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SAS, Zoltan; VANDEVENNE, Niels; Doherty, Rory; Vinai, Raffaele; Kwasny, Jacek; Russell, Mark; Sha, Wei; Soutsos, Marios & SCHROEYERS, Wouter (2019) Radiological evaluation of industrial residues for construction purposes correlated with their chemical properties. In: Science of the total environment, 658, p. 141-151.

DOI: 10.1016/j.scitotenv.2018.12.043 Handle: http://hdl.handle.net/1942/27647

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14	Abstract
15	This study characterises the naturally occurring radionuclide (NOR) contents of a suite of secondary raw

materials or industrial residues that are normally disposed of in landfills or lagoons but now are increasingly used in green concretes. This includes ashes from a variety of industrial processes and red mud from aluminium production, as well as air pollution control residue and cement kiln dust. The chemical composition of the samples was determined with X-ray fluorescence spectroscopy (XRF). The Ra-226, Th-232 and K-40 activity concentrations were obtained by gamma spectrometry, and the results were compared with recently published NOR databases. The correlation between the NOR contents and the main chemical 22 composition was investigated. The radioactive equilibrium in the U-238 chain was studied based on the 23 determination of progeny isotopes. The most commonly used calculation methods (activity concentration 24 index and radium equivalent concentration) were applied to classify the samples. The radon exhalation rate 25 of the samples was measured, and the radon emanation coefficient was calculated. Significant correlation 26 was found between the NORs and certain chemical components. The massic exhalation demonstrated a 27 broad range, and it was found that the emanation coefficients were significantly lower in the case of the 28 residues generated as a result of high-temperature combustion processes. The results showed a weak 29 correlation between the Ra-226 concentration and the radon exhalation. This emphasizes that managing the 30 Ra-226 content of recycled material by itself is not sufficient to control the radon exhalation of recycled 31 materials used in building products. The investigated parameters and their correlation behaviour could be 32 used to source apportion materials found during the process of landfill mining and recovery of material for 33 recycling.

34

35 Keywords: gamma spectrometry; radon emanation; radon exhalation; recycling; red mud

# 36 Highlights

37	•	The NOR contents of the surveyed residues fit well with recent NOR databases
38	٠	The radioactive equilibrium in the decay chains fits well with the literature data
39	•	Strong correlation was found between the NOR contents and certain chemical elements
40	•	The chemical composition can be used as a source apportionment tool for NOR content
41	•	The emanation was low for residues generated under high-temperature processes
42		

## 43 1. Introduction

44 The depletion of raw materials and demand for low carbon material resources has resulted in the urgent 45 need for new eco-innovative building materials. The market need for efficient, economical and safe 46 production of new building products requires a comprehensive model of the properties of primary and 47 secondary raw materials, and existing building products to facilitate the creation of a circular economy. "The transition to a more circular economy, where the value of products, materials and resources is 48 49 maintained in the economy for as long as possible, and the generation of waste minimised, is an essential 50 contribution to the EU's efforts to develop a sustainable, low carbon, resource efficient and competitive 51 economy" (European Commission, 2015). These material resources are often recycled from secondary raw 52 materials or industrial residues rather than from pristine sources. Valorisation alongside carbon capture 53 technologies can offer an opportunity for a circular economy approach to building materials (Pan et al., 54 2018). Alkali-activated materials (AAMs) are alternative low-carbon binders and can be produced through 55 the reuse of industrial residues as secondary raw materials. These residues have traditionally been disposed of in brownfield landfills and lagoons which are now being mined to recover the valuable materials. 56

57 These residues often serve as precursors for production of AAM. Ideally the activators should be also 58 residues or secondary raw materials with high pH (Tong et al., 2018). Here we focus on the residues that 59 can be used in the production of AAMs. Globally, about 46% of CO<sub>2</sub> emissions originated as a result of the 60 fossil fuel combustion, with 31% emitted from coal combustion power plants (Olivier et al., 2016). The amount of generated residue depends on the non-combustible mineral content, which can vary between 5-61 30% (Kovacs et al., 2017). As a result of combustion, the NOR contents of the coal are enriched in the 62 63 residues (Table 1). A tenfold enrichment factor, compared to the initial NOR contents of the coal, is common 64 in residues (Somlai et al., 1996). Owing to this phenomenon, residues, including the coarse bottom ash 65 (BA), also called coal slag, and the fine, fly ash (FA), contain elevated (Kovacs et al., 2017; Kardos et al., 2015) and occasionally extremely high concentrations of Ra-226 (Somlai et al., 2006; Somlai et al., 1996) 66 above the 1000 Bg/kg clearance level defined in the EU BSS (European Union, 2014). The use of BA and 67

FA in construction materials always increases the risk to residents. The iron production process produces 68 slag as a residue. The NOR contents of the ground granulated blast-furnace slag (GGBFS) (Table 1) depend 69 on the materials used during the process such as iron ore, sinter, flux limestone, dolomite, and coke. 70 71 Aluminium production from bauxite produces red mud. The red mud still contains valuable compounds. 72 Huge efforts are made to find economical technology to valorise them. However, when reused on an industrial scale it will still be subject to an 'end of waste criteria' depending on the country where this 73 74 occurs. Globally, this is estimated at 150 million tons per year (Davris et al., 2015). The safe reuse of red 75 mud has not been resolved yet, due to its heavy metal and its elevated NOR contents (Table 1). The unsafe 76 storage of the red mud can endanger eco-systems and humans, as was demonstrated by disasters that 77 happened in 2010 at Aika, Hungary (Somlai et al., 2010; Gelencsér et al., 2011; Mayes et al., 2016) and in 78 2016 at Luoyang, Henan province, China, the latter fortunately without human injury (Liu, 2016). Red mud 79 needs to be checked for its NOR contents when it is used in building materials (Kovacs et al., 2017). Cement 80 kiln dust (CKD) presents a significant landfill and disposal problem (Gunning et al., 2010). There was no information found in the current literature regarding the NOR contents of the CKD. However, for 81 82 comparison, cement data can be used as a proxy with the assumption that the CKD generated from the same 83 stream as cement production is composed of the same unreacted raw material (US EPA, 2016). Municipal 84 residue, clinical residue and sewage sludge produce significant amounts of ash (Rani et al., 2008). The ash, e.g. household waste ash (HWA), incinerated sewage sludge ash (ISSA) and dust, e.g. air pollution control 85 86 (APC) residue, originate as a result of the scrubbing of emissions, with the residue often classified as 87 hazardous (Kourti et al., 2010; Rani et al., 2008). Numerous studies have dealt with their reuse in the cement 88 and concrete industry (Cyr et al., 2007; Donatello and Cheeseman, 2013; Wongsa et al., 2017; Müller and Rübner, 2006). As a result of the incineration, the radionuclides mainly remain in the solid residues 89 (Carvalho, 2017). A study performed in Germany (Puch et al., 2005) measured the NOR contents of the 90 91 HWA and compared them with the world averages published in RP-112 (European Commission, 1999). 92 The radionuclide contents of ISSA mainly depend on the treated wastewater. The NORs and also artificial 93 radionuclides, most notably I-131, Tl-201, and Sr-89 (all short half-lived medical isotopes), can accumulate

94 in the sludge and after the incineration remain in the inert inorganic particles of the ISSA. A survey, 95 involving 313 Publicly Owned Treatment Works across the USA, concluded that elevated levels of radioactive materials were found in some sewage sludge and ash samples, but the survey did not indicate a 96 97 widespread problem (ISCORS, 2005). Rice kusk ash (RHA), a residue of biomass-based electricity 98 generation, originates from rice mills. The husk consists of approximately 40% cellulose, 30% lignin and 99 20% silica and is burned in power plants producing a residue with a hard, abrasive nature. The high silica 100 content (~90-95%) and the reactive nature of the amorphous silica content makes it usable as a pozzolana 101 (He et al., 2013). Information in the scientific literature about the NOR contents in RHA is currently missing. 102 This circular approach requires cross-disciplinary collaboration between academics, industry, and the 103 authorities. Large quantities of specific secondary raw materials can be utilised in AAMs as solid binders 104 of performance comparable to Portland cement (Ascensão et al., 2017; Bondar and Coakley, 2014; Puertas 105 et al., 2015; Vinai et al., 2016). For new forms of concrete, the use of AAMs incorporating industrial 106 residues reduces CO<sub>2</sub> emissions by up to 80% (Aiken et al., 2017). Although economically viable, market 107 uptake and widespread application of these new types of recycled materials are currently hampered by public 108 health concerns related to immobilisation of potentially toxic compounds (Sas and Vandevenne, 2015) and 109 in particular radiation exposure from naturally occurring radionuclides (NORs) that can be present in these 110 materials (Kovacs et al., 2017).

111 With existing construction materials and raw materials, the contents of NOR (U-238, Th-232 series and 112 their progenies, K-40) and their effects can have significant health implications. Despite the relatively low 113 NOR contents generally found in buildings, the radionuclides present can cause long-term exposure to the 114 inhabitants, due to prolonged indoor residence times. Two main exposure pathways can be differentiated 115 when considering the built environment. The primary pathway leading to internal exposure is as a result of 116 the decay of the incorporated radionuclides from the U-238 and Th-232 decay series that leads to the 117 formation of radon & thoron. The exposure factor, related to this pathway, is the inhalation of radon/thoron (Rn-222, Rn-220) and their progenies (from soil and construction materials) which can get stuck in the lungs 118 119 and irradiate cells. Radon, a radioactive noble gas, can diffuse out of the building materials and is currently 120 the second most common cause of lung cancer after smoking (Axelsson et al., 2015; World Health 121 Organization, 2009). Depending on the internal structure and the parent element concentration (Ra-226), 122 the amount of radon which can exhale from a given building material matrix can vary greatly. The secondary 123 pathway, the external exposure caused mainly by gamma radiation emitted from the decay of NOR also 124 needs to be considered. Owing to their high penetration capacity, high energy gamma photons can exit walls, 125 floors, and ceilings that contain NOR materials. This depends on several factors including the energy of the 126 gamma photons, the thickness of the walls, the material density, the homogeneity and concentration of the 127 radionuclides. A constant dose rate is formed as a result of the NORs in buildings. The gamma exposure 128 can also depend on the position of the residents within rooms, but typically to a small extent (International 129 Atomic Energy Agency, 2012; Risica et al., 2001). Screening of potential industrial residues prior to 130 recycling ensures the avoidance of recycled building materials with increased radioactivity, and, in this way, 131 the industrial residue streams for the circular economy are checked in advance to assure safe recycling 132 (Kovacs et al., 2017).

133 To avoid an elevated risk for residents in houses, the EU has laid down Council Directive 2013/59/Euratom 134 (European Union, 2014) as Basic Safety Standards (EU-BSS) for protection against the dangers arising from 135 exposure to ionising radiation. Annex VIII of the directive defines the requirement for maximum allowable 136 excess dose from the NOR contents of building materials. Furthermore, the reference level for indoor radon 137 was set at 300 Bq/m<sup>3</sup> average radon concentration. However, uniform requirements and a standardised 138 method for screening the radon release from building materials before they are placed on the market are still 139 missing, which presents a significant challenge for future research. The NOR contents of construction 140 materials, their raw materials and residues depend on the origin of the materials. The processing technology 141 can also lead to a strong fluctuation in the NOR concentration, even in the case of the same residue repository 142 (Croymans et al., 2017b).

Table 1 presents global information about the NOR contents of BA, FA, GGBFS, HWA and RM based on
the NORM4Building (Schroeyers et al., 2018) and By-BM (By-Products for Building Materials) (Sas et al.,

- 145 2017) NOR databases. In relation to the other residues that this article considers, namely APC, CKD, ISSA,
- 146 RHA, there are no records yet in the NOR databases (Sas, 2017; Sas et al., 2017; Schroeyers et al., 2018).
- 147

148

### Table 1: Naturally occurring radionuclide (NOR) contents (Bq/kg) of studied residues

## 149 according to NORM4Building and By-BM databases

Material	Database		Ra-2	26		Th-2	32	K-40			
		Min	Max	Average	Min	Max	Average	Min	Max	Average	
BA	By-BM	16	3152	845	11	290	845	7	1100	253	
FA	NORM4B	11	1000	188	1	200	91	17	1100	343	
	By-BM	14	1028	235	1	250	96	44	3001	505	
GGBFS	NORM4B	100	323	201	25	148	66	158	500	298	
	By-BM	8	399	183	3	330	83	7	388	162	
HWA	By-BM	11	25	18	8	21	13	159	213	83	
RM	NORM4B	97	1700	389	45	1800	553	15	583	216	
	By-BM	97	1047	311	118	1350	324	5	583	155	

150

151 There is a fundamental difference between the two NOR databases. The By-BM database operates with 152 individually reported sample information, including information on how the samples were measured, which 153 enables further statistical analysis of the data. The disadvantage of this dataset is that it operates with a 154 limited amount of records (currently a few thousand). The dataset contains the number of the samples with 155 the minimum, maximum, and the average or median activity concentrations of samples. The 156 NORM4Building dataset has a greater number of records but consists mainly of averaged data. This type of 157 information does not allow the precise weighting of the data, but the great number of entries provides an 158 overall insight into the materials.

Here we evaluate new radiological and chemical analysis of residues or secondary raw materials commonly used in the manufacture of alkali-activated materials by determination of NOR contents by gamma spectrometry and calculation of I-index and radium equivalent. We investigate radioactive disequilibrium in the radioactive decay chain of Th-232 and U-238 and determine massic exhalation and radon emanation factor for the residues.

## 164 2. Materials and methods

## 165 **2.1 Sample preparation**

166 Samples were collected from different European countries and originate from various industrial activities 167 (Table 2). The sources of the samples are not revealed, as the present scientific research is not for judging 168 them. The samples were homogeneous within each source, represented by a unique Sample ID in Table 2. 169 FA 7 was originated from the same site as FA 1 and GGBFS 2 came from the same site as GGBFS 1. This 170 is the reason why FA 7 and GGBFS 2 were not examined with XRF. Fig. 1 gives exact compositions of all 171 these sample materials. All ashes are siliceous. Note that the data shown in Table 1 are from literature data 172 forming the two databases, while the samples listed in Table 2 are for the original experimental studies, the results of which are reported in this paper. The samples were dried to constant mass in a drying cabinet at a 173 174 temperature of 105°C and powdered. A typical sample weight used for subsequent analysis post drying was 175 1 kg. The powdered samples were divided to three portions. For the gamma spectrometry analysis and the 176 radon exhalation measurement, typically 0.3–0.5 kg samples were used respectively depending on their 177 density. For the XRF characterization 10 g samples were used.

178

Sample ID	Material	Industry
APC	Air pollution control residue	Municipal waste incineration
BA	Bottom ash	Coal combustion thermal power plant
CKD 1, 2, 3	Cement kiln dust	Cement production
FA 1, 2, 3, 4, 5, 6, 7	Fly ash	Coal combustion thermal power plant
GGBFS 1, 2	Ground granulated blast-furnace slag	Ferrous industry
HWA	Household waste ash	Municipal waste incineration
ISSA	Incinerated sewage sludge ash	Sewage sludge incineration
RHA	Rice husk ash	Rice milling industry
RM 1, 2	Red mud	Aluminum production

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181

## 2.2 Determination of major components with XRF

182 In this study, the main chemical composition was determined by X-ray fluorescence (XRF) analysis. The 183 measurements were performed on a fused glass bead sample, for removing both grain size and mineralogical 184 effects. The samples were heated under air atmosphere up to 1200°C in a platinum crucible with lithium 185 borates. During the process, oxides of the metal contents are formed and the results are reported in that form. 186 The equipment used was a PANalytical Axios Advanced XRF spectrometer which runs on a 4KW Rh tube 187 using WDS and a sample to flux ratio of 1:10. The results, which were quoted as weight percent, were 188 analysed using PANalytical SuperQ software using reference samples and artificial analogues. LOI was 189 determined by igniting the materials at 950°C for 1.5 hours.

## 190 **2.3 Determination of NOR with gamma spectrometry**

191 The samples were put into polystyrene containers with metal cap and stored for 27 days to achieve secular 192 equilibrium between Ra-226 and Rn-222. The NOR contents of the investigated materials were determined

193 by gamma spectrometry using a calibrated high purity broad energy germanium detector (Canberra BE5025-194 7500SL) with a 50% nominal relative efficiency. The detector was shielded with a copper-lined lead shield 195 specific for low-activity measurements. All samples were measured for 80 000 s using the same poly(methyl 196 methacrylate) sample holder to fix the samples in position 5 mm above the endcap of the detector, leaving 197 an air-filled gap between the sample and the detector. Canberra's Genie 2000 software was used for data 198 acquisition. Canberra's LabSOCS software was used to perform the efficiency calibration with self-199 absorption correction. The 1 sigma error was calculated by the sofware. The determined radionuclides and 200 their details are presented in Table 3.

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## Table 3: Details of radionuclides measured by gamma spectrometry

Nuclide	Decay chain	Determined isotope	Energy (keV)	Intensity (%)
Pb-214	U-238	Ra-226	351.9	35.6
Bi-214	U-238	Ra-226	609.3	45.5
Th-234	U-238	U-238	63.3	3.8
Pb-210	U-238	Pb-210	46.5	4.3
Ac-228	Th-232	Th-232	911.2	26.2
Pb-212	Th-232	Th-232	238.6	43.6
K-40	-	K-40	1460.8	10.6
Cs-137	-	Cs-137	661.7	85.0

203

#### 204 **2.4 Calculation of commonly used indexes**

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#### 2.4.1 Radium equivalent index

The radium equivalent index (Ra<sub>eq</sub>) (Beretka and Mathew, 1985) is based on the assumption that the dose rate contribution of unit activity of Ra-226, Th-232 and K-40 with their belongings decay chains are different. The dose criterion in the case of  $Ra_{eq}$  is 1.5 mGy/year absorbed dose which corresponds to a value of 1.0 mSv annual effective dose. The calculation of  $Ra_{eq}$  assumes that 259 Bq/kg of Th-232 and 4810 Bq/kg of K-40 cause a dose rate equivalent to 370 Bq/kg of Ra-226 (Beretka and Mathew, 1985; Nuccetelli et al., 2017). The  $Ra_{eq}$  can be calculated according to the following equation:

212 
$$Ra_{eq} = A_{Ra-226} + 1.43A_{Th-232} + 0.077A_{K-40}$$
(1)

where  $A_{Ra-226}$ ,  $A_{Th-232}$ , and  $A_{K-40}$  are the activity concentration of Ra-226, Th-232, and K-40, respectively. The current Chinese and Russian legislation is derived from this approach (Nuccetelli et al., 2017).

215 <u>2.4.2 Activity concentration index (I-index)</u>

216 To characterise construction materials the calculation of the I-index is one of the most commonly used 217 screening tool based on the Mikka Markannens model, presented in RP112 (European Commission, 1999). 218 The I-index is derived to indicate whether the annual dose due to the excess external gamma radiation in a 219 building may exceed 1.0 mSv. This calculation method operates with the assumption that all the walls, the 220 ceiling and also the floor of the room are made from 20 cm thick concrete with 2350 kg/m<sup>3</sup> density. The 221 computation considers the occupancy factor, the annual indoor spent time, and the dose conversion factor. 222 The targeted 1.0 mSv dose excess can be the result of exposure to respectively 276 Bq/kg Ra-226, 231 223 Bq/kg Th-232 or 3176 Bq/kg of K-40. In the final formula of the I-index, the values computed above are 224 rounded to the nearest full 100 Bq/kg (Ra-226 and Th-232) or 1000 Bq/kg (K-40). The latest European 225 Basic Safety Standard (EU-BSS) in Article 75, Annex XIII (European Union, 2014) introduces a screening 226 index which is based on the abovementioned computation to identify building materials that are of concern 227 from the radiological protection point of view. The I-index can be calculated according to the following 228 formula (European Commission, 1999; Nuccetelli et al., 2017):

229 
$$I = \frac{C_{Ra}}{300Bq/kg} + \frac{C_{Th}}{200Bq/kg} + \frac{C_K}{3000Bq/kg}$$
(2)

where  $C_{Ra}$ ,  $C_{Th}$ ,  $C_K$  are the Ra-226, Th-232 and K-40 activity concentrations expressed in Bq/kg.

In the European Union, the member states were required to harmonise their national legislation according to the EU-BSS at the latest in February 2018. It is important to note that the calculation of the I-index only allows for a conservative screening. To more accurately predict the dose contribution as a result of recycled building materials in a given building, the thickness and the density also have to be taken into consideration (Nuccetelli et al., 2015). A recently published dose model (Croymans et al., 2017a) with expanded gamma lines from NORs is applicable in non-standard rooms.

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## 2.5 Massic radon exhalation and emanation factor of surveyed samples

238 The massic exhalation (Friedmann et al., 2017) of surveyed samples was determined with an accumulation chamber technique. The granulated (<10 mm grain size) (Friedmann et al., 2017), dry samples were 239 240 enclosed in radon-tight acrylic accumulation chambers equipped with stainless steel valves. To effectively 241 remove the radon from the samples, including pores, the chambers were evacuated in a vacuum chamber 242 and after purged with intensive radon-free airflow. The exhaled radon was determined with RD200 (200 cm<sup>3</sup> chamber volume) ionisation chamber manufactured by FTLab. Circulation was used for 10 minutes 243 244 with 5 L/min flow rate. To avoid the disequilibrium of the radon and its progenies, and the contribution of 245 thoron (Jonas et al., 2016), the first result obtained from the 60 minutes of the measurement was ignored. In 246 the accumulation time function, the activity of the decay of the exhaled radon was corrected, and the massic 247 exhalation was calculated according to the following formula (Sas et al., 2015b):

248 
$$E_{Mass} = \frac{C_t \cdot V}{m \cdot t} \cdot \frac{\lambda \cdot t}{1 - e^{-\lambda t}}$$
(3)

where  $C_t$  = accumulated radon concentration in the measurement kit during sampling [Bq m<sup>-3</sup>],  $E_{Mass}$  = massic exhalation rate [mBqkg<sup>-1</sup> h<sup>-1</sup>], t = accumulation time [h], V = volume of the accumulation kit [m<sup>3</sup>], m = mass of the sample [kg],  $\lambda$  = decay constant of radon [h<sup>-1</sup>]. Error values were derived from the sensitivity of the instrument, using information provided by manufacturer. The emanation factors of the surveyed samples were calculated from the Ra-226 activity concentration obtained by gamma spectroscopy and the equilibrium radon concentration calculated from the massic exhalation results (International Atomic Energy Agency, 2013):

256 
$$\varepsilon = \frac{Rn_{eq}}{C_{Ra-226}} \cdot 100 \tag{4}$$

257 where  $\varepsilon$  = emanation factor (%), Rn<sub>eq</sub> = equilibrium radon concentration and C<sub>Ra-226</sub> = Ra-226 activity 258 concentration.

# 3. Results and discussion

## 260 **3.1 Chemical composition of surveyed samples obtained by XRF**

261 The main chemical compositions of the studied residues are illustrated as a heat-map in Fig. 1. Dark red 262 represents the dominant components in the samples. The  $SiO_2$  content was the highest with 90.8 wt% in the 263 case of the rice husk ash sample (RHA) which fits the reported data (He et al., 2013). In the case of those fly ash and bottom ash samples, the SiO<sub>2</sub> ranged between 42.7-56.0 wt%, the Al<sub>2</sub>O<sub>3</sub> content varied between 264 265 18.4-30.0 wt% (highest among all residues studied) and the  $Fe_2O_3$  ranged between 4.9-18.7 wt%. The fly 266 ash samples were all siliceous and not calcareous. The CaO content was dominant in the case of all CKD, 267 APC and GGBFS 1 samples (32.6-49.5 wt%). In the case of both red mud samples, the composition fits 268 well with the scientifically reported data (Wang and Liu, 2012). The most dominant components in the red 269 mud were Fe<sub>2</sub>O<sub>3</sub> (35.8-43.8 wt%, highest among all residues studied), Al<sub>2</sub>O<sub>3</sub> (16.3-25.1 wt%), SiO<sub>2</sub> (8.6-270 13.8 wt%), TiO<sub>2</sub> (5.1-10.2 wt%, highest among all residues studied), CaO (4.5-5.6 wt%) and Na<sub>2</sub>O (4.7-7.7 271 wt%) which mainly originates from the NaOH solution used in the Bayer process (Kovacs et al., 2017).

Sample ID	Si02	TiO2	AI203	Fe2O <sub>3</sub>	Mno	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> 0	P205	SO <sub>3</sub>	V205	Cr203	SrO	Zr02	BaO	Nio	CuO	ZnO	PbO	IOI
APC	6.43	0.79	2.59	0.73	0.08	1.05	32.59	3.55	3.20	0.85	16.38	0.01	0.03	0.05	0.01	0.06	0.00	0.07	1.78	0.05	14.40
BA	56.02	0.83	18.39	7.97	0.09	1.73	5.36	2.61	0.88	0.68	0.23	0.03	0.01	0.18	0.04	0.34	0.01	0.01	0.01	0.00	4.63
CKD 1	16.37	0.21	3.73	2.21	0.06	0.88	46.62	4.35	0.37	0.13	13.67	0.01	0.01	0.07	0.01	0.04	0.00	0.01	0.06	0.03	9.90
CKD 2	14.57	0.27	3.84	2.07	0.06	0.75	49.53	9.12	1.07	0.09	4.28	0.01	0.00	0.02	0.00	0.02	0.01	0.05	0.04	0.05	13.17
CKD 3	11.83	0.24	3.49	2.39	0.18	1.60	45.44	8.29	0.93	0.05	4.61	0.06	0.01	0.03	0.01	0.02	0.01	0.03	0.01	0.02	20.21
FA 1	50.24	0.98	25.84	11.27	0.08	1.86	3.15	2.91	0.89	0.22	0.12	0.08	0.02	0.10	0.03	0.32	0.02	0.02	0.03	0.01	3.05
FA 2	53.64	0.91	20.31	9.26	0.07	1.83	4.33	2.19	1.14	0.43	0.39	0.04	0.01	0.18	0.04	0.33	0.01	0.01	0.02	0.00	4.54
FA 3	48.70	0.98	29.97	6.99	0.07	1.45	2.80	3.26	0.66	0.68	0.58	0.05	0.02	0.14	0.04	0.42	0.03	0.03	0.02	0.01	3.97
FA 4	55.45	1.07	23.90	4.86	0.05	1.72	4.43	1.89	0.81	0.72	0.73	0.03	0.01	0.18	0.00	0.43	0.01	0.01	0.02	0.01	3.19
FA 5	55.77	0.83	19.84	5.79	0.08	2.03	4.46	2.42	1.24	0.53	0.55	0.03	0.01	0.15	0.04	0.35	0.01	0.01	0.02	0.01	5.44
FA 6	42.73	0.91	27.90	18.72	0.04	0.98	4.13	1.45	0.11	0.40	0.71	0.04	0.02	0.10	0.03	0.25	0.01	0.01	0.03	0.01	2.18
GGBFS 1	34.74	0.62	13.80	0.34	0.46	7.63	41.13	0.69	0.30	0.00	2.54	0.01	0.00	0.08	0.04	0.42	0.00	0.00	0.00	0.00	0.00
HWA	35.22	0.89	12.47	10.57	0.16	2.39	19.59	1.07	4.21	1.74	1.43	0.06	0.05	0.16	0.04	0.33	0.04	0.24	0.48	0.07	7.34
ISSA	34.19	1.26	13.53	15.02	0.19	3.46	9.21	2.36	1.25	16.98	0.31	0.02	0.03	0.05	0.03	0.23	0.02	0.10	0.33	0.02	1.46
RHA	90.78	0.07	1.16	0.71	0.14	0.54	0.78	2.00	0.08	1.28	0.04	0.00	0.00	0.00	0.01	0.07	0.00	0.00	0.01	0.00	2.59
RM 1	8.58	10.17	16.25	43.76	0.05	0.07	5.64	0.09	4.68	0.32	0.16	0.23	0.25	0.01	0.35	0.21	0.01	0.00	0.01	0.01	9.33
RM 2	13.75	5.07	25.13	35.78	0.02	0.41	4.54	0.57	7.72	0.03	0.39	0.09	0.10	0.00	0.13	0.76	0.06	0.00	0.01	0.02	5.25
0																					100

272

273

Fig. 1: Main chemical components (wt%) of studied residues illustrated on a heat-map chart

## **3.2 NOR contents**

The activity concentration values obtained with gamma spectrometry of the NOR and the Cs-137 contents are presented in Table 4. Compared to the world average of NORs in construction materials (Ra-226 = 50 Bq/kg, Th-232 = 50 Bq/ kg and K-40 = 500 Bq/kg) (European Commission, 1999), the obtained average values of the residues were 1.84, 1.8 and 1.5 times higher, respectively.

There is no easy way to compare the different materials. They are associated with different raw materials and different processes. The NOR isotopes are trace elements and their behavior depends on the processes. These materials are completely independent from each other. It is not a straightforward mechanism in general. So, the results were compared in this paper only to the records of the NORM databases. A source apportionment tool can be a first step to build a dataset to provide possibility to draw conclusion for the mechanisms.

# Table 4: Naturally occurring radionuclide (NOR) and Cs-137 contents of surveyed materials

285

28	86	
20	0	

where the 1 sigma error was calculated by the LabSOCS software

ID	Ra-226	Th-232	K-40	Cs-137
APC	10±1	7±1 (min.)	1025±43	6.1±0.4
BA	113±8	68±5	623±27	-
CKD 1	15±1	11±1	1348±57	0.9±0.1
CKD 2	15±1	8±1	2712±113 (max.)	4.9±0.4
CKD 3	15±1	8±1	2631±110	3.0±0.3
FA 1	139±10	82±6	743±31	1.4±0.2
FA 2	108±7	59±4	542±23	-
FA 3	89±6	94±7	763±32	-
FA 4	115±8	98±7	482±21	-
FA 5	89±6	60±4	577±25	-
FA 6	201±14 (max.)	97±7	349±15	-
FA 7	129±9	76±5	674±29	1.3±0.1
GGBFS 1	126±9	44±3	117±6	-
GGBFS 2	129±9	47±3	122±6	-
HWA	32±2	18±1	242±11	1.4±0.1
ISSA	65±5	60±4	563±24	11±1 (max.)
RHA	6±1 (min.)	16±1	505±22	-
RM 1	186±13	452±31 (max.)	37±2 (min.)	-
RM 2	168±11	398±27	174±8	-
Average	92	90	749	2

287

In Table 4, a dash line indicates no detectable data, i.e., the measured intensity was below the detection 288 289 limit. The results of different studied materials were compared with the similar material records in the NORM4Building (Schroevers et al., 2018) and By-BM (Sas et al., 2017) NOR databases. The result of the 290 291 comparison is illustrated in Fig. 2.



292

293 Fig. 2: Comparison of obtained naturally occurring radionuclide (NOR) contents with datasets of NOR databases with the distribution of the data and the computed average values all illustrated 294



- 301 Th-232 contents were significantly lower than the average values of the cement records collected in the
- 302 databases. The K-40 contents were significantly higher compared to the database records.

## 303 **3.3 I-index and radium equivalent concentration of studied residues**

- 304 The I-index and the radium equivalent concentration were calculated based on the obtained NOR content.
- 305 However, this calculation provides only a conservative screening value, since neither the density nor the
- thickness of the construction materials are taken into consideration. The results are illustrated in Fig. 3.





309

**Fig. 3**: Activity concentration index (I-index) and radium equivalent index (Ra<sub>eq</sub>) concentration of surveyed residues compared with naturally occurring radionuclide (NOR) datasets

The I-index values varied between 0.27-2.89 with an average of 1.00. The I-index of five siliceous fly-ash and two red mud samples were found with above the EU recommended 1.0 I-index value (European Union, 2014). The Ra<sub>eq</sub> concentration of the residues was lower than 370 Bq/kg for all cases, except the red mud samples. However, the Ra<sub>eq</sub> concentration seems to be considerably more permissive compared to the I-

index: it has to be highlighted that 370 Bq/kg Raeg concentration is equivalent to 1.2 times the I-index value 314 315 which is about 20% higher than the I-index recommended value of 1.0. In the case of the I-index, the targeted 316 excess external dose from the building materials is 1.0 mSv/a. The dose contribution of the ICRP 115 317 (Tirmarche et al., 2010) and EU-BSS (European Union, 2014) recommended 300 Bq/kg average radon 318 concentration which corresponds to approximately 10 mSv/year effective dose (Paquet et al., 2017). Clearly, 319 the acceptable excess dose from the gamma exposure is significantly lower relative to the acceptable radon 320 exposure. The comparison of the calculated values is presented in Fig. 4. The trendline was placed with its 321 95% confidence bands to represent the uncertainty in an estimate of a curve or function based on limited or 322 noisy data. As confidence intervals are constructed and only refer to a single point, they are narrower (at 323 this point) than a confidence band which is supposed to hold simultaneously at many points (Härdle et al., 324 2004).



325

Fig. 4: Relationship between the calculated I-indexes and radium equivalent concentrations of studied
 residues with 95% confidence bands

328

329 However, certain samples do not fulfil the criteria of I-index. It has to be noted that both the Ra<sub>eq</sub> and the I-330 index are used for only screening of construction materials. Individually, none of the studied residues are 331 suitable for direct use as a 100% building material. This means the final I-index and the  $Ra_{eq}$  of any building 332 material that contains a proportion of these residues have to be calculated to incorporate the residues and 333 other components of any building material based on their total NOR contents (Sas et al., 2017; Schroeyers 334 et al., 2018). According to the databases, the aggregates and the cement used for concrete production have 335 significantly lower NOR contents resulting in a lower I-index. The mixing of the industrial residues with 336 other construction material components (aggregates/cements) dilutes the NOR contents and allows the final 337 NOR contents of the recycled construction materials to be under levels defined by different national 338 legislation (Sas et al., 2015a; Nuccetelli et al., 2017).

# 339 3.4 Radioactive equilibrium of U-238 and Th-232 decay chains of the studied industrial residues

341 The radioactive equilibrium state of U-238 decay chain was investigated. The U-238 content was obtained 342 from the Th-234 content (63.3 keV gamma line) of the studied samples. The Pb-210 activity concentrations 343 were obtained via the 46.5 keV gamma peak. To check the equilibrium condition in the chain, the Ra-226 344 activity concentrations were used as a reference value. However, in the case of the Th-232 chain, the most 345 significant possibility for disequilibrium may occur between the Th-232 and Ra-228 owing to the 5.74 years 346 half-life of Ra-228. Since direct measurement of Th-232 via gamma and alpha spectrometry was not 347 possible, its content was not determined. There was no information about the date when the residues were 348 generated so exact age of the samples was also not known. Owing to these facts, the disequilibrium state 349 was not investigated in the case of Th-232 chain. The disequilibrium state of U-238 chain related to Ra-226 350 content is presented in Fig. 5.





Fig. 5: Equilibrium state of U-238 decay chain related to Ra-226 content

353 The calculated values showed that the U-238 disappeared in the case APC and the RHA samples and in the 354 case of CKD 2 the U-238 content was 45.1% lower compared to Ra-226 activity concentration. The 355 disequilibrium state of RHA suggests that the uranium uptake or bioaccumulation by the rice from soil is 356 extremely low. Significant U-238 enhancement was found in the case of HWA and ISSA samples. Both 357 samples originate as a result of incineration of materials containing significant amounts of various organic compounds. Pb and the Po are relatively volatile elements in high-temperature combustion environments as 358 359 is the case for coal combustion, cement production, and incineration of wastes. In this study, all the samples 360 are generated from high-temperature treatment, except for red mud, which is produced by the Bayer-process. 361 Owing to the high temperature, the volatile radionuclides condensate on the fine ash particles (Ozden et al., 362 2018) which can result in elevated levels of Pb-210 in the fly ash type residues with decreased levels in the 363 bottom ash residues. The bottom ash residues, the BA, and both GGBFS and HWA samples had significantly 364 lower Pb-210 content compared to their Ra-226 content. The fine ash type residues had significantly 365 increased Pb-210 content compared to Ra-226 except for all FA samples. The Pb-210 content of all CKD samples was extremely high with 13-16 times higher Pb-210 content compared to the Ra-226 activity 366 367 concentration. This can be explained by the condensation of these isotopes in the kiln during the cooling 368 phase of operation and their subsequent release during preheating when the CKD accumulates these 369 isotopes. However, the exact mechanism should be investigated in more detail in future research projects. 370 The APC, ISSA and RHA samples had also increased Pb-210 content with a factor of 6.7, 2.5 and 2.1, 371 respectively, which fits with the conclusion based on the volatility of Pb and Po. The FA samples did not 372 show significant Pb-210 accumulation which is not unusual in the case of FA residues. Relatively low 373 enrichment factors can also be found in the literature (Ozden et al., 2018).

374

## **3.5** Correlation between NOR contents and chemical composition

375 The correlation between the NOR isotopes and the chemical composition results is presented in Fig. 6. In 376 the figure, the dark colours indicate the strong correlation between the NOR isotopes and the chemical 377 composition data. From the results it can be concluded that the Ra-226 concentration has a strong positive 378 correlation with the Al<sub>2</sub>O<sub>3</sub>, BaO and Fe<sub>2</sub>O<sub>3</sub> contents and strong negative correlation was found with the  $K_2O$ 379 content. In the case of Th-232, the Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> contents had strong positive 380 correlation with Th-232. The K-40 content showed strong correlation with the CaO and, of course, with the 381 K<sub>2</sub>O content. Strong negative correlation was found when compared with the BaO content. No correlation 382 with the  $P_2O_5$  content was observed for any of the NORs. Owing to the various industrial processes and the 383 results of the heat map, it can be concluded that the NOR isotope contents can be expected to correlate with 384 the oxides mentioned above.

385

	AI203	BaO	CaO	Cr203	CuO	Fe <sub>2</sub> 0 <sub>3</sub>	K <sub>2</sub> 0	MgO	MnO	Nazo	Nio	P205	bbo	sio2	so3	SrO	Tio2	V205	ZnO	ZrO2	Pearson Correlation (R)
Ra-226	0.82	0.71	-0.57	0.44	-0.39	0.69	-0.62	0.08	-0.12	0.27	0.36	-0.10	-0.57	0.05	-0.55	0.18	0.53	0.50	-0.38	0.54	-0.80-1.00 - very strong negative -0.60-0.79 - strong negative
Th-232	0.43	0.57	-0.41	0.84	-0.27	0.93	-0.49	-0.30	-0.32	0.75	0.52	-0.08	-0.23	-0.30	-0.34	-0.32	16.0	0.79	-0.23	0.86	-0.40-0.59 -moderate negative -0.20-0.39 - weak negative 0.00-0.19 - very weak positive 0.00-0.19 - very weak positive 0.20-0.39 - weak positive
K-40	-0.55	-0.64	0.70	-0.37	-0.01	-0.45	66'0	-0.22	-0.09	-0.28	-0.28	-0.11	0.42	-0.37	0.40	-0.30	-0.38	-0.28	0.03	-0.42	0.40-0.59 -moderate positive 0.60-0.79 - strong positive 0.80-1.00 - very strong positive

386

387 388

Fig. 6: Comparison between the naturally occurring radionuclide (NOR) isotopes and main chemical compositions illustrated on a heat-map type diagram

The purpose of the correlation analysis was to examine the possibility of using the information about the chemical composition as a source apportionment tool for NORs. This is useful considering the future recovery of materials from old landfills, lagoons, or illegal dumps where information on the original material is not available. Based on the Pearson correlation results, the strong correlation, either positive or negative, shows that the concept is promising to predict the level of the expected NOR content. However, the conclusion was drawn from 19 samples, so the extension of the dataset and further correlation analysis could strengthen the concept.

396

## **3.6 Radon emanation and massic exhalation features of the studied samples**

397 After the gamma spectrometry measurements, the massic radon exhalation of the samples was determined, 398 and their radon emanation factor was calculated with the obtained Ra-226 content. The obtained results are 399 illustrated in Fig. 7. The massic exhalation of the residues varied between 0.7 mBqkg<sup>-1</sup>h<sup>-1</sup> and 121.0 mBqkg<sup>-</sup> 400  $^{1}$  h<sup>-1</sup> with an average of 16.1 mBqkg<sup>-1</sup> h<sup>-1</sup>. The emanation factor was obtained between 0.6-8.6%. The average 401 of the emanation factor was 2.7%. This variation of the emanation factor of certain materials can be 402 explained by the different emanation coefficients, which depends on the characteristic of the material matrix 403 (Hegedus et al., 2016; Kovacs et al., 2016; Sas et al., 2015b). The results generally match those reported in 404 various publications (International Atomic Energy Agency, 2013). The two highest massic exhalation rates 405 were found in the case of the red mud samples which can be explained by their significantly higher Ra-226 406 content and their relatively high emanation coefficient. In the case of the fly ash samples, seven samples 407 were analysed from different origins. The calculated emanation factors were under 2% in all the seven cases 408 which fit well with the literature data (International Atomic Energy Agency, 2013; Sas et al., 2014).





The massic radon exhalation depends on the Ra-226 content and the emanation factor of the matrix
(International Atomic Energy Agency, 2013). That is why the belonging values and their correlation were
also investigated. The results of the comparison are illustrated in Fig. 8.





416 Fig. 8: Correlation between the Ra-226 and massic exhalation results and Ra-226 and emanation factor
417 with 95% confidence bands

However, during the analysis, the fitting of a linear trendline showed a weak correlation between the Ra-226 and the massic exhalation. The relatively low number of the samples does not make possible to state the relationship between these parameters explicitly. Furthermore, the emanation factor also influences the massic exhalation. Between the Ra-226 and the emanation factor no correlation was found which proves that they are independent parameters. Measuring the Ra-226 content by itself does not allow an assessment to verify whether the radon exhalation of building materials is increased or reduced.

## 424 4. Conclusions

From the results, there were no extraordinary NOR contents in the case of any of the samples. Compared with recently published NOR databases the values were close to the average values of the datasets. The highest NOR contents were found in the case of the red mud samples which emphasize the importance ofthe detemination of its NOR contents before reusing it for construction material purposes.

The radioactive equilibrium state in the decay chains fits well with the scientifically reported data. In the case of all the cement kiln dust, 13-16 times higher Pb-210 content compared to the Ra-226 activity concentration was observed which requires further investigation to find out the exact reason for the accumulation.

433 Significant positive correlation was found between the Ra-226 and the Al<sub>2</sub>O<sub>3</sub>, BaO and Fe<sub>2</sub>O<sub>3</sub> contents and 434 strong negative correlation were found with the K<sub>2</sub>O content. Strong negative correlation was observed with 435 the CaO content. Th-232 had a strong positive correlation with the Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and 436 ZrO<sub>2</sub> content. The K-40 content had a strong positive correlation with the CaO and the K<sub>2</sub>O content while 437 strong negative correlation was found with the BaO content.

The massic exhalation demonstrated a broad range. The highest values were found in the case of the red mud samples. The emanation coefficients were significantly lower in the case of the residues generated as a result of high-temperature processes. Compared with literature data (International Atomic Energy Agency, 2013), all the obtained emanation factors are regular.

These emanation coefficients, chemical correlations together with the radioactive equilibrium state could be used to source apportion materials found during the process of landfill mining and recovery of material for recycling, by, for example, mixing more active materials with less active materials to achieve an overall acceptable mix from the radioactivity point of view.

### 446 Acknowledgements

447 The project leading to this paper has received funding from the European Union's Horizon 2020 research 448 and innovation programme under the Marie Sklodowska-Curie grant agreement No 701932. R. Doherty's 449 time was also supported by the European Union's Horizon 2020 research and innovation programme under

- 450 the Marie Sklodowska-Curie grant agreement No 643087. The authors would also like to acknowledge
- 451 networking support by the COST Action TU1301 (www.norm4building.org).

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