variations in activity concentrations indicate that using one-time sampling or applying a low frequency of sampling is inappropriately for the considered industrial case. One-time sampling leads to a misleading conclusion regarding the radiological output of the production process in particular in complex systems. Consequently drawing conclusions to ensure radiation protection should be performed cautiously and the complexity and variability of the facility or industry should be taken into account. Over the long time, production processes tend to change in time due to innovations, regulations and economic factors. These factors will impact both input and output and subsequently can also influence the radiological content of the residues. The frequency of the radiological monitoring should be optimized for a given plant in order to ensure radiation protection, especially when the residues are aimed towards reuse in public applications. The authors recommend monitoring depending on the frequency of the discharge of these residues.

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Figures

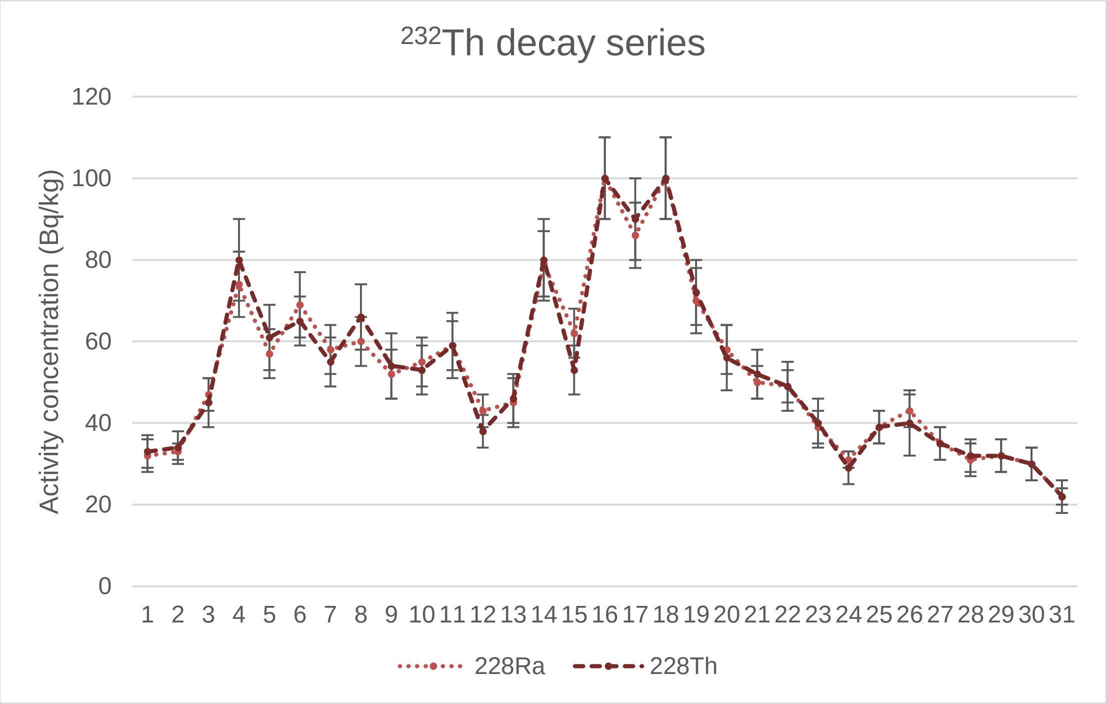

Figure 1: Activity concentration of 31 slag samples for the ^{232}Th decay series (coverage factor, k=2). Samples were collected at 31 consecutive days of slag production.

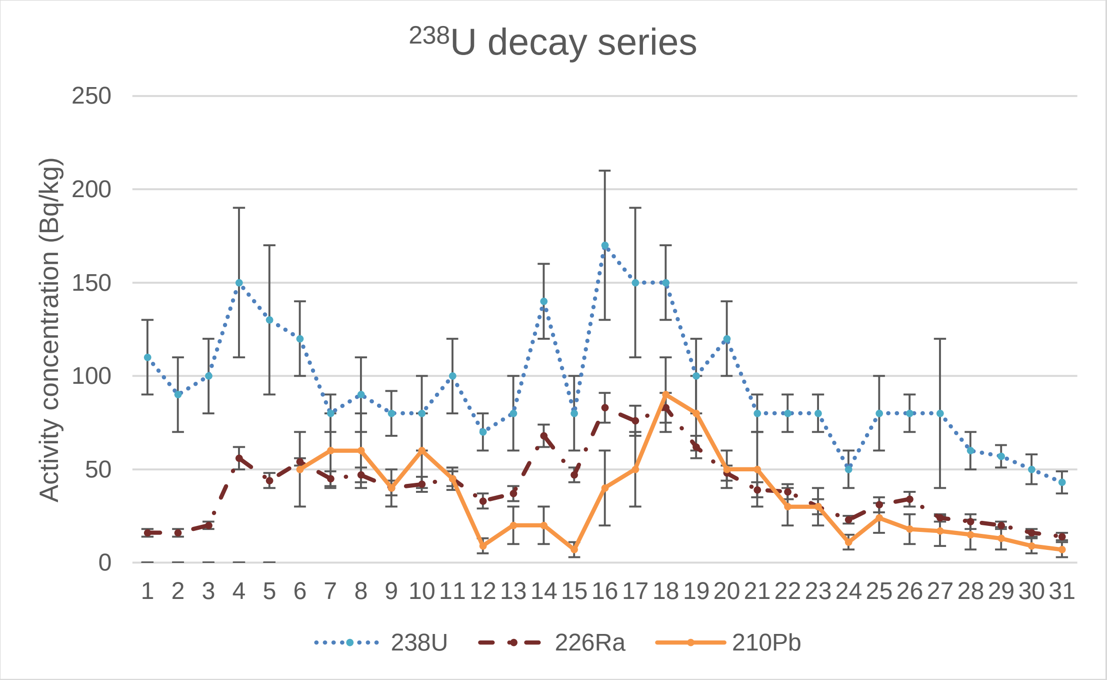

Figure 2: Activity concentration of 31 slag samples for the ^{238}U decay series (coverage factor, k=2). Samples were collected at 31 consecutive days of slag production.

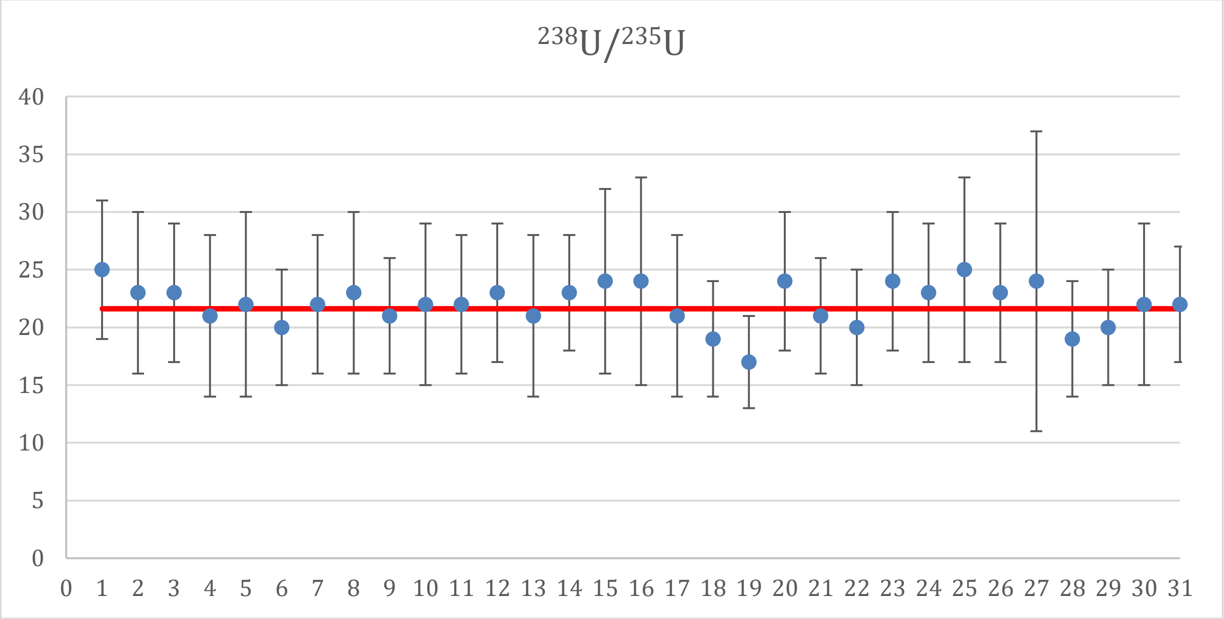

Figure 3: ^{238}U/^{235}U of slag 1 – slag 31, with ^{238}U via ^{234m}Pa (k=2). Red line indicates natural uranium ratio of 21.6. Samples were collected at 31 consecutive days of slag production.

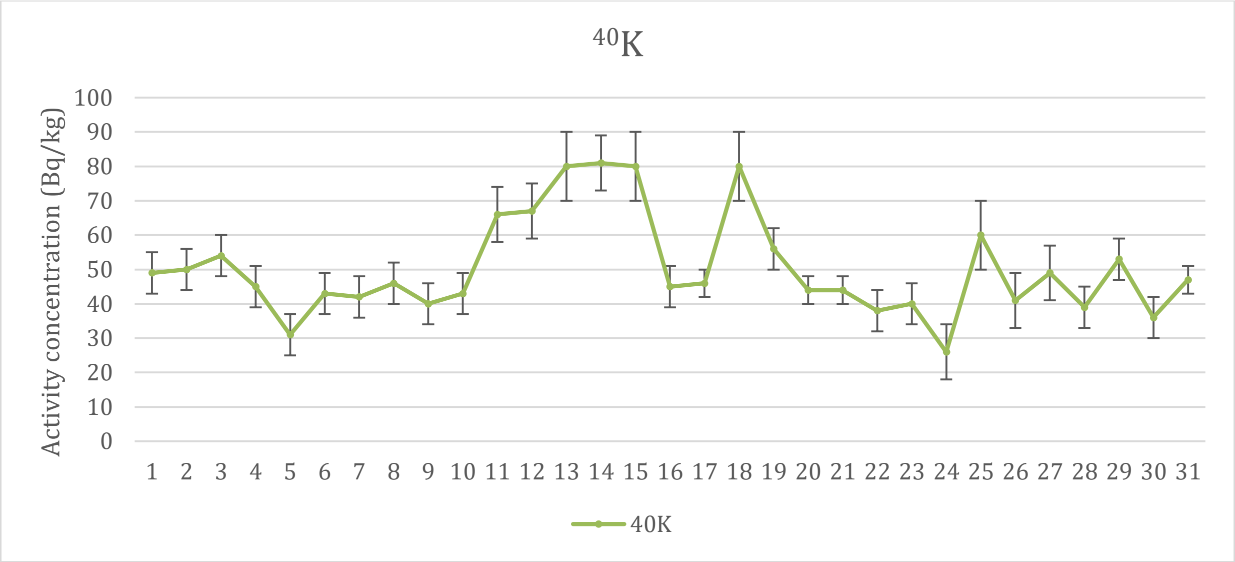

Figure 4: Activity concentration of slag 1 – slag 31 for ^{40}K (coverage factor, k=2). Samples were collected at 31 consecutive days of slag production.

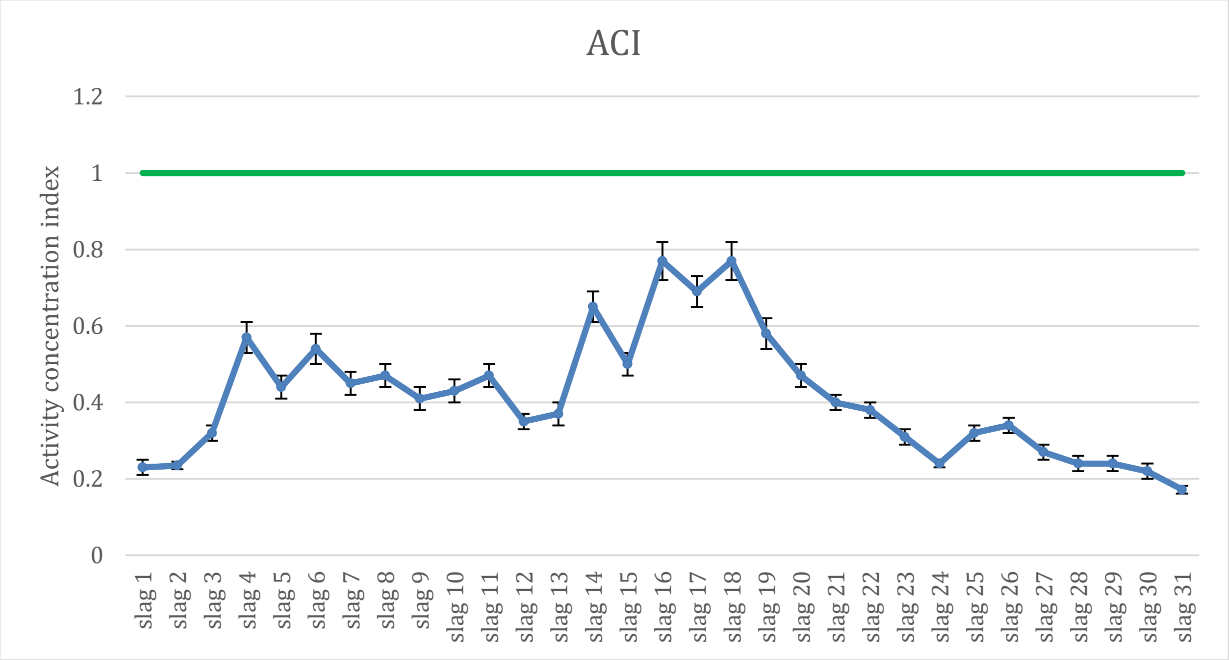

Figure 5: Activity concentration index for slag 1 – 31 (k=2). Samples were collected at 31 consecutive days of slag production.

Tables

Table 1: Overview of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in metallurgical slags in Bq/kg. N is the number of samples.

Slag type	N	^{226}Ra	^{232}Th	^{40}K	Slag origin	Reference
Tin slag*	/	1100	/	/	Germany	Leopold and Weiss, 2003
Tin slag◊	/	/	11000		United Kingdom - The Netherlands	Ryan et al., 2004
Tin slag	/	2000	/	/	Malaysia	Omar, 2000
Tin slag	12	492 - 1153	720 - 1532	11230 - 23183	Malaysia	Ismail et al., 2011
Tin slag	4	/	12100 - 14200	/	United Kingdom	Gilmore and Jackson, 1992
Tin slag	3	500 - 3400	800 - 7300	/	Malaysia	Omar et al., 2008
Tin slag	/	4570	420	/	Malaysia	Kontol et al., 2007
Tin slag	3	20000 - 69000	34000 - 130000	/	Brazil	Garcia, 2009
Tin slag	/	1000	4000	/	United Kingdom	European Commission, 1997
Tin slag	/	1000 - 1200	230 - 340	330	Germany	Lehmann, 1996
Tin melting slag*	/	5500	15000	/	Germany	Leopold and Weiss, 2003
Nickel smelt slag	3	16.7 -364	7.9 - 82	78.1 - 888	Poland	Zak et al., 2008

Nickel slag	/	52	78	76	Germany	Lehmann, 1996
Niobium slag	/	/	80000	/	/	European Commission, 1997
Niobium slag	/	3300 - 5000	17000 - 118000	/	Brazil	Pires do Rio et al., 2002
Lead slag	/	270	36	200	Germany	Lehmann, 1996
Copper slag*	/	2000	/	/	Germany	Leopold and Weiss, 2003
Copper slag	8	287 - 401	44 - 73	674 - 900	Poland	Zak, 1995
Copper smelt slag●	80	236.6 - 517.8	25.7 - 183	615.4 - 1250.6	Poland	Zak et al., 2008
Copper slag*	/	530	183	1459	Poland	Skowronek and Dulewski, 2005
Copper slag	23	237 - 336	26 - 76	615 -1251	Poland	Zak et al., 1993
Copper slag (old production)	/	861 - 2100	18 - 78	300 - 730	Germany	Lehmann, 1996
Copper slag (new production	/	490 - 940	41 - 60	530 - 760	Germany	Lehmann, 1996
Copper slag primary process	/	/	13	/	/	RP-122 part II
Copper slag secondary process	/	17	15	/	/	RP-122 part II
Steel slag	/	88	49	/	United Kingdom	Crockett et al., 2003; Hughes and Harvey, 2008
Steel Slag	1	8.62	3.73	5.14	Romania	Ene and Pantelica, 2011
Steel slag	/	/	150	/	The Netherlands	Van Der Steen, 2004
Steel slag	1	62	21	51	China	Wendling et al., 2013
Steel slag	3	184 - 213	156 - 182	<17 - 25	Qatar	Taha et al., 2014
Steel slag	10	15.2 - 21.4	12.9 - 15.1	45.3 - 62.9	Croatiä	Sofilic et al., 2011
Steel slag	/	5 - 31	0 - 5	/	/	RP-122 part II
Steel slag	/	100 -600	/	/	Slovenia	Smodis et al., 2006
Steel and Iron slag	/	150	150	/	/	European Commission, 1997

Steel slag□	/	196	29.6	148	Romania	Tanase and Tanase, 2003
Steel slag	5	51 - 114	28.6 - 35.5	118 - 145	Romania	Sahagia et al., 2014
Non-Iron slag	/	20 -30	10 - 15	20	South Korea	Jeong et al., 2014
Iron slag	2	107.4 - 113.9	95.2 - 109.6	2.27 - 18.9	Saudi Arabia	Alamoudi and Almehmadi, 2013
Iron slag	/	10 - 220	10 - 90	10 - 150	South Korea	Jeong et al., 2014
Iron slag	12	15 - 22	/	/	Scandinavia	Broden et al., 2001
Iron slag	/	64 - 380	30 - 98	/	/	RP-122 part II
Iron slag	6	4 - 234	2 - 196	8 - 105	Slovenia	NORM4Building database, 2016
EAF slag	3	14.6 - 17.1	6.7 - 13.1	15.3 - 36.9	Croatiä	Sofilic et al., 2010
EAF slag	12	18.3 -21.6	12.3 - 15.4	45.3 - 63.8	Croatia	Sofilic et al., 2010
EAF slag	/	25	5	10	Greece	Xirouchakis and Manolakou, 2011
Blast furnace slag	/	160 - 165	35-40	/	Belgium	Vanmarcke et al., 2010
Blast furnace slag	40	13.7 - 310.1	3.8 - 330	18.1 - 290.1	Turkey	Ugur et al., 2013
Blast furnace slag	1	166	47.6	232.3	Spain	Chinchon-Paya et al., 2011
Blast furnace (boiler) slag	368	12.4 - 351.1	2.2 - 115	18.0 - 1400	Poland	Zak et al., 2008
Blast furnace slag	4	116 - 223	83 - 141	136 - 196	China	Wendling et al., 2013
Blast furnace slag	12	8 -308	1.6 - 337.3	18.4 - 388.9	Turkey	Turhan, 2008
Blast furnace slag	/	251.2	24.8	361.7	Croatia	Sofilic et al,. 2011
Blast furnace slag	2	143.4 - 150.9	45.6 - 45.8	75.7 - 76.8	/	Puertas et al., 2015
Blast furnace slag	5	105 - 129	32.4 - 102	97.2 - 209	Finland	Mustonen, 1984
Blast furnace slag	5	323 ± 18.6	39.8 ± 7.2	158 ± 16	Egypt	Sharaf et al., 1999
Blast furnace slag	/	88.3 - 142.0	26.8 - 46.0	188 - 269	Hungary	Gallyas and Torok, 1984
Blast furnace slag	/	186.69 ± 2.38	35.87 ± 1.67	295.91 ± 9.08	Turkey	Baltas et al., 2014

Blast furnace slag†	42	18.5 - 458.8	/	225.7 - 2227.4	Poland	Pensko et al., 1980
Blast furnace slag*	/	2100	340	1000	/	RP-112
Blast furnace slag◊	/	270	70	240	/	RP-112
Blast furnace slag	/	131 - 139	4	157 - 177	Ukraine	NORM4Building database, 2016
Metallurgical slag	/	251	115	1400	Poland	Skowronek and Dulewski, 2005
Metallurgical slag	6	41 - 124	41 - 106	166 - 395	Slovakia	Cabanekova, 1996
Metallurgical slag	2	162 - 173	25 - 52	179 - 219	Romania	Muntean et al., 2014
Metallurgical slag	40	13 - 341	2 -115	36 - 889	Poland	Zak, 1995
Metallurgical slag	8	10.8 - 38.8	2.7 - 21.8	7.3 - 63.3	/	Sofilic et al., 2004
Metallurgical slag	160	33 - 351	12 - 102	14 - 825	Poland	Zak et al., 1993
Metallurgical slag + dross ‡	43	10.0 - 436.0	9.5 - 55.6	75.7 - 649.6	Slovakia	Cabanekova, 2008

* Mentioned as maximum value

◊ Mentioned as typical values

□ Mentioned as average value

● Could contain samples reported by Zak et al. 1993 and Zak 1995

† Could contain boiler slag data and is converted from pCi/g

‡ Could contain doubles with Cabanekova 1996

Table 2: Exemption/clearance levels reported in EU-BSS ∣ IAEA (equilibrium situation) and RP-122 part II (disequilibrium situation)

Radionuclide	**EU-BSS ∣ IAEA***	**RP-122 part II**
	Exemption/clearance level (Bq/kg)	**Exemption/clearance level (Bq/kg)**
^{238}U	1000	5000
^{226}Ra	1000	500**
^{210}Pb	1000	5000**
^{228}Ra	1000	5000**
^{228}Th	1000	500**
^{235}U	1000	1000**

^{40}**K**	10000	5000

* The activity concentration criterion of the EU-BSS ∣ IAEA assumes equilibrium (European Council, 2014; IAEA, 2004).

** To indicate that the derived clearance level also includes daughter nuclides (European Commission, 2002).

Table 3: HPGe detectors used for gamma-ray analysis.

	Ge-3	**Ge-4**	**Ge-5**	**Ge-8**	**Ge-T5**
Crystal type	P-type, coaxial	P-type, coaxial	P-type, planar	P-type, planar	P-type, coaxial
Relative efficiency	60%	100%	50%	19%	46%
Shielding	10 cm copper + 14 cm lead	7.5 cm copper + 15 cm lead	5 cm copper + 15 cm lead	5 cm copper + 15 cm lead	1 mm copper+ 10 cm lead
Top dead layer	0.7 mm	0.5 µm	0.5 µm	0.5 µm	0.6 mm
Samples measured	Slag 5, Flue dust samples	Slag 4, 6, 9, 11, 14, 20, 22, 26, 29, 31	Slag 1, 2, 3, 7, 12, 15, 17, 18, 19, 21, 23, 27,30	Slag 8, 10, 13, 16, 24, 25, 28	Feedstock materials
FWHM of QA at 661.6	1.55	1.57	1.31	1.23	1.41
FWHM of QA at 1332	1.89	1.96	1.75	1.64	1.86

Table 4: minimum and maximum activity concentrations, ratio of the maximum over the minimum activity concentration and ratio of different long living radionuclides over each other for feedstock material, flue dust and non-ferrous fayalite slag samples (k=2).

Radionuclide	**Feedstock material (5 samples)**			**Flue dust (9 samples)**		
	Activity concentration (Bq/kg)			**Activity concentration (Bq/kg)**		
	min	**max**	**Ratio max/min**	**min**	**max**	**Ratio max/min**
^{238}**U**	770 ± 90	2100 ± 300	2.7 ± 0.5	21 ± 8	50 ± 10	2 ± 1
^{226}**Ra**	410 ± 40	1600 ± 200	3.9 ± 0.6	0.8 ± 0.2	3.3 ± 0.2	4 ± 1
^{210}**Pb**	6000 ± 2000	22000 ± 7000	4 ± 2	300 ± 200	900 ± 300	3 ± 2
^{228}**Ra**	770 ± 70	2100 ± 200	2.7 ± 0.4	1.4 ± 0.2	2.8 ± 0.2	2.0 ± 0.3
^{235}**U**	27 ± 4	74 ± 8	2.7 ± 0.5	0.8 ± 0.2	2.3 ± 0.2	2.9 ± 0.8
^{228}**Th**	800 ± 100	2000 ± 400	2.2 ± 0.6	1.2 ± 0.2	3 ± 2	3 ± 2
^{40}**K**	10 ± 8	90 ± 10	9 ± 7	49 ± 6	210 ± 20	4.3 ± 0.7
^{228}**Ra/**^{228}**Th**	0.9 ± 0.2	1.0 ± 0.2		0.96 ± 0.09	1.5 ± 0.4	
^{238}**U/**^{226}**Ra**	1.2 ± 0.2	1.9 ± 0.3		10 ± 3	30 ± 10	
^{210}**Pb/**^{226}**Ra**	8 ± 3	20 ± 7		110 ± 30	900 ± 300	

Radionuclide	**Non-ferrous fayalite slag (31 samples)**		
	Activity concentration (Bq/kg)		
	min	**max**	**Ratio max/min**

^{238}U	42 ± 4	180 ± 40	4 ± 1
^{226}Ra	14 ± 2	83 ± 8	6 ± 1
^{210}Pb	7 ± 4	90 ± 20	13 ± 7
^{228}Ra	22 ± 2	100 ± 10	4.5 ± 0.6
^{235}U	2.0 ± 0.4	8 ± 2	4 ± 1
^{228}Th	21 ± 2	100 ± 10	4.7 ± 0.7
^{40}K	26 ± 8	80 ± 10	3.1 ± 0.5
^{228}Ra/^{228}Th	0.9 ± 0.2	1.1 ± 0.2	
^{238}U/^{226}Ra	1.7 ± 0.4	7 ± 2	
^{210}Pb/^{226}Ra	0.14 ± 0.09	1.4 ± 0.5	