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1 Variation of natural radionuclides in non-ferrous fayalite 2 slags during a one-month production period

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- 11

12 Highlights

- 13 • Natural radionuclides monitored in non-ferrous slag during 1
14 month production.
- 15 • Large activity concentration fluctuations of natural occurring
16 radionuclides.
- 17 • Disequilibrium in the ²³⁸U decay series and equilibrium in
18 the ²³²Th decay series.
- 19 • Extensive comparison between different types of metallurgical
20 slags.
- 21 • Continuous monitoring of the produced slag is advised to assure
22 safe application.

23
24
25

26 **Abstract**

27

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

40 ^{235}U and ^{40}K using HPGe detectors. Secular equilibrium was observed for the slags,
41 flue dust and feedstock samples in the ^{232}Th decay chain, in contrast to the ^{238}U
42 decay chain. During the month in question the ratios of maximum over minimum
43 activity concentration were 3.1 ± 0.5 for ^{40}K , 4 ± 1 for ^{238}U , 6 ± 1 for ^{226}Ra , 13 ± 7
44 for ^{210}Pb , 4.5 ± 0.6 for ^{228}Ra and 4.7 ± 0.7 for ^{228}Th for the slags. Even with the
45 activity concentration of the feedstock material ranging up to 2.1 ± 0.3 kBq/kg for
46 ^{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
47 2.0 ± 0.4 kBq/kg for ^{228}Th , none of the slag samples exceeded the
48 exemption/clearance levels of the EU-BSS and RP-122 part II, which can
49 respectively provide guidance under equilibrium and in absence of equilibrium.
50 As each NORM-processing industry has its own complexity and variability, the
51 observed variations point out that one should approach one-time measurements
52 or low frequency monitoring methods cautiously. Low frequency measurements
53 should be optimised depending on the discharge of the batches. A follow up of the
54 industrial process and its output can provide important insights to assure a
55 limited public exposure upon application of these industrial residues.
56 Finally a comparison is made with reported data on other metallurgical slags and
57 the use of the slags in building materials is evaluated using the Activity
58 Concentration Index (ACI) proposed by the EU-BSS.

59

60 **1. Introduction**

61

62 Each year over 400 million tons of metallurgical slags, a by-product from metal
63 producing industries, are produced world-wide (van Oss, 2013). Due to the
64 presence of Naturally Occurring Radionuclides (NORs) in the raw materials used
65 by the metallurgical industries the produced metallurgical slag can contain
66 enhanced concentrations of NORs. In Table 1 an overview is given on the activity
67 concentrations of ^{226}Ra , ^{232}Th and ^{40}K for different types of metallurgical slags
68 reported in the literature. These activity concentrations are found in the intervals
69 2-69 kBq/kg, 2-130 kBq/kg and 2-23 kBq/kg for ^{226}Ra , ^{232}Th and ^{40}K , respectively.
70 It must be noted that this list is not exhaustive and some data originate from
71 samples of the 1980's. In several cases the number of measured samples is not
72 specified and not all considered NORs (^{226}Ra , ^{232}Th and ^{40}K) are reported. The data

73 and nomenclature are shown as mentioned in the corresponding reference. Data
74 on other radionuclides mentioned in the corresponding reference is not shown in
75 Table 1. The two main classes of metallurgical slags are non-ferrous and ferrous
76 slags (Piatak et al., 2015a). Especially for non-ferrous slags such as Sn, Nb and Cu
77 slags, higher activity concentrations can be found reaching up to (Table 1):

- 78 • 69 kBq/kg ^{226}Ra , 130 kBq/kg ^{232}Th and 23 kBq/kg ^{40}K for Sn slag,
- 79 • 5 kBq/kg ^{226}Ra and 118 kBq/kg ^{232}Th for Nb slag
- 80 • 2.1 kBq/kg ^{226}Ra , 0.1 kBq/kg ^{232}Th and 1.3 kBq/kg ^{40}K for Cu slag.

81 Non-ferrous slags typically consist mainly out of Fe and Si whereas the ferrous
82 slags are typically rich in Ca and Si (Piatak et al., 2015a). The production of non-
83 ferrous slag is limited to approximately 12% of the total worldwide slag
84 production (National Slag Association, 2013). Non-ferrous industries that process
85 niobium ores or work on tin, lead or copper smelting and therefore produce Nb,
86 Sn, Pb and Cu slags are specifically considered in Council directive
87 2013/59/Euratom, known as the European Basic Safety Standards (EU-BSS), as
88 practices involving naturally-occurring radioactive materials (NORM). In addition
89 residues of steel production are regulated by the EU-BSS for use in building
90 materials. In Table 1, it is also demonstrated that a large range of activity
91 concentrations can be found for a given type of metallurgical slag. For example for
92 Sn slag, the activity concentrations range from 0.5 - 69 kBq/kg for ^{226}Ra , 0.2 - 130
93 kBq/kg for ^{232}Th and 0.3 - 23 kBq/kg for ^{40}K . The measured activity
94 concentrations for different non-ferrous slags are in several cases higher than the
95 activity concentrations for exemption or clearance of NORs in solid materials in
96 secular equilibrium with their progeny, proposed by the EU-BSS (European
97 Commission, 2014). The EU-BSS exemption/clearance levels were chosen in
98 accordance with the exemption/clearance levels of the IAEA “Application of the
99 concepts of exclusion, exemption and clearance”. A global level benefits the
100 industries processing and transporting these materials from an administrative
101 and legislative point of view. These EU-BSS | IAEA levels are 1 kBq/kg for natural
102 radionuclides from the ^{238}U and ^{232}Th decay series and 10 kBq/kg for ^{40}K (Table
103 2) however these levels are only applicable if secular equilibrium in the decay
104 series is obtained. The EU-BSS allows higher values in case of disequilibrium but

105 does not specify which levels are recommended. RP (Radiation Protection)-122
106 specifies these values and applies of a summation rule for the radiological
107 evaluation (Table 2) (European Commission, 2002).

108

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

114

$$115 \quad ACI = \frac{AC_{Ra226}}{300 \text{ Bq/kg}} + \frac{AC_{Th232}}{200 \text{ Bq/kg}} + \frac{AC_{K40}}{3000 \text{ Bq/kg}} \quad (1)$$

116

117 With A_c as activity concentration of the mentioned radionuclide expressed in
118 Bq/kg.

119

120 According to the EU-BSS this index allows estimating the requirement that upon
121 application of these building materials the public exposure is below the effective
122 dose limit of 1 mSv a year. An ACI value below 1 assumes that the dose limit of 1
123 mSv a year is not exceeded. The application of metallurgical slags in building
124 materials is gaining interest and the applications depend on the chemical
125 composition, cooling path, availability, price, etc. (Piatak et al., 2015a). Usage of
126 metallurgical slags in tiles, in railway ballast, in roofing materials, in coloured glass
127 and in cementitious materials are reported (Piatak et al., 2015b). The main usage
128 is as a raw material in asphalt and concrete mixtures for road construction –
129 mainly for ferrous slag (Piatak et al., 2015b). Recently the application of non-
130 ferrous slag as a binder to produce inorganic polymers building materials was
131 reported (Pontikes et al., 2013). Inorganic polymers (IPs) are novel types of
132 building materials with lower CO₂ emissions in comparison to concrete (Provis,
133 2014). IPs can be used in similar applications as conventional concrete (Provis and
134 Van Deventer, 2014). In addition, other reuse and recycle options are reported,
135 like usage as sand blasting material, as reprocessing material for secondary metal
136 recovery and for environmental remediation (Al-jabri et al., 2011; Piatak et al.,
137 2015b). Despite these applications, still large fractions of slags currently ends up
138 on landfills (Piatak et al., 2015a).

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

153

154 **2. Methods and materials**

155

156 **2.1 Samples**

157

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

165

166 **2.1.1 Non-ferrous fayalite slag samples**

167

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

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

180

$$181 \text{ Composition daily sample} = \sum_{i=1}^n \frac{\text{Quantity production batch } i}{\text{Quantity day production}} * 100\% \quad (2)$$

182

183 All cycle samples were dry and milled to powders by disk milling. In total 31 slag
184 mixtures were produced corresponding to 31 consecutive days of slag production.
185 Each slag mixture dry mass varied between 80 g and 140 g. The samples of a first
186 batch of slag samples were measured after a period of approximately 470 days
187 after sample collection. Samples from a second batch (indicated as second batch),
188 in total two fayalite slags samples, were sampled at a later date, prepared in the
189 exact same way as the first batch and measured after a period of approximately
190 180 days after sample collection.

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

193

194 **2.1.2 Flue dust samples**

195

196 The flue dust is recovered by leading the off-gasses through fabric filter units.
197 These are cleaned at regular time intervals by which the dust is transferred to dust
198 silos for temporary storage. By the cleaning action and the subsequent fluidization
199 of the dust for transport purposes, the dust is already mixed in the silos. Trucks
200 are loaded directly from those silos. At several places of the truckload, grab
201 samples are collected and mixed to form a homogeneous sample for
202 measurements. Nine different batches of dust samples were monitored during the
203 one month production period, containing mainly Zn, and minor amounts of other

204 non-ferrous metals. The dry mass of the collected samples ranged from 42 g to 76
205 g. The samples were measured after a period of approximately 470 days after
206 sample collection.

207

208 **2.1.3 Feedstock samples**

209

210 All feedstock materials are monitored upon arrival via a detection portal. As a
211 result of this screening one type of feedstock material with elevated activities is
212 selected for further investigations in the framework of this study. The considered
213 feedstock material is mainly a metallic by-product of a primary non-ferrous metal
214 producer, containing iron (> 70%), and minor amounts of other metals. The
215 radioactivity is primarily resulting from slag inclusions, which are difficult to
216 separate from the metal phase. The considered feedstock material is a minor
217 fraction of the total feedstock materials used in the production process. Samples
218 for measurement were produced by mixing delivered lots (size from 25 to 50 ton)
219 homogeneously by mobile cranes, and subsequently performing several “coning
220 & quartering” actions until a homogeneous and representative sample of about
221 500 kg is reached. This sample is further downsized by the same techniques using
222 manual actions until a sample of circa 50 kg remains. Grab samples of this final
223 sample were used for measurements. Five different batches of feedstock materials
224 were monitored during the one month production period. The dry mass of these
225 samples ranged between 260 g and 570 g. The samples were measured after a
226 period of approximately 470 days after sample collection.

227

228 **2.2 Radiological analysis**

229

230 Measurements were performed on different HPGe-detectors of the Radionuclide
231 Metrology Laboratory of JRC-Geel in Belgium. All detectors are located in the 225
232 m deep underground laboratory Hades located on the premises of the Belgian
233 Nuclear Centre SCK•CEN in Mol, Belgium except for Ge T-5 which is located above
234 ground. The detector details are listed in Table 3. The low background count rates
235 of the underground detectors were in the order of 200 to 400 counts per day in
236 the energy interval 40 to 2700 keV. The background count rate of individual peaks

237 was mostly below 1 count per day. This low background is particularly important
238 when measuring NORs that are known to be present in all detector systems. All
239 samples for gamma-ray spectrometric analysis were transferred to radon tight
240 Teflon containers and stored for at least 21 days to reach secular equilibrium
241 between ^{226}Ra and daughters. The slag and flue dust samples were positioned 2
242 mm above the endcap of each HPGe-detector except for detector Ge-8 where the
243 samples were placed directly on the endcap. The feedstock samples were
244 positioned 11 mm above the endcap of the HPGe-detector. The measurement
245 times ranged from 2 to 7 days and the dead time was always below 1%.

246

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

256

257 The radionuclides occurring in natural decay series of ^{238}U and ^{232}Th , as well as
258 ^{235}U and ^{40}K were investigated by their emitted gamma rays. An overview of the
259 used gamma lines is found in Croymans et al. 2016 (Croymans et al., 2016).

260

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

265 The 186 keV peak is a doublet with contributions from ^{235}U (185.7 keV) and ^{226}Ra
266 (186.2 keV). By subtracting the contribution from ^{226}Ra , which activity was
267 determined from its daughters ^{214}Pb and ^{214}Bi , from the 186 keV doublet peak, the
268 activity of ^{235}U is calculated. In addition this result was confirmed by the other
269 three main gamma lines of ^{235}U i.e. 143.8 keV, 163.4 keV and 205.3 keV. As natural

270 isotopic abundance is expected for ^{235}U in these "non-nuclear" samples, one can
271 see the measured $^{238}\text{U}/^{235}\text{U}$ activity ratio as a quality control of the measurement.

272

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

279

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

288

289 The ACI was calculated for slag 1 to 31 using the activity concentration of ^{226}Ra ,
290 ^{232}Th and ^{40}K (Equation 1). The EU-BSS assumes equilibrium between ^{232}Th and
291 ^{228}Ac , and therefore the activity concentration of ^{228}Ac is used. The ACI calculation
292 performed here assumes that the building material is constructed solely of the
293 non-ferrous slag. Novel developments in IP production allow developing building
294 materials solely out of non-ferrous fayalite slag (Kriskova et al., 2015).

295

296 Uncertainty of the ACI is calculated like in Equation 3

297

$$298 \quad u(I) = \sqrt{\left(\frac{1}{300}\right)^2 u^2 (Ac_{226Ra}) + \left(\frac{1}{200}\right)^2 u^2 (Ac_{232Th}) + \left(\frac{1}{3000}\right)^2 u^2 (Ac_{40K})} \quad (3)$$

299

300 Where I is the activity concentration index, $u(\text{Ac})$ is the uncertainty of the activity
301 concentration of the mentioned radionuclide.

302

303 **3. Results & Discussion**

304

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

310

311 **3.1 Assessment of radiological equilibrium in samples**

312

313 **3.1.1 The ^{232}Th decay series**

314

315 The activity concentrations of the relatively short-lived ^{224}Ra , ^{212}Pb , ^{212}Bi and ^{208}Tl
316 (corrected for its branching) were equal within the measurement uncertainties.
317 Their weighted mean value gave the activity concentration for ^{228}Th ($t_{1/2}= 1.9126$
318 years). The activity concentration of the short-lived ^{228}Ac was in equilibrium with
319 its mother ^{228}Ra ($t_{1/2}= 5.75$ years). Looking at Table 4 the ratio of ^{228}Ra over ^{228}Th
320 equals 1 in the feedstock material samples, flue dust samples and slag samples.
321 For the slags, this equilibrium is not likely to have been established in the
322 relatively short time (~ 470 days, two-thirds of the $t_{1/2}$ of ^{228}Th , and ~ 180 days, a
323 quarter of the $t_{1/2}$ of ^{228}Th ; respectively for Batch 1 and 2) between the production
324 and the measurement. This means that Ra is not separated from Th during the
325 industrial process of non-ferrous metal production. Th and Ra are both lithophilic
326 and will therefore end up in the slag phase (Bourdon et al., 2003; White, 2013).
327 The affinity for silicates of both radionuclides confirms the unaffected equilibrium
328 during the industrial process. Often in literature, equilibrium is assumed between
329 ^{232}Th and ^{228}Ra , here the activity of ^{228}Ra is shown since this one is actually
330 measured.

331

332

333 **3.1.2 The ^{238}U decay series**

334

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

347

348 This disequilibria is also present in the investigated feedstock material but less
349 distinct, with a minimum and maximum ratio $^{238}\text{U}/^{226}\text{Ra}$ of 1.2 ± 0.2 and 1.9 ± 0.3
350 respectively (table 4). Looking at another output material of the industrial
351 process, the flue dust demonstrates an even more outspoken absence of equilibria
352 with a minimum and maximum $^{238}\text{U}/^{226}\text{Ra}$ ratio of respectively 10 ± 3 and $30 \pm$
353 10 . It must be noted that the ^{238}U (maximum 50 ± 10 Bq/kg) and ^{226}Ra (maximum
354 3.3 ± 0.2 Bq/kg) activity concentrations of the flue dust samples are low in
355 comparison with ^{238}U (minimum 42 ± 4 Bq/kg) and ^{226}Ra (minimum 14 ± 2 Bq/kg)
356 activity concentrations of the slag samples (Table 4). In addition, per ton slag
357 approximately 25 kg of flue dust is produced. This means transport of ^{238}U and
358 ^{226}Ra to the flue gasses is limited. The activity concentrations of ^{238}U and ^{226}Ra in
359 the metallic fractions are low - this is confirmed by the company, however no data
360 can be made publicly available. Regarding the lithophile properties of U and Ra
361 and their limited absolute transport, it is believed that other sources of NORs
362 which have a higher degree of disequilibrium than the measured feedstock
363 material are present and consequently explain the relatively high level of
364 disequilibria in the slag samples.

365

366 The activity concentrations ratios of ^{210}Pb over ^{226}Ra in the non-ferrous slags
367 range between 0.14 ± 0.09 and 1.4 ± 0.5 (Table 4). In nine cases an absence of

368 equilibrium is observed and the activity concentration of ^{210}Pb is lower than the
369 activity concentration of ^{226}Ra . However in slags 6 to 11, slags 17 to 23, slag 25
370 and slags 27 to 29 equal activity concentrations are measured (Figure 2). It is
371 important to note that the observed equal activity concentrations of ^{226}Ra and
372 ^{210}Pb cannot originate from the instalment of equilibrium of ^{210}Pb with ^{226}Ra
373 during or after processing, since the half-life of ^{210}Pb is 22.23 years. Table 4 shows
374 that for the flue dust the minimum and maximum ratios $^{210}\text{Pb}/^{226}\text{Ra}$ are 110 ± 30
375 and 900 ± 300 respectively and for the feedstock material they are 8 ± 3 and $20 \pm$
376 7 respectively. So the absence of equilibrium is already present in the feedstock
377 material but is less pronounced for the slag samples and more pronounced for the
378 flue dust samples. An enrichment in Pb concentration and enhanced ratios
379 $^{210}\text{Pb}/^{226}\text{Ra}$ in dust samples were also observed by Khater and Bakr which studied
380 the transport of ^{210}Pb transport in metallurgical industries (Khater and Bakr,
381 2011). The transport of Pb towards flue dust and fumes can be subscribed to the
382 volatile nature of Pb. In addition the ratio ^{210}Pb over ^{226}Ra in the slags samples is
383 influenced by the transport of Pb towards the metallic phase i.e. the produced
384 metal alloy. This transport is depending on the reduction potential in the furnace
385 of the investigated smelter facility. Strong reducing conditions favor the transport
386 of Pb towards the metal phase.

387

388 No ^{210}Pb was measured in slags 1 to 5 and the Minimum Detectable Activity (MDA)
389 with a confidence limit of 95% was below 20 Bq/kg for slags 1 to 4 and 160 Bq/kg
390 for slag 5. The MDA of slag 5 is higher due to the thicker dead layer of detector Ge-
391 3, which impacts the FEP for the low-energy gamma-ray of ^{210}Pb .

392

393 The ratio of activity concentrations $^{238}\text{U}/^{235}\text{U}$ of all slags agreed within the
394 uncertainties (except for slag 19) with the expected value of 21.6. The measured
395 $^{238}\text{U}/^{235}\text{U}$ ratios (Figure 3) indicate therefore the expected natural isotopic
396 composition. This is an important quality control measure, which indicates that
397 the gamma-spectrometric measurements were robust.

398

399 **3.1.3 ^{40}K**

400

401 Potassium-40 is not a part of a decay series and has lithophilic properties (White,
402 2013). The ^{40}K activity concentrations in the slags vary between 26 ± 8 Bq/kg and
403 80 ± 10 Bq/kg (Figure 4 and Table 4).

404

405 **3.2 Temporal variation in the activity concentrations**

406

407 The ratios of the maximum measured activity concentration over the minimum
408 activity concentration for each long living radionuclide in the different materials
409 (Table 4) indicate significant fluctuations. For the slags, the lowest ratio was $3.1 \pm$
410 0.5 for ^{40}K and the highest ratio was 13 ± 7 for ^{210}Pb whereas for the flue dust
411 samples the lowest ratio was 2.0 ± 0.3 for ^{228}Ra and the highest ratios was $4.3 \pm$
412 0.7 for ^{40}K . The variations in the non-ferrous slag and flue dust samples can be
413 explained as the smelter facility uses a mixture of primary and secondary raw
414 materials. The radiological content of the input materials is strongly depending on
415 the origin and as the data of the investigated feedstock material (Table 4 and
416 Figure 4) suggests also variations occur even when the origin of the input material
417 is the same (IAEA, 2003). For the feedstock materials the lowest observed
418 maximal/minimal ratio was 2.2 ± 0.6 for ^{228}Th and the highest observed ratio was
419 9 ± 7 for ^{40}K .

420

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

430 These measures will only bear information on a specific time and not on the
431 variation of the activity concentrations. Drawing conclusions based on a one-time
432 sampling or low frequency sampling in order to ensure radiation protection of
433 general public and workers should be performed cautiously. The authors

434 recommend performing radiological measurements depending on the frequency
435 of the discharge of the residues taking into account the complexity and variability
436 of the facility/industry.

437

438 **3.3 Comparison of activity concentrations with the literature.**

439

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

455

456 **3.4 Evaluation in function of legislative criteria**

457

458 **3.4.1 Evaluation considering the exemption and clearance levels**

459

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

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

469

470 **3.4.2 Evaluation for use as building material considering the ACI**

471

472 Figure 5 shows the variation of the ACI when the fayalite slag is solely used
473 (100%) to construct a building material. No day production batch exceeded the
474 index value of 1, therefore every day production batch can be used as an building
475 material. It must be noted that the highest observed activity concentrations (slag
476 18) are approximately a factor 12, 10 and 120 below the exemption/clearance
477 levels of the EU-BSS for respectively ^{226}Ra , ^{232}Th and ^{40}K , however the index has a
478 value of approximately 0.8. So being well below the exemption/clearance levels
479 does not necessarily imply that is in accordance with the limits applying to
480 building materials.

481

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

486

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

496

497 **4. Conclusion**

498

499 The current study monitored different materials processed in a non-ferrous
500 smelter facility, which fits within the framework of the EU-BSS. Equilibria are
501 discussed for the ^{232}Th and ^{238}U decay series. The ^{232}Th decay series was found to
502 be in equilibrium for all the slags, measured feedstock material and flue dust. This
503 was not the case for ^{238}U decay series due to lack of equilibrium in the feedstock
504 material and the impact of the industrial process. The activity concentrations of
505 the slags were all below the provided exemption/clearance levels of the EU-BSS
506 and RP-122 part II, and are also low in comparison to slags reported in literature.
507 The activity concentrations of the flue dust samples were all except for ^{210}Pb
508 below the exemption/clearance levels. For the feedstock material only ^{40}K and
509 ^{235}U were below the exemption/clearance levels. In addition the ACI is not a
510 restriction regarding the use of these non-ferrous slags to produce building
511 materials.

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

530

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532

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538

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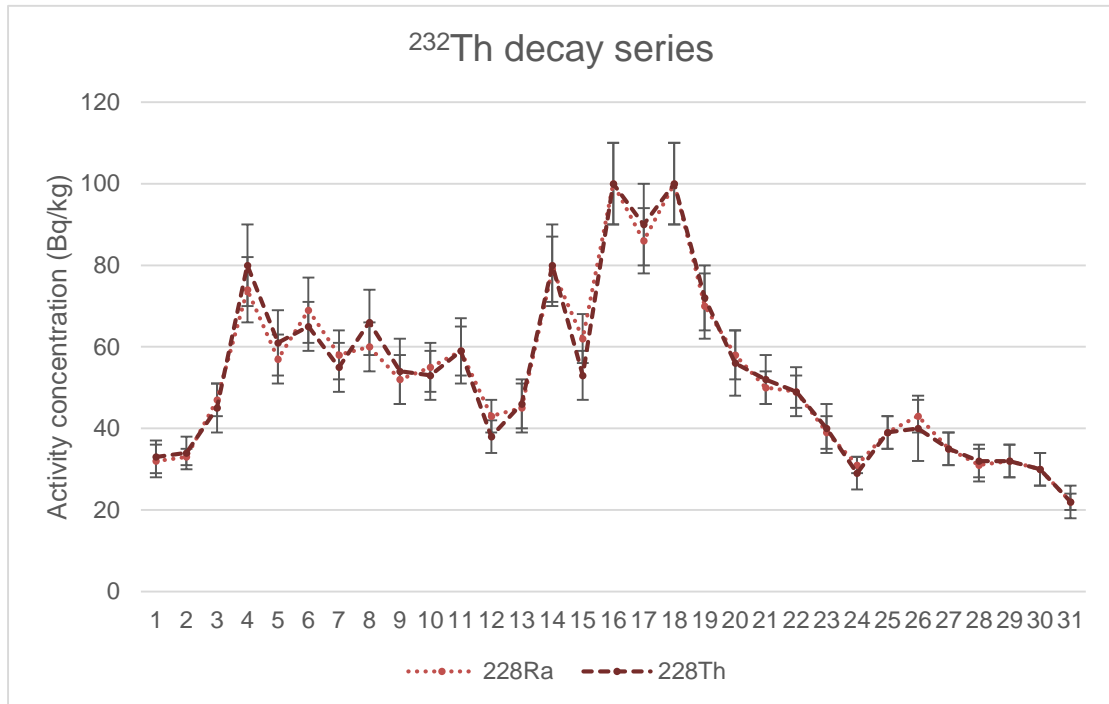
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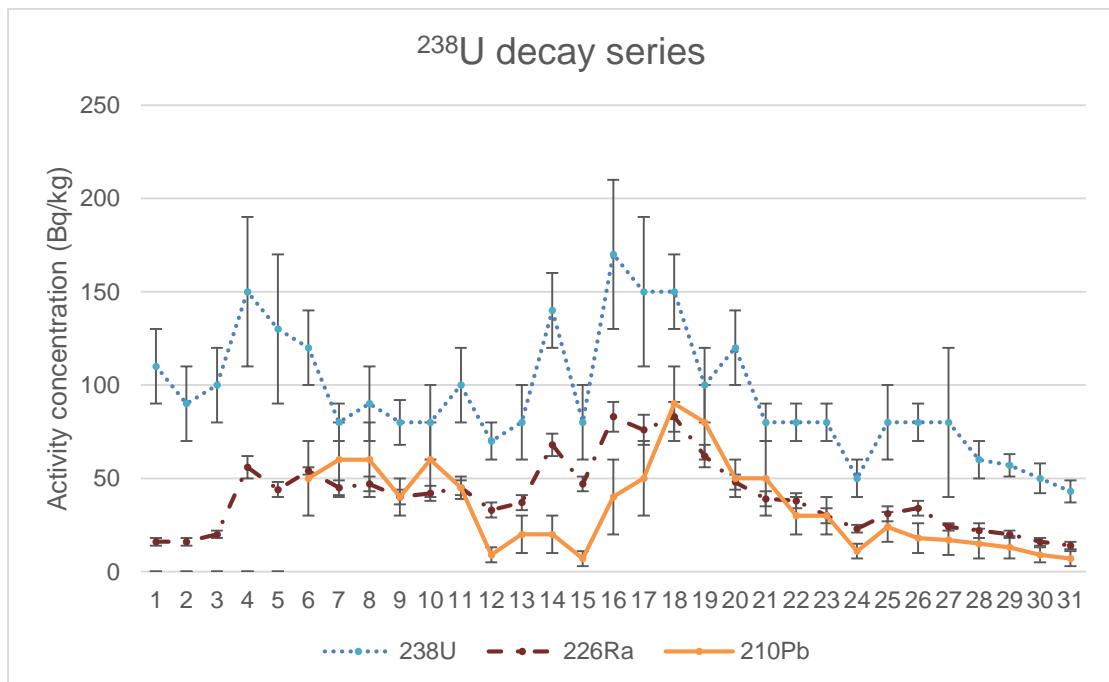
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733 **Figures**
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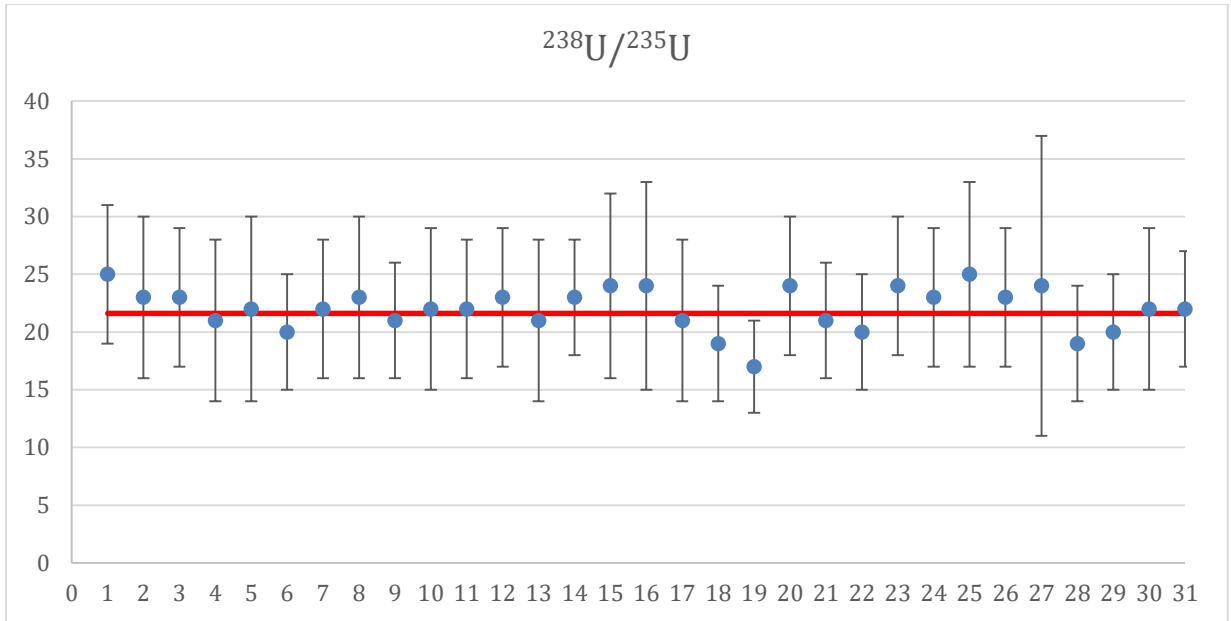
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Figure 1: Activity concentration of 31 slag samples for the ^{232}Th decay series (coverage factor, $k=2$). Samples were collected at 31 consecutive days of slag production.



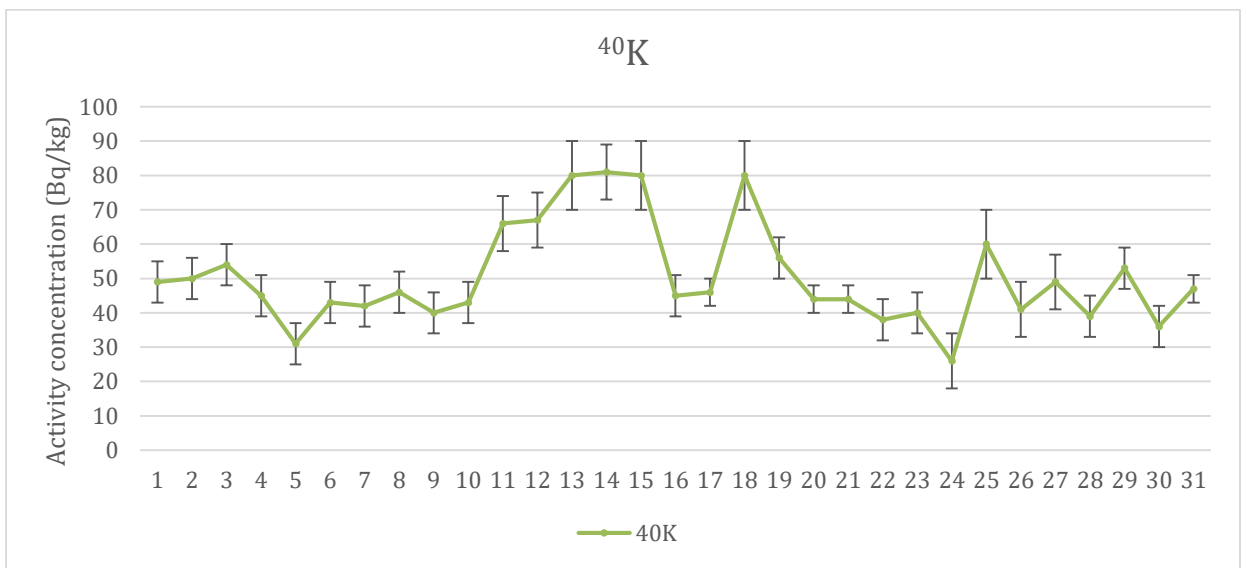
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Figure 2: Activity concentration of 31 slag samples for the ^{238}U decay series (coverage factor, $k=2$). Samples were collected at 31 consecutive days of slag production.



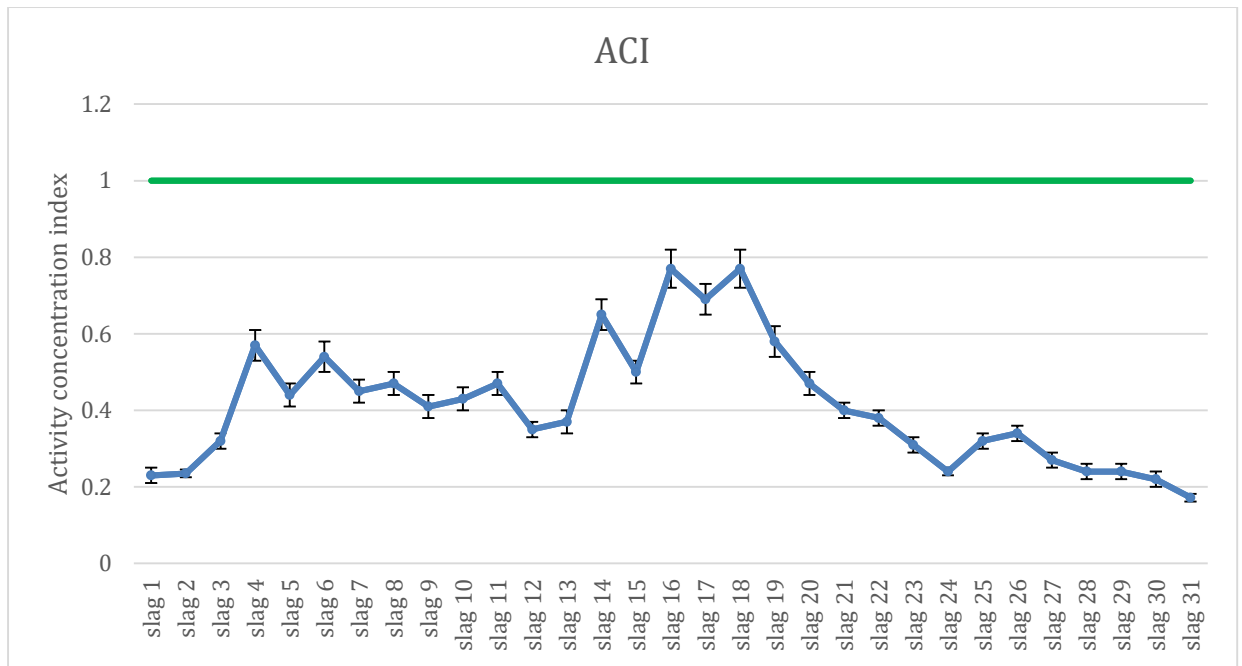
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Figure 3: $^{238}\text{U}/^{235}\text{U}$ of slag 1 – slag 31, with ^{238}U via $^{234\text{m}}\text{Pa}$ ($k=2$). Red line indicates natural uranium ratio of 21.6. Samples were collected at 31 consecutive days of slag production.



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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.



752

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

755

756 **Tables**

757

758 Table 1: Overview of the activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K in metallurgical slags in
759 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	Croatia	Sofilic et al., 2011
Steel slag	/	5 - 31	0 - 5	/	/	RP-122 part II
Steel slag	/	100 - 600	/	/	Slovenia	Smoldis 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 Almeahmadi, 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	Croatia	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	Cabaneckova, 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	Cabaneckova, 2008

760 * Mentioned as maximum value

761 ◊ Mentioned as typical values

762 □ Mentioned as average value

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

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

765 ‡ Could contain doubles with Cabaneckova 1996

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767 Table 2: Exemption/clearance levels reported in EU-BSS | IAEA (equilibrium situation) and RP-
768 122 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
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769 * The activity concentration criterion of the EU-BSS | IAEA assumes equilibrium (European
770 Council, 2014; IAEA, 2004).

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

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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

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Table 4: minimum and maximum activity concentrations, ratio of the maximum over the minimum

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activity concentration and ratio of different long living radionuclides over each other for feedstock

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material, flue dust and non-ferrous fayalite slag samples (k=2).

Radionuclide	Feedstock material (5 samples)			Flue dust (9 samples)		
	Activity concentration (Bq/kg)		Ratio max/min	Activity concentration (Bq/kg)		Ratio max/min
	min	max		min	max	
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	

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

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

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