

COMPARISON OF ANALYSIS METHODS
FOR THE CHARACTERISATION OF THE RADIOACTIVE
CONTENT OF METALLURGICAL SLAG USED WITHIN
THE EURAMET-EMRP JRP IND04 MetroMetal*

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Abstract. This paper presents the methods developed for the initial radioactive content description of a metallurgical slag sample to be used for the preparation of standard sources - reference materials within the EURAMET-EMRP JRP IND04 MetroMetal: Ionising radiation metrology for the metallurgical industry. The obtained results regard:

– The comparative measurement of the natural radionuclide content of several samples of Romanian metallurgical slag, analysed in the Radionuclide Metrology Laboratory (RML), as compared with those used in the usual analyses performed on site by the Arcelor Mittal Company staff, collaborator of the project.

– The proposed method will be applied for the measurement of the natural radionuclide content of processed Spanish metallurgical slag.

– A comparison of the methods and results is presented.

Key words: EURAMET.EMRP-JRP IND04, metallurgical samples, natural radioactivity measurement.

1. INTRODUCTION

IFIN-HH is the Romanian Designated Institute (DI), by the Romanian Bureau of Legal Metrology (BRML), for field of ionizing radiations. The Radionuclide Metrology Laboratory (RML) from IFIN-HH is the owner of the primary standard of radionuclide activity unit, becquerel (Bq), and in this quality it

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applied for obtaining the statute of the owner of the National Romanian Standard for radionuclide activity unit. It is also accredited as a calibration and testing laboratory in the field of radioactivity measurements by the Romanian Accreditation Association (RENAR), and is notified by CNCAN, according to the requirements of the EN ISO/IEC 17025:2005 standard. Its technical capability in performing calibration operations is attested also by the publication of calibration and measurement capability (CMC) files on the CIPM-MRA, Annex C, address: <http://kcdb.bipm.org/AppendixC/default.asp>. It participates regularly at international key and supplementary comparisons on the radioactive standard solutions or other radioactive matrices. The most recent comparisons, to be found in the Key Comparison data Base (KCDB), are:

– CCRI(II)-S8 Supplementary Comparison on ^{40}K , ^{137}Cs and ^{90}Sr activity content in dried bilberry material, organized by EC-JRC - Institute for Reference Materials and Measurements (IRMM), Belgium, during 2010-2011 (<http://kcdb.bipm.org/>). [1]

– CCRI(II)-K2.Tc-99/ 2012. Key comparison on the measurement of a ^{99}Tc solution, organized by NPL, UK, on behalf of BIPM [2].

– CCRI(II)-S9 “Supplementary Comparison on ^{137}Cs and ^{40}K Activity Concentrations in KRIS Rice Powder Reference”, organized by KRIS, Republic of Korea, during 2011-2012 [3].

– CCRI(II)-S10.LASCE “Large area sources comparison exercise”, organized by ENEA, Italy, during 2012–2013 [4].

For these reasons, our laboratory was accepted as a partner in the EURAMET-EMRP (European Organization of National Metrology Institutes – EURAMET, European Metrology Research Program) Joint Research Project **JRP IND04 – Ionizing Radiation Metrology for Metallurgical Industry.MetroMETAL, 2012-2014.**

The coordinator is Dr. Eduardo Garcia Torano, CIEMAT – Spain, and IFIN-HH responsible is Dr. Maria Sahagia; we participate in WP2 (preparation of standard sources), WP3 (gamma-ray spectrometry measurements and corrections) and WP5 (application at end-users). The WP2 accomplishment requires that adequate methods were developed, in order to be applied for the preparation of spiked standards; one important step is the initial radioactive content description of a metallurgical slag sample to be used for the preparation of standard sources-reference materials, by spiking with the radionuclides: ^{60}Co , ^{137}Cs and ^{226}Ra . Due to the technological processes in metallurgical industry, the cast steel does not contain any natural radionuclide, but it can be contaminated with artificial contaminants, such as ^{60}Co , ^{137}Cs , ^{192}Ir and ^{226}Ra , due to the accidental melting of unidentified industrial orphan sources. By difference of it, the metallurgical slag contains always natural occurring radionuclides, whose content must be carefully determined when the material is used for the preparation of reference materials, and accidentally artificial contaminants.

At this stage, our involvement in the project regards mainly finding the most precise method for the determination of the initial content of slag in natural radionuclides. Such studies were systematically performed at the Arcelor Mittal Galati SA (former ISPAT SIDEX), Romania, collaborator of the JRP [5, 6].

2. DESCRIPTION OF THE EQUIPMENT, SAMPLES AND METHODS

2.1. EQUIPMENT

The method used in analysis is the high resolution gamma-ray spectrometry, based on high-resolution semiconductor detector HPGe and associated electronics. The IFIN-HH spectrometer is described in detail in the RML working procedure code AC-PL-LMR-0100 [7]. The spectrometric system, designed for low level radioactivity measurements, has a graded shielding made of lead (10 cm thick), tin (1 mm) and copper (1 mm) in order to reduce the background radiations. The main technical parameters of the system are (measured values): energy resolution (FWHM) of 1.67 keV at 1.33 MeV (^{60}Co) and 0.64 keV at 122 keV (^{57}Co); relative efficiency 28.9 %; the peak-to-Compton ratio, ^{60}Co , is 62:1. The integral background rate for the interval (50–1500) keV is 1.2 s^{-1} . The energy and efficiency calibrations of system were done by using volume radioactive standard sources, produced and certified by RML-calibration laboratory, in order to assure the national and international traceability of the measurements [8]. For the measurement of the slag samples, the calibration was done with volume homogeneous standard sources in SARPAGAN geometry, with a soil matrix. Due to the low activity of the analyzed samples, all the measurements were made directly on top the detector. All the corrections, necessary for the gamma-ray spectrometry measurements, were performed by using validated software: coincidence summing corrections and efficiency transfer coefficients for various geometries and densities (GESPECOR) [9], background subtraction (GammaVision, the manufacturer software used for spectra acquisition) [10], deconvolution of multiple peaks (COLEGRAM) [11] and decay corrections from the measurement to the reference date. The measurements were made according to the RML working procedure code AC-PL-LMR-061 [12]. The method and equipment were previously tested, with good results, by participating at the “Environmental Radioactivity Proficiency Test Exercise 2008”, organized by the National Physical Laboratory from UK [13].

The equipment used at Arcelor Mittal-Galati SA is described in [5, 6] and consists mainly from the following components. The HPGe detector is a model Oxford CPVDS-12185-M with coaxial p semiconductor, having the preamplifier included [6]. The crystal dimensions are: diameter 51.6 mm and height 41.0 mm, mounted in an aluminium capsule, 1 mm thick, with the external diameter 76 mm; the operational high voltage is +3600 V. The main parameters are: relative

efficiency: 18 %; FWHM: 1.68 keV at 1332 keV and 0.720 keV at 122 keV; ratio peak / Compton is 53:1. The shielding of the system contains: 12 mm of stainless steel, 100 mm of lead, 0.5 mm of cadmium and 1.5 mm of copper. The volume of the measurement chamber is 4 l, allowing the measurement of samples in Marinelli geometry, and the integral background rate for the interval (50–1500) keV is 0.76 s^{-1} .

The auxiliary electronic chain is an “Oxford Instruments Inc.” (USA) model and contains: a high voltage power supply (HVPS), an amplifier and a multichannel analyzer type PCA Multiport E/R, which contains the necessary software for data processing and communication with the central computer. The computer is of type Gateway, having the software packages installed: PCAME vers. 2.42 GammaTrac™ vers. 1.22 of the “Oxford Instruments Inc.” (USA). These software packages are used for the qualitative and quantitative analysis of the spectra. The calibration of the system was done with a ^{152}Eu standard source of the same type as for the RML from IFIN-HH, produced by the same laboratory.

2.2. SAMPLES

The samples to be analyzed consist from slag batches, collected in different periods of time from Arcelor Mittal SA (ISPAT SIDEX), Galați, as follows: The samples measured at IFIN-HH were collected within the period January – February 2013, in a total number of 5 and those measured at Arcelor Mittal were collected during the period: 1997–2003 and include some hundreds of samples [5]. From these samples, which consist from fine white powder, in both cases, at IFIN-HH cylindrical volume sources were prepared by precise weighing. Measurement samples resulted, with the following characteristics: diameter 73 mm, height 38 mm (SARPAGAN), except sample no.3, 36 mm height, similar with the geometry of the standard sources, having total masses from 217.4 g up to 245.7 g and density 1.40 g cm^{-3} . They were considered to have an equivalent atomic number similar to the soil.

At IFIN-HH, a different measurement was performed on another slag sample, provided by CEPROCIM SA, coming from another siderurgy unit; it consists from fine red powder. A Marinelli source was prepared, using a Marinelli type baker, with a total mass $660 \pm 20 \text{ g}$ and a density of 1.30 g cm^{-3} .

2.3. MEASUREMENT METHODS

Method used at IFIN-HH. The gamma-ray spectra of the samples, characterized generally by low levels of radioactivity, were measured during acquisition times of 18 000 s to 23 000 s. The background of the installation was measured and subtracted from the samples’ spectra. The nuclear decay data necessary for the computations were adopted from the BIPM-5 Monographie [14], values recommended by BIPM to be used by all the metrology laboratories. The activity concentration, A , was computed according to Eq. 1, while the corresponding uncertainty – from Eq. 2:

$$\Lambda = \frac{(A - A_F) \cdot F_C \cdot F_D}{t \cdot s \cdot \varepsilon \cdot F_T} \cdot \frac{1}{m}, \quad (1)$$

$$U_{\Lambda} = k \cdot u_{\Lambda} = k \cdot \sqrt{s_{A-A_F}^2 + u_s^2 + u_{\varepsilon}^2 + u_{F_C}^2 + u_{F_D}^2 + u_{F_T}^2 + u_m^2}, \quad (2)$$

where A and A_F are the net areas of the considered peak from the gamma-ray spectrum of the sample (corresponding to the total absorption of the gamma-ray quanta with a given energy), respectively the same peak from the installation background spectrum (if it is the case); t is the measurement time (the same for sample and background, expressed in seconds); F_C , F_T and F_D are the multiplicative coefficients for coincidence summing corrections, efficiency transfer corrections (if the sample geometry is different from that of the standard source used) and for the decay during the reference time and the time of the sample measurement start; s is the emission probability of the considered gamma-rays; ε is the detection efficiency corresponding to the energy of the considered peak, determined with a standard source, according to the calibration certificate; m is the mass of the sample (in kilograms). For the radionuclides emitting several gamma radiations, with different energies, the activity was calculated as arithmetic mean of the measurement of significant radiations. In Eq. (2), k is the coverage factor, u_{Λ} is the composed activity uncertainty, s_{A-A_F} is the type A (statistical) uncertainty component of the peak net area uncertainty, while u_s , u_{ε} , u_m , u_{F_C} , u_{F_T} , and u_{F_D} are the type B components (systematic) of the uncertainties for the emission probability, efficiency, mass and correction factors for coincidence summing, efficiency transfer, respectively decay during the reference time and the time of the measurement start. The uncertainty of the measurement time and the decay during the measurement time are considered negligible.

Method used at Arcelor Mittal. The measurement of samples was described in [5], [6] and was performed in time intervals between 5000 s and 86400 s, assuring values of minimum detectable activity for ^{40}K and ^{226}Ra from 5.58 to 1.25 Bq, calculated according to [15]. The calculations were done by the installed program, having implemented the formulae (1), (2), except the correction for coincidence summing correction. The decay data are included in the program library.

3. RESULTS AND DISCUSSIONS

The results are expressed as activity concentration, in Bq kg^{-1} , for all detected gamma-ray emitting radionuclides, which belong to the natural radioactive series: ^{238}U (^{234}Th , $^{234\text{m}}\text{Pa}$, ^{226}Ra , ^{214}Pb , ^{214}Bi), ^{232}Th (^{228}Ac , ^{228}Th , ^{212}Pb , ^{212}Bi , ^{208}Tl), as well as ^{235}U and ^{40}K . All results are presented in Table 1

- **IFIN-HH analyses:**

– Slag samples from Arcelor Mittal. One can see that the measurements were performed almost in conditions of equilibrium between ^{226}Ra and its daughters: ^{222}Rn , ^{214}Pb and ^{214}Bi . The activities determined for ^{214}Pb and ^{214}Bi are statistically the same, as it should be. The determination of ^{226}Ra activity was done after the independent determination of ^{235}U content and its contribution extraction from the ^{226}Ra full absorption peak, 186.2 keV. For all the 5 samples from Arcelor Mittal the ^{226}Ra content is almost similar, as in case of the small reported values the activity must be considered as the maximum value of uncertainty interval, due to the existing equilibrium relations. Consequently, one may calculate mean values from the 5 samples and one may conclude from the mean values: The content of ^{238}U is the same with $^{234\text{m}}\text{Pa}$ and ^{234}Th in equilibrium, calculated from the arithmetic mean of the two values as: (91 ± 18) Bq/kg. The content of ^{226}Ra is (84 ± 13) Bq/kg, almost in equilibrium with its daughters. The content of ^{232}Th , similar with that of ^{228}Ac , ^{212}Pb and ^{212}Bi , is (34.3 ± 1.1) Bq/kg. The content of ^{235}U is (5.4 ± 1.6) Bq/kg, in a good agreement with the natural proportion of ^{235}U in natural uranium. The content of ^{40}K is (130 ± 5) Bq/kg. The critical activity, as compared with the exclusion from the regulatory control levels (Radioprotection Security Norm 01, CNCAN Table 2B), regards ^{226}Ra content, which is two times higher than the exclusion level, 40 Bq/kg, and the ^{232}Th activity with an exclusion limit of 1 Bq/kg.

– Slag from CEPROCIM SA. In this case, the content of naturally occurring radionuclides is lower and is situated at levels as follows. ^{238}U : (25 ± 1) Bq/kg; ^{226}Ra : (34 ± 13) Bq/kg, a value practically at the exclusion limit; ^{235}U : (3.2 ± 0.8) ; ^{232}Th : (53 ± 5) Bq/kg; ^{40}K : (716 ± 43) Bq/kg. Comparatively with the Arcelor Mittal slag, the content of elements from uranium series is lower, close to the exclusion limit; the content in thorium series and ^{40}K is higher. A slight concentration of ^{137}Cs , artificial radionuclide, of <1 Bq/kg was found, at the limit of the Minimum Detectable Activity (MDA), which is much lower than the exclusion limit, 800 Bq/kg.

• **Arcelor Mittal (ISPAT SIDEX) analyses.** In this case the contents of naturally occurring radionuclides, reported for one sample, where uncertainties are also reported, are situated at levels as follows. ^{238}U : (89 ± 22) Bq/kg, deduced from ^{234}Th measured activity; ^{232}Th : (45 ± 5) Bq/kg; ^{40}K : (172 ± 20) Bq/kg. The activity of ^{235}U is not reported, but it can be deduced as being at the level of (4.1 ± 1.0) Bq/kg. All these values, from a sample measured in 2003, are not so different from those collected in 2013 and measured at IFIN-HH. The reported activity of ^{226}Ra seems to be much higher, comparatively with the contents of the other radionuclides. The cause can be due to two reasons: either the ^{226}Ra is in total non equilibrium with its daughters, or a certain contribution can be due to ^{235}U , with gamma-ray energy 185.7 keV, presence in the ^{226}Ra full absorption energy peak (FAP) of 186.21 keV. Having in mind the ^{235}U activity one can calculate the contribution of this activity in the full absorption peak area. The calculations were based on the following equations:

The FAP corresponding to the reported value of $\Lambda_{\text{Ra-226}} = 187 \text{ Bq/kg}$, with a detection efficiency of the system deduced as $\varepsilon = 2.48 \times 10^{-3} \text{ s}^{-1}/(\text{Bq/g})$, and applying relation (1), is $(A-A_F)_{\text{total}} = 0.01643 \text{ s}^{-1}$. The ^{235}U activity, $\Lambda = 4.1 \text{ Bq/kg}$, would result in a contribution of $(A-A_F)_{\text{U-235}} = 0.00580 \text{ s}^{-1}$. The real activity of ^{226}Ra in the sample in Table 1, column 3 is then: $\Lambda_{\text{Ra-226}} = (121 \pm 30) \text{ Bq/kg}$, instead of reported 187 Bq/kg ; correspondingly, the average and maximum activities, columns 1 and 2, are: $\Lambda_{\text{Ra-226 avg}} = 127 \text{ Bq/kg}$ and $\Lambda_{\text{Ra-226 max}} = 130 \text{ Bq/kg}$.

The conclusions from the measurements are:

- The measurements done at IFIN-HH are more precise than those from Arcelor Mittal due to the followings: use of a higher quality HPGe detector; use of the GESPECOR program, including the coincidence summation correction, application of the ^{235}U activity correction in the FAP corresponding to ^{226}Ra .

- The samples collected and measured within the period 1997–2003, measured at Arcelor Mittal have a slightly higher concentration in natural radionuclides, than those collected in 2013 and measured at IFIN-HH, but in the sets of samples from both periods the ^{226}Ra and ^{232}Th activity remains higher than the exclusion level, even after the application of the ^{235}U activity correction.

- As reported in the papers [5], [6], the high content in natural radionuclides in the slag from Arcelor Mittal is due to the raw materials used in the technological process, by difference of the slag from CEPROCIM SA.

4. CONCLUSIONS

- Comparative measurements were performed in two different laboratories, in order to fully characterise the furnace slag samples.

- Three types of slag were analysed.

- The samples from Arcelor Mittal have a higher content in natural radionuclides than the sample from CEPROCIM.

- All these measurements and comparisons are a preparatory step in the characterization of slag to be used for the preparation of standard ^{226}Ra sources implied in the EURAMET-EMRP, JRC IND04 MetroMetal.

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