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Research Paper

Migration of trace elements and radioisotopes to various fractions of solid wastes generated as a result of the sewage sludge incineration process

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ABSTRACT

The research was aimed at providing new knowledge in the field of chemical characteristics of solid waste generated in the process of combustion of sewage sludge in fluidized bed furnaces. The research material consisted of disposed fluidized beds (DFB), sewage sludge ash (SSA) and air pollution control residues (APC) from three Polish installations for the thermal treatment of sewage sludge. Natural radionuclides as well as anthropogenic isotope ^{137}Cs were determined in the tested materials and the migration of a wide spectrum of trace elements to various waste fractions generated in the process of sewage sludge combustion was examined. It was observed that both radioisotopes and most of the trace elements determined accumulate in SSA and DFB, while the APC fraction contains a much smaller amount of them. The exceptions are mercury and selenium, whose volatile compounds migrate to the exhaust gas dedusting system and accumulate in the APC fraction (up to 40 mg/kg and 13 mg/kg, respectively). A potential threat from the ^{226}Ra isotope in SSA is identified in the context of the management of this waste in the production of building materials because the typical activity of ^{226}Ra in SSA collected from areas with very low Ra content in natural environment exceeds 1.5–6 times the activity of this isotope in conventional cement mixtures. When managing SSA and DFB, special attention should be paid to the content of metalloids such as As, B and Se, due to the high content of mobile forms of these elements in the mentioned materials.

1. Introduction

The sewage sludge combustion process is one of the most dynamically developed sewage sludge management technologies in developed countries. The use of this technology brings a number of benefits, both in the economic sphere and in the aspect of environmental protection. Combustion of sewage sludge allows energy recovery and waste volume reduction by up to 90 % (Cieślik and Konieczka, 2017), and the resulting waste is, unlike sewage sludge, completely safe in terms of microbiology and chemically stabilized. The waste obtained through the aforementioned process is usually stored, although the secondary use of some of them is postulated, according to the circular economy doctrine introduced in the EU countries. Incineration of sewage sludge is usually carried out in installations using fluidized bed furnace technology, so this variant of the combustion process will be the subject of investigation in this work.

Waste generated during the combustion of sewage sludge in fluidized bed furnaces can be divided into three main fractions. The first is sewage sludge ash (SSA), which is a mineral residue of the combustion process. The second fraction is air pollution control (APC) residues, consisting of contaminated sorbents used at the exhaust gas treatment stage and fine particles not separated from the exhaust gas stream at the first set of filters (where SSA is separated). The last fraction is disposed fluidized bed (DFB) which is, by definition, mainly contaminated silica. The fluidized bed in fluidized bed furnaces is replaced regularly, usually once a year. A simplified diagram of the sewage sludge thermal treatment

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installation is presented in the drawing in Graphical Abstract.

Due to the majority share of SSA in the total mass of solid waste generated (usually 60–90 %), this fraction is the best studied in terms of chemical composition and physicochemical properties and is most often subjected to attempts at secondary management. Among the potential applications of SSA, the most frequently mentioned are the use of this material as a source of phosphorus and a raw material for the production of phosphorus fertilizers (Cieślik and Konieczka, 2017; Fang et al., 2018; Franz, 2008; Guedes et al., 2014; Herzel et al., 2016; Hu et al., 2023; Li et al., 2015; Xu et al., 2012; Yang et al., 2023), as a additive to building materials or as a replacement of cement (Baeza-Brotons et al., 2014; Danish and Ozbakkaloglu, 2022; Garcés et al., 2008; Haustein et al., 2022; Świerczek et al., 2021; Zdeb et al., 2022), as a sorbent of some gases and ions (Elouear et al., 2009; Fernández Ferreras et al., 2010; Gil-Lalaguna et al., 2015; Pan et al., 2003) or as an agent for land reclamation (Cieślik et al., 2015; Lin et al., 2018). In the case of implementing the proposed SSA management routes, it is crucial to have in-depth knowledge of the content of potentially hazardous substances in this material in order to be able to estimate the environmental risk associated with taking such actions. The main threats related to the development of SSA include the high content of certain heavy metals (in particular Fe, Pb, Cu, Zn, Cr and Ni) (Franz, 2008; Herzel et al., 2016; Kępys et al., 2021; Pazos et al., 2010). Moreover, it has been proven that some metals contained in SSA (e.g. Cu or Zn) may have significant mobility and susceptibility to leaching (Xiao et al., 2015). There are also studies on the determination of the content of rare earth elements and trace d-block metals in SSA (Jackson et al., 2010; Krüger et al., 2014; Smol et al., 2020; Zhang et al., 2002). Research conducted in Europe after the Chernobyl disaster (1986) and in Japan after the accident at the Fukushima Dai-Ichi nuclear power plant in 2011 also proved that both sewage sludge and SSA may contain significant amounts of particularly problematic, anthropogenic radioisotopes ^{137}Cs and ^{90}Sr with long half-lives (30 and 29 years respectively) (Fischer and Yokoo, 2014; Kamei-Ishikawa et al., 2013b; Kozai et al., 2015; Tsushima et al., 2013). Moreover, ^{137}Cs isotope are considered partly mobile in various types of waste (Matsuzuru et al., 1977; Ogawa et al., 2021). Therefore, the problem of the mobility of radioisotopes should not be considered in isolation from the mobility of a wide range of elements, which can cause serious threats to the environment. To the authors' knowledge, no research has been conducted so far that would include a broad analysis of the content of natural radioisotopes in SSA, the presence of which may, however, be significant due to the research-proven content of uranium and thorium in this material, which is typically at the level of several mg/kg (Smol et al., 2020). Therefore, the presented concept is considered a significant novelty.

Moreover, APC and DFB fractions have not been the subject of extensive research so far, and their chemical characteristics are poorly known. Literature reports are suggesting a very low activity concentration of ^{137}Cs and a number of heavy metals (most often in the form of chlorides) in the exhaust stream resulting from the combustion of sewage sludge in fluidized bed furnaces (Lee et al., 1993; Tsushima, 2017). Taking into account the above-mentioned studies, it can be hypothesized that the content of metals and radioisotopes in the APC fraction should be trace. It should be noted, that the cited studies (Lee et al., 1993) were conducted on a very limited scope (only five elements tested) and did not include the analysis of highly volatile species (e.g. Hg species). According to the current state of knowledge, APC and DFB fractions are considered difficult to recycle and are subject to landfill. APC is disposed of in hazardous waste landfills, while DFB is disposed of in non-hazardous waste landfills.

The aim of this work is to supplement and gain new knowledge on the chemical characteristics of solid waste resulting from the incineration of sewage sludge in fluidized bed furnaces by conducting a broad analysis of the content of trace elements and the activity of natural and artificial radioisotopes in all three waste fractions (SSA, APC and DFB). Based on the obtained analysis results, the degree of migration of individual tested chemical entities to specific waste fractions is assessed, and on this basis (also taking into account their mobility) the potential, possibilities and limitations related to the management of the mentioned materials are estimated.

2. Methodology

2.1. Materials

The research material consists of samples of three waste fractions (SSA, APC and DFB) generated in the process of combustion of sewage sludge in fluidized bed furnaces, collected in 2014–2021 from three different installations for the thermal processing of sewage sludge located in Poland (Gdańsk Wschód, GOŚ Łódź and GOŚ Dębogórze), which is dictated the fact that the content of determined species may change significantly over the years These installations collect sewage sludge from municipal sewage treatment plants located in large urban agglomerations. Estimated daily sewage flows are GOŚ Łódź – 210,000 m^3/d, Gdańsk Wschód – 95,000 m^3/d, GOŚ Dębogórze – 55,000 m^3/d. The total numbers of samples are 16 samples of SSA, 11 samples of APC and 5 samples of DFB.

2.2. Radioisotopes activity analysis

To determine the activity concentration of radioisotopes in the tested materials, the gamma-ray spectrometry technique was used using two spectrometers equipped with semiconductor germanium detectors (HPGe type XTRa) with relative efficiencies of 30 % and 40 %. Energy calibration was performed using a certified source containing a mixture of gamma radioisotopes with emission energies covering the range from 60 to 1836 keV. Due to the lack of the radioactive standard source with geometry appropriate to the described application, it was decided not to perform efficiency calibration using a standard source with a specific geometry. Instead, the measurement geometry was simulated in Canberra's Laboratory Sourceless Calibration Software (LabSOCS). The LabSOCS program (together with a characterized detector) is used when it is impossible to provide a measurement geometry that would fully correspond to the measured samples (density, matrix, etc.). This software is able to mathematically simulate (create) a performance curve for a given type of sample and a given measurement geometry. Previous research proves that the LabSOCS software is a very good replacement for classic efficiency calibration using radioactive sources with specific geometry, and the results obtained using both methodologies are characterized by low discrepancies (4–10 %). (Bronson, 2003; Shyti, 2019; Stanić et al., 2019). Measurements of the activity concentration of radioisotopes in studied samples were carried out in closed, polypropylene containers in the shape of a truncated cone with a volume of 125 cm^3. Each time, from about 50 g to about 150 g of the sample was used for measurement (depending on the density of the tested material, which corresponded to filling the container to about 100 cm^3). The time of each measurement was 80,000 s. The following densities of the tested materials were assumed to simulate the measurement geometry in the LabSOCS program: 0.50 g/cm^3 for APC, 1.06 g/cm^3 for SSA and 1.50 g/cm^3 for DFB. The density of the materials entered into the software was determined by the measurement of the bulk density of tested materials by measuring the mass of material contained in a container of a given volume. The average bulk density values calculated for every fraction of tested waste were used. Analysis reports were generated using Genie2000 software, with the measurement uncertainty being one standard deviation (2.7–24 Bq/kg ^{40}K; 0.16–0.86 Bq/kg ^{137}Cs; 1.9–7.6 Bq/kg ^{226}Ra; 2.5–30 Bq/kg ^{210}Pb and 0.73–3.1 Bq/kg ^{228}Ac).

2.3. Trace elements analysis

As part of the presented research, the total content of selected trace elements in SSA, APC and DFB was determined, as well as the share of

individual fractions of these elements, separated on the basis of their mobility in the environment, in SSA and DFB. In order to determine the total content of elements, the samples were digested in aqua regia (10 ml of aqua regia per 0.5 g of sample) using microwave-assisted digestion (200 °C, 35 min). After that 1 ml of a sample was evaporated (80 °C, 3 h) and diluted in 10 ml of 2 % HNO_3 solution. To dissolve all residues after evaporation all samples (sealed in teflon containers) were treated in ultrasound bath for 20 min. and heated at 80 °C for another 20 min. Metal fractionation was performed using a modified BCR sequential extraction model (Rauret et al., 1999). The content of trace elements in extracts and solutions obtained as a result of digestion was determined using the Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) model, 7700 Agilent Technologies. In the case of mercury, fractionation of this element was waived (due to the low content of the analyte in the samples and the possibility of its loss by evaporation), and the total mercury content was determined using the Cold-Vapor Atomic Absorption Spectrometry (CV-AAS) technique. This analytical technique does not require a prior sample digestion. For this part of the analysis, approx. 10 mg of APC samples and 50 mg of SSA and DFB samples were put into special, previously roasted measuring cells. All reagents used for samples and calibration preparation were ICP purity. The validation parameters are presented in Table S1 (Supplementary Materials). The uncertainty of the determination of the elements (as coefficients of variation from four measurements) was estimated in the range of 0.30–1.7 % depending on the element in the case of ICP-MS analysis and in the range of 0.45–10 % for Hg determination using the CV-AAS technique.

3. Results and discussion

3.1. Radioisotopes

The content of radionuclides in tested materials was presented in Figs. 1 and 2. For analytical results presentation, the box-plot charts were used in which the minimum and maximum value of the variable is presented, as well as the median value (horizontal line in the box) and average value (the „X" symbol in the box).

The only anthropogenic radionuclide registered in the gamma radiation spectra of the tested material samples is an isotope ^{137}Cs. Activity concentration of ^{137}Cs in solid residues from the process of thermal utilization of sewage sludge are shown in Fig. 1. Based on the available data on environmental contamination in Poland with the ^{137}Cs isotope, it can be concluded that the sewage treatment plants, from which the research material came, are located in areas slightly contaminated with ^{137}Cs (Isajenko et al., 2022) and according to predictions, samples of the tested materials are characterized by trace activity concentration of this isotope, of the order of several Bq/kg. Based on the analysis of the obtained results, it is concluded that the vast majority of radiocesium contained in sewage sludge during combustion goes to the sewage sludge ash (SSA) fraction. The DFB fraction was characterized by approximately 1.5–2 times (depending on the sewage treatment plant) lower activity concentration of ^{137}Cs, while in each case an unmeasurable activity of this isotope was recorded in the APC fraction. The explanation for this phenomenon seems to be known. It has already been proven that only about 10 % of cesium entering sewage treatment plants is retained in the form of sewage sludge (with almost 100 % subsequent conversion to SSA during combustion) (Kamei-Ishikawa et al., 2013a). This state of affairs allows us to conclude that the cesium contained in SSA does not pose any threat in the context of the mentioned waste management methods if the sewage sludge being combisted comes from areas slightly or moderately contaminated with the ^{137}Cs isotope.

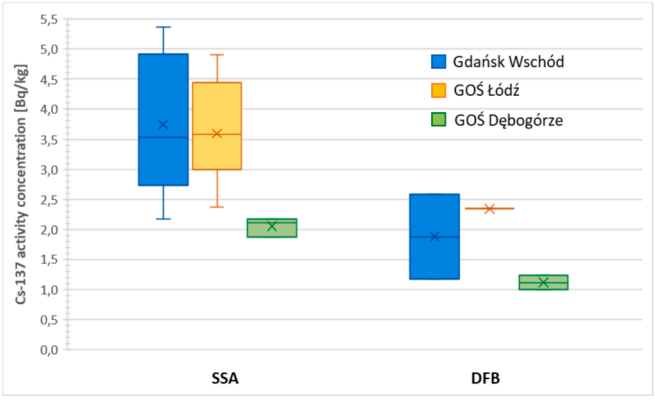

Fig. 1. Activity concentration of ^{137}Cs in the tested samples of sewage sludge ash (SSA) and disposed fluidized bed (DFB) according to the origin of the samples (sampling places).

Natural radioisotopes are responsible for the vast majority of the activity of the tested waste materials (Fig. 2A–C). The average activity concentration of the ^{40}K isotope in the samples were: 336–429 Bq/kg in SSA, 10–91 Bq/kg in APC and 149–287 Bq/kg in DFB. The activity concentration distribution of ^{40}K according to the type of waste is therefore similar to the ^{137}Cs, which can be justified by the similar chemical properties of potassium and cesium compounds. The solubility, oxidation–reduction potential, alkaline-acid properties and melting and boiling points of the majority of cesium salts are very similar in comparison with their potassium equivalents. Due to these reasons, the behavior of cesium and potassium which are present in wastewater is expected to be similar during the wastewater treatment as well as sewage sludge combustion process. Uranium and thorium and isotopes from their series are not intentionally used in households or on a large scale in industry. Therefore, the presence of these elements and isotopes from their radioactive series in waste from sewage sludge incineration is natural and their amount may be correlated with the radiochemical characteristics of the surrounding environment. The migration of radioisotopes that are elements of the natural radioactive series: the uranium-radium series (^{226}Ra, ^{210}Pb) and the thorium series (^{228}Ac) turned out to be different depending on the sewage treatment plant from which the tested materials came. For waste from the "Gdańsk Wschód" sewage treatment plant (Fig. 2A), the highest activity concentration of the mentioned radioisotopes was recorded in DFB samples, while in the case of waste from other treatment plants (Fig. 2B and C), the highest activity concentration of isotopes from uranium and thorium series was characterized by the SSA fraction. However, in each case, the activity concentration of the studied isotopes in the APC fraction was the lowest of all three waste fractions tested. An important observation noted is the fact that the tested materials were characterized by relatively low variability in activity concentration of studied isotopes within each sampling site (as evidenced by the close distances between individual quartiles in box plots), which indicates a relatively stable radionuclides content in the waste over time. 2014–2021 (sampling period).

It should be noted that in sewage sludge ash and in the case of DFB samples originating from the Gdańsk Wschód and GOŚ Łódź sewage treatment plants, the typical activity concentration of the ^{226}Ra and ^{228}Ac isotopes is 3.2–5.2 times higher and 1.9–2.2 times higher, respectively, than the typical activity concentration of these isotopes in the soil in the surrounding areas (Table 1) (Isajenko et al., 2012). Moreover, the activity concentration of the ^{226}Ra isotope in the tested SSA samples is 1.5–6 times higher than the activity concentration of this isotope in typical, conventional cement mixtures (19–45 Bq/kg). (Madruga et al., 2019; Papastefanou et al., 2005; Trevisi et al., 2012). This means that if SSA is considered as a replacement for conventional cement for the production of concrete, the obtained building material will be characterized by higher activity of the ^{226}Ra isotope compared to its conventional counterparts. The ^{226}Ra isotope is a precursor of the ^{222}Rn isotope (product of alpha decay of ^{226}Ra), which is one of the common and dangerous indoor air pollutants. Therefore, the use of SSA in construction materials as the replacement for cement (Danish and Ozbakkaloglu, 2022; Świerczek et al., 2021) for the production of

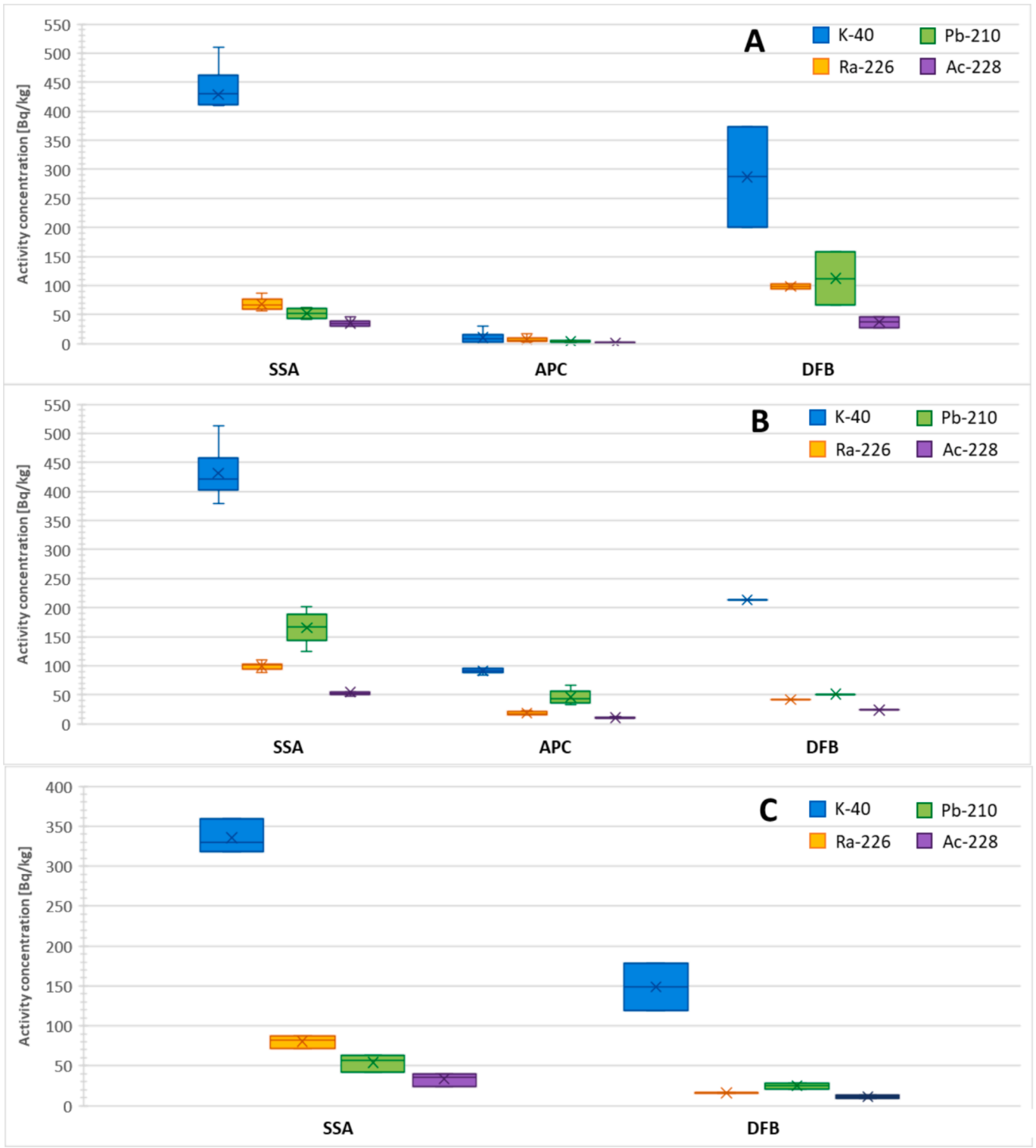

Fig. 2. Activity concentration of natural radioisotopes in samples of sewage sludge ash (SSA), air pollution control residues (APC) and disposed fluidized beds (DFB) from the following sewage sludge thermal treatment plants: Gdańsk Wschód (A), GOŚ Łódź (B), GOŚ Dębogórze (C).

buildings could potentially lead to an increase in the concentration of the ^{222}Rn isotope in indoor air and thus pose a potential threat to health through a harmful effect on the lung epithelium of living organisms (Kim and Yu, 2014). It should be noted that the research presented in this work concerns ashes generated from sewage sludge produced in northern and central Poland. The natural environment (including soil) in these areas is characterized by anomalously low concentrations of uranium (and therefore radium) compared to different parts of Europe (Joint Research Centre, 2019). Therefore, it is highly probable that ashes from thermal treatment of sewage sludge generated in other countries where the natural environment is richer in chemical species included in the ^{238}U radioactive series may contain much higher amounts of radium. In such a case, potential building materials doped with SSA may have a significantly higher ^{226}Ra content. The Activity Concentration Index

Table 1
Comparison of the activity concentration of ^{226}Ra and ^{228}Ac in the tested waste materials and in the soil. Average values for a given category of samples were used to calculate the ratios.

Gdańsk Wschód	Soil(Pomeranian Voivodeship) [Bq/kg]	SSA/Soil ratio	APC/Soil ratio	DFB/Soil ratio
^{226}Ra	19	3.6	0.35	5.2
^{228}Ac	17	2.1	<0.12	2.2
GOŚ Łódź	**Soil(Łódź Voivodeship) [Bq/kg]**	**SSA/Soil ratio**	**APC/Soil ratio**	**DFB/Soil ratio**
^{226}Ra	13	7.7	1.4	3.2
^{228}Ac	13	4.3	0.80	1.9
GOŚ Dębogórze	**Soil(Pomeranian Voivodeship) [Bq/kg]**	**SSA/Soil ratio**	**APC/Soil ratio**	**DFB/Soil ratio**
^{226}Ra	19	4.3	–	0.85
^{228}Ac	17	2.0	–	0.69

(ACI) for construction materials is defined as ACI = C_{Ra226}/300 Bq/kg + C_{Th232}/200 Bq/kg + C_{K40}/3 000 Bq/kg, where C is the activity concentration of radionuclide [Bq/kg]. According to the European directive Euratom 2013/59 in building materials, the Activity Concentration Index (ACI) must be <1 to be suitable for their use in construction. The possibility of using SSA as a replacement for cement, based on ACI, cannot be estimated because it applies to building materials and not their individual components while in this case, such a component would be SSA. However, it is clearly visible that using SSA from tested Polish thermal treatment plants as a replacement for cement would not lead to exceeding the ACI limit. Moreover, a vital issue is the law limit of $_{222}$Rn in indoor air. The same directive (European directive Euratom 2013/59) sets a limit of $_{222}$Rn in indoor air at 300 Bq/m^3. The correlation between the $_{226}$Ra in SSA and $_{222}$Rn in indoor air in the hypothetical buildings constructed using SSA as a cement replacement is difficult to estimate. It depends on many variables for instance the percentage of cement replaced by SSA and wall density and thickness. Taking into account the above, according to the authors, the problem of potential contamination of indoor air with the ^{222}Rn isotope in buildings constructed using building materials doped with SSA requires thorough analysis as part of future scientific research.

In order to check the correlation between the content of ^{238}U and ^{232}Th, i.e. two main, potentially dangerous natural radioisotopes (excluding ^{40}K with low radiotoxicity), an analysis of the Pearson correlation coefficients of the tested isotopes derived from the isotopes ^{238}U (^{226}Ra and ^{210}Pb) and ^{232}Th (^{228}Ac) was performed. A quite strong correlation was found between the ^{238}U decay products and the ^{232}Th decay product in the case of SSA ($|r| > 0.71$) and a very strong correlation in the case of DFB ($|r| > 0.90$) (Table 2). The analysis of Pearson's correlation coefficients in APC samples was abandoned due to the very low activities of the tested isotopes in this waste fraction and, consequently, the high measurement uncertainty. Based on the analysis of the results, it was found that the content of uranium and thorium in the tested samples of waste materials was correlated.

3.2. Trace elements

Table 3 presents the total content of the tested chemical elements in all types of solid waste generated in the process of combustion of sewage sludge in fluidized bed furnaces. The vast majority of the elements determined during sewage sludge incineration accumulate in the sewage sludge ash (SSA) fraction. Some elements (Se and Hg) are largely transferred to the APC waste fraction during the combustion of sewage sludge. This is because these elements easily form a number of highly volatile (under combustion conditions) chemical species, and therefore to a large extent, they end up in the exhaust gas stream. Particular attention should be paid to the fact that the APC fraction from the Gdańsk Wschód thermal treatment plant generally contains fewer tested elements compared to the APC fraction from the Łódź GOŚ station. This dependence may result from technological differences, a different type of sorbent used in the exhaust gas treatment system and a different amount of sorbent used. This observation allows to formulate the conclusion that the chemical composition of the APC fraction may be significantly variable depending on the flue gas treatment technology used and should be individually examined when developing possible ways of managing this waste, although APC should always be treated as hazardous waste due to its very high mercury content (reaching up to 40 mg/kg in the studied case). It is observed, that in the majority of cases, the content of selected elements in SSA oscillates around the concentration of a given element in DFB. However, in the case of Ag, Cd and Pb the content of these elements could vary in SSA compared to DFB and it seems to depend on the sampling place. In some rare cases (Ba, Bi), DFB is characterized by a higher content of mentioned elements in comparison with SSA independently on the sampling place (on average 1.5–5.7 times and 2.6–5.8 times, respectively). It should be remembered that the fluidized bed in the installations discussed is replaced relatively rarely (usually once a year) and therefore comes into contact with a significant amount of sewage sludge and ash during use. This is a possible explanation for the similar chemical composition of both waste fractions.

It should be noted that the chemical composition of SSA is highly variable (Fig. 3). Very high values of the coefficient of variation CV were obtained, among others, for highly toxic elements such as Sb, Pb, and Cd. Strong variability of the content of toxic elements in SSA may constitute a serious technological challenge in the context of secondary use of this waste fraction, due to the environmental threat that is difficult to predict without prior appropriate analyses.

The results of fractionation of the tested elements constituting SSA and DFB are presented in Fig. 4. However, fractionation of metals in APC was abandoned due to the high content of alkaline sorbents in this waste fraction, as the BCR sequential extraction technique is not suitable for highly alkaline matrices. Similar results were obtained for the relative content of individual fractions of the tested elements in SSA and in DFB, but it was observed that some elements, such as Rb, Sr, V, Ag, Cd, As, B and Br, may be to some extent more strongly immobilized in DFB than in SSA. In general, metalloids and non-metallic elements (Se, As, B and Br) were characterized by the highest mobility in the tested waste materials, however, it should be noted that the content of these elements in the tested DFB and SSA samples does not differ from the typical concentrations of these elements in the soil (Shacklette and Goerngen, 1984). Therefore, even with the content of significant amounts of mobile forms, the environmental risk associated with the development of DFB and SSA should be low. However, the possibility of the presence of increased concentrations of metalloids in some types of industrial wastewater should be taken into account. SSA obtained by combustion of industrial or municipal sewage containing industrial sewage rich in metalloids may contain much higher amounts of these elements. This possibility should be taken into account when developing SSA management methods, taking into account the high mobility of the mentioned elements proven in the presented research. Fractionation results of elements such as Au, Cs, In, Sn and Tl are not presented in Fig. 4, due to the concentrations below the limit of quantification (<LOQ, see Table S1 in Supplementary Materials) of the mentioned elements in fractions F1, F2 and F3. These elements were determined only in the F4 fraction, which suggests their very low mobility in both SSA and DFB. A particularly

Table 2
Table of Pearson correlation coefficients |r| between the content of tested natural radioisotopes.

SSA	^{226}Ra	^{210}Pb	^{228}Ac	**DFB**	^{226}Ra	^{210}Pb	^{228}Ac
^{226}Ra	1.00	0.77	0.72	^{226}Ra	1.00	0.84	0.91
^{210}Pb	0.77	1.00	0.74	^{210}Pb	0.84	1.00	0.98
^{228}Ac	0.72	0.74	1.00	^{228}Ac	0.91	0.98	1.00

Table 3
The total content of selected trace elements in the tested waste fractions, taking into account the location of the sewage sludge thermal treatment plant. Results presented as average value (range).

Element [mg/kg]	*Gdańsk Wschód*			*GOŚ Łódź*			*GOŚ Dębogórze*	
	SSA	APC	DFB	SSA	APC	DFB	SSA	DFB
Ag	10.0(0.44–16.9)	<0.40 (<0.060–1.5)	21(11–30)	11.8(2.7–21.8)	<3.2(<0.060–6.7)	<0.060	20.8(4.2–37.0)	13(6.4–20)
As	5.1(3.7–7.0)	<0.21 (<0.16–0.32)	5.4(0.30–11)	5.9(2.7–7.1)	2.2(1.5–3.5)	0.47	2.7(0.7–4.6)	0.67(0.40–0.87)
Au	0.71(0.41–1.0)	<0.15	<0.93 (<0.15–1.7)	0.81(0.35–1.1)	<0.25 (<0.15–0.39)	<0.15	0.63(0.41–1.0)	0.40(0.35–0.45)
B	23(16–33)	5.5(1.4–13)	22(4.3–40)	29(24–41)	6.4(3.6–10)	1.6	16(3.6–24)	7.9(1.6–14)
Ba	169(52–449)	22(4.0–59)	254(137–370)	101(69–139)	8.1(1.8–11)	571	208(113–305)	920(683–1156)
Bi	5.3(2.7–7.4)	<0.015	14(13–15)	13(5.6–19)	3.1(2.2–3.9)	35	10(5.4–17)	58(54–62)
Br	<0.90(<0.48–2.0)	<2.5(<0.48–9.4)	<1.2(<0.48–1.9)	1.9(0.88–3.2)	<1.4(<0.48–3.7)	<0.48	0.79(0.65–1.0)	0.63 (<0.48–0.78)
Cd	2.4(1.0–8.2)	<0.0063	1.6(0.88–2.3)	3.7(1.7–6.6)	<0.0063	2.8	1.2(1.2–1.3)	3.0(2.6–3.4)
Co	5.1(3.7–6.8)	<0.040 (<0.0064–0.24)	5.5(1.9–9.0)	12(9.0–19)	2.2(1.7–3.6)	3.6	3.4(3.1–3.9)	3.6(3.0–4.1)
Cs	0.85(0.61–1.6)	<0.028	0.38(0.21–0.56)	1.1(0.75–1.5)	0.14 (<0.028–0.30)	0.38	0.42 (0.36–0.53)	<0.028
Cr	95(82–117)	3.6(0.77–13)	73(60–86)	1046(451–1434)	133(70–200)	632	72(45–94)	70(62–78)
Ga	4.3(2.7–7.1)	<0.058	2.4(1.1–3.6)	4.6(2.7–9.9)	0.65(0.43–1.1)	1.7	2.9(1.6–4.3)	1.5(1.4–1.6)
Hg	0.13(0.058–0.25)	4.6(0.83–12)	0.069 (0.00057–0.14)	0.16(0.056–0.23)	21(6.4–40)	0.00053	0.13 (0.098–0.15)	0.055 (0.0085–0.10)
In	<0.42 (<0.012–0.90)	<0.012	0.41(0.33–0.48)	0.25 (<0.012–0.51)	<0.012	0.69	0.36 (0.24–0.44)	1.8(1.7–1.9)
Pb	231(86–483)	0.62(0.28–1.1)	55(45–65)	111(74–131)	19(6.6–26)	36	60(32–79)	150(88–213)
Rb	14(11–25)	<0.49 (<0.012–1.0)	8.4(4.1–13)	16(10–23)	3.3(2.4–4.9)	5.4	7.3(6.3–9.2)	2.6(1.7–3.6)
Rh	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028
Sb	2.2(0.10–4.2)	<0.27(<0.10–1.1)	1.8(0.38–4.1)	20(5.4–32)	4.4(0.10–12)	<0.10	2.0(1.0–2.9)	0.59(0.47–0.71)
Se	1.8(1.4–2.2)	2.7(0.4–7.1)	<1.5 (<0.078–2.9)	2.2(1.6–3.3)	9.8(6.9–13)	<0.078	1.3(0.4–2.1)	0.36(0.35–0.36)
Sn	76(0.20–185)	0.61(<0.011–4.1)	48(42–54)	49(9.5–87)	4.6(<0.011–11)	–	42(24–70)	102(98–105)
Sr	457(426–500)	44(5.6–99)	304(147–461)	507(428–570)	75(35–96)	268	355(118–476)	407(355–459)
Te	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Ti	753(411–1125)	35(5.5–115)	592(285–899)	383(283–671)	415(101–592)	947	702(513–956)	290(289–291)
Tl	<0.045 (<0.0060–0.28)	<0.0060	0.11 (<0.0060–0.23)	<0.12 (<0.0060–0.25)	<0.21 (<0.0060–0.27)	<0.0060	<0.0060	<0.0060
V	16(12–27)	1.1(0.30–4.1)	12(2.9–21)	25(15–37)	4.4(3.0–7.6)	6.4	8.2(6.1–11)	4.6(3.9–5.3)

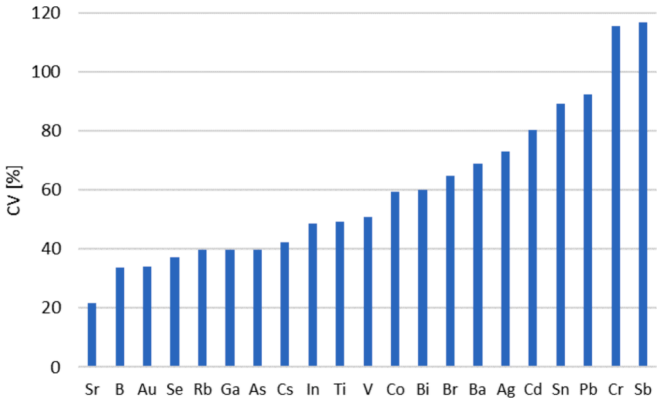

Fig. 3. Coefficient of variation diagram (CV) for the content of individual elements in the tested samples of sewage sludge ash (SSA).

important observation is the fact of low mobility of cesium, which is important in the context of assessing the risk associated with the management of SSA contaminated with the ^{137}Cs isotope, especially those generated in sewage treatment plants operating in areas with a high activity concentration of ^{137}Cs in the environment. For technical reasons, fractionation of radioisotopes using the BCR sequential extraction technique is complicated and often even impossible. The obtained metal fractionation results may therefore be helpful in trying to assess the mobility of some identified natural radioisotopes. As discussed in the previous section, the ^{226}Ra isotope was identified as one of the most hazardous in the context of SSA development as an additive to construction materials. This isotope may also pose a threat when using SSA as a phosphorus fertilizer or as a recultivation agent, due to the potential possibility of changing the soil chemistry in terms of radiochemistry. Due to the similarity of the chemical properties of radium and barium, the mobility of ^{226}Ra should be similar to that of barium. This element occurs in SSA and DFB almost exclusively in the form of the immobile fraction F4 and with a few percent share of the reducible fraction (F2). Therefore, probably ^{226}Ra also occurs in the discussed waste materials, mostly in immobilized forms, which significantly reduces the environmental risk associated with the management of SSA and DFB in ways in which these materials would come into contact with the soil environment.

4. Conclusion

As part of the presented research, a broad analysis of the chemical composition of all three fractions of solid waste generated in the process of thermal utilization of sewage sludge in fluidized bed furnaces was made: disposed fluidized bed (DFB), sewage sludge ash (SSA) and air pollution control residues (APC). The research proved that the APC fraction is characterized by the lowest radioactivity (from both natural radioisotopes and the ^{137}Cs isotope) compared to the DFB and SSA fractions. It was observed that the SSA fraction may be characterized by the activity concentration of the ^{226}Ra isotope several times higher than the typical activity concentration of this isotope in soil, although this isotope occurs in both SSA and DFB, probably mainly in immobile forms. For this reason, a potential threat from ^{226}Ra contained in SSA was identified only when this material is used as an additive to building

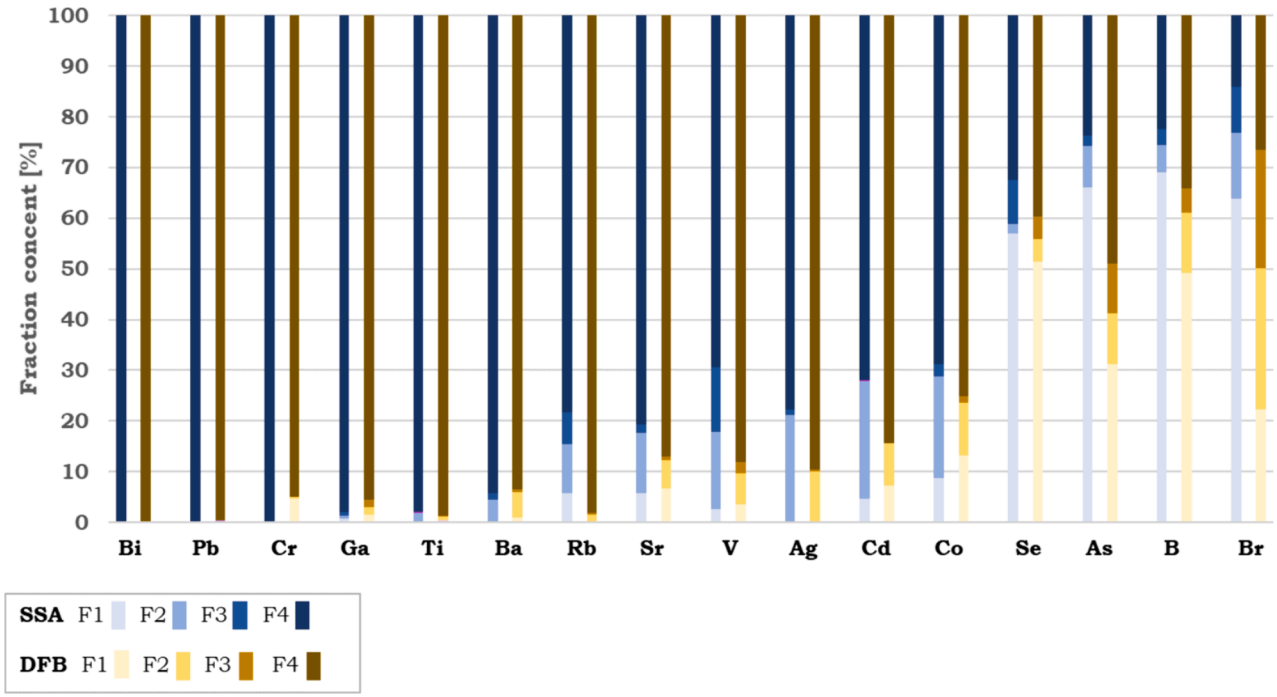

Fig. 4. Content of the fraction of the tested elements in sewage sludge ash (SSA) and disposed fluidized bed (DFB), determined using the BCR sequential extraction technique.

materials (due to the possibility of increasing the concentration of ^{222}Rn in indoor air). The authors draw attention to the need to measure the activity concentration of ^{226}Ra in SSA obtained from sewage sludge collected in areas with a higher content of uranium in the soil than in Poland and to perform appropriate research to verify the hypothesis about the possible threat from this radioisotope using SSA in the production of building materials. As in the case of radioisotopes, the vast majority of the tested trace metals and metalloids contained in sewage sludge remain in the SSA fraction during combustion or settle on a fluidized bed (DFB). The exceptions are highly volatile mercury and selenium compounds, which during the combustion of sewage sludge enter the exhaust gas stream and settle on sorbents, thus causing a relatively high content of the mentioned elements in the APC fraction. Fractionation of the tested elements in DFB and SSA using the BCR sequential extraction technique led to the conclusion that metalloids (As, B, Se) and Br are characterized by high mobility in the tested materials. This phenomenon should be taken into account when developing methods for the management of DFB and SSA when there is a suspicion that sewage sludge subjected to incineration may have contained increased amounts of the above-mentioned elements.

CRediT authorship contribution statement

Oskar Ronda: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Bartłomiej Michał Cieślik:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Barbara Piotrowska:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Krzysztof Isajenko:** Writing – review & editing, Supervision, Resources, Methodology. **Satoki Okabayashi:** Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Koichi Chiba:** Writing – review & editing, Supervision, Resources. **Motohiro Tsuboi:** Writing – review & editing, Validation, Supervision, Resources, Methodology. **Justyna Płotka-Wasylka:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

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References

Baeza-Brotons, F., Garcés, P., Payá, J., Saval, J.M., 2014. Portland cement systems with addition of sewage sludge ash. Application in concretes for the manufacture of blocks. J. Clean. Prod. 82, 112–124. https://doi.org/10.1016/j.jclepro.2014.06.072.

Bronson, F.L., 2003. Validation of the accuracy of the LabSOCS software for mathematical efficiency calibration of Ge detectors for typical laboratory samples. J. Radioanal. Nucl. Chem. 255, 137–141. https://doi.org/10.1023/A:1022248318741.

Cieślik, B., Konieczka, P., 2017. A review of phosphorus recovery methods at various steps of wastewater treatment and sewage sludge management. The concept of "no solid waste generation" and analytical methods. J. Clean Prod. 142, 1728–1740. https://doi.org/10.1016/j.jclepro.2016.11.116.

Cieślik, B.M., Namieśnik, J., Konieczka, P., 2015. Review of sewage sludge management: standards, regulations and analytical methods. J. Clean. Prod. 90, 1–15. https://doi.org/10.1016/j.jclepro.2014.11.031.
Danish, A., Ozbakkaloglu, T., 2022. Greener cementitious composites incorporating sewage sludge ash as cement replacement: a review of progress, potentials, and future prospects. J Clean Prod 371, 133364. https://doi.org/10.1016/j.jclepro.2022.133364.
Elouear, Z., Bouzid, J., Boujelben, N., 2009. Removal of nickel and cadmium from aqueous solutions by sewage sludge ash: study in single and binary systems. Environ Technol 30, 561–570. https://doi.org/10.1080/09593330902824940.
Fang, L., Li, J., Donatello, S., Cheeseman, C.R., Wang, Q., Poon, C.S., Tsang, D.C.W., 2018. Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation. Chem. Eng. J. 348, 74–83. https://doi.org/10.1016/j.cej.2018.04.201.
Fernández Ferreras, J., García Posadas, H., Rico Gutierrez, J.L., Renedo Omaechevarría, J., 2010. Use of ash from sewage sludge in the preparation of desulfurant sorbents. Int. J. Chem. React. Eng. 8 https://doi.org/10.2202/1542-6580.2102.
Fischer, H.W., Yokoo, Y., 2014. Preliminary comparison of radioisotope concentration in sewage sludge after the fukushima and chernobyl accidents. Energy Proc. 59, 256–262. https://doi.org/10.1016/j.egypro.2014.10.375.
Franz, M., 2008. Phosphate fertilizer from sewage sludge ash (SSA). Waste Manag. 28, 1809–1818. https://doi.org/10.1016/j.wasman.2007.08.011.
Garcés, P., Pérez Carrión, M., García-Alcocel, E., Payá, J., Monzó, J., Borrachero, M.V., 2008. Mechanical and physical properties of cement blended with sewage sludge ash. Waste Manag. 28, 2495–2502. https://doi.org/10.1016/j.wasman.2008.02.019.
Gil-Lalaguna, N., Sánchez, J.L., Murillo, M.B., Gea, G., 2015. Use of sewage sludge combustion ash and gasification ash for high-temperature desulphurization of different gas streams. Fuel 141, 99–108. https://doi.org/10.1016/j.fuel.2014.10.036.
Guedes, P., Couto, N., Ottosen, L.M., Ribeiro, A.B., 2014. Phosphorus recovery from sewage sludge ash through an electrodialytic process. Waste Manag. 34, 886–892. https://doi.org/10.1016/j.wasman.2014.02.021.
Haustein, E., Kuryłowicz-Cudowska, A., Łuczkiewicz, A., Fudala-Książek, S., Cieślik, B. M., 2022. Influence of cement replacement with Sewage Sludge Ash (SSA) on the heat of hydration of cement mortar. Materials 15, 1547. https://doi.org/10.3390/ma15041547.
Herzel, H., Krüger, O., Hermann, L., Adam, C., 2016. Sewage sludge ash — a promising secondary phosphorus source for fertilizer production. Sci. Total Environ. 542, 1136–1143. https://doi.org/10.1016/j.scitotenv.2015.08.059.
Hu, S., Yi, K., Li, C., Ma, S., Liu, J., Yang, W., 2023. Efficient and selective recovery of iron phosphate from the leachate of incinerated sewage sludge ash by thermally induced precipitation. Water Res. 238, 120024 https://doi.org/10.1016/j.watres.2023.120024.
Isajenko, K., Piotrowska, B., Stawarz, O., Wojtkowski, K., 2022. https://www.gios.gov.pl/images/dokumenty/pms/monitoring_promieniowania_jonizujscego/raport_cez_2021.pdf (Access: 26.09.2023) [WWW Document]. Monitoring promieniowania jonizującego realizowany w ramach państwowego monitoringu środowiska w latach 2020-2022.
Isajenko, K., Piotrowska, B., Fujak, M., Kardaś, M., 2012. Radiation atlas of Poland 2011. Biblioteka Ochrony Środowiska, Warsaw.
Jackson, M.T., Prichard, H.M., Sampson, J., 2010. Platinum-group elements in sewage sludge and incinerator ash in the United Kingdom: assessment of PGE sources and mobility in cities. Sci. Total Environ. 408, 1276–1285. https://doi.org/10.1016/j.scitotenv.2009.09.014.
Joint Research Centre, 2019. https://remon.jrc.ec.europa.eu/About/Atlas-of-Natural-Radiation/Digital-Atlas/Uranium-in-soil/Uranium-concentration-in-soil-; Access: 26.09.2023 [WWW Document]. European map of uranium in soil, January 2019.
Kamei-Ishikawa, N., Ito, A., Tagami, K., Umita, T., 2013a. Fate of radiocesium in sewage treatment process released by the nuclear accident at Fukushima. Chemosphere 93, 689–694. https://doi.org/10.1016/j.chemosphere.2013.06.012.
Kamei-Ishikawa, N., Ito, A., Umita, T., 2013b. Fate of stable strontium in the sewage treatment process as an analog for radiostrontium released by nuclear accidents. J. Hazard. Mater. 260, 420–424. https://doi.org/10.1016/j.jhazmat.2013.05.038.
Kępys, W., Śliwka, M., Pawul, M., 2021. Assessment of Ecotoxicity of Incinerated Sewage Sludge Ash (ISSA). Minerals 11, 849. https://doi.org/10.3390/min11080849.
Kim, J.T., Yu, C.W.F., 2014. Hazardous materials in buildings. Indoor Built. Environ. 23, 44–61. https://doi.org/10.1177/1420326X14524073.
Kozai, N., Suzuki, S., Aoyagi, N., Sakamoto, F., Ohnuki, T., 2015. Radioactive fallout cesium in sewage sludge ash produced after the Fukushima Daiichi nuclear accident. Water Res. 68, 616–626. https://doi.org/10.1016/j.watres.2014.10.038.
Krüger, O., Grabner, A., Adam, C., 2014. Complete survey of german sewage sludge ash. Environ. Sci. Technol. 48, 11811–11818. https://doi.org/10.1021/es502766x.
Lee, J.-K., Lee, K.-H., Chun, H.-S., 1993. Behavior of trace metals in fluidized-bed incineration of sewage sludge. J. Chem. Eng. Jpn. 26, 179–182. https://doi.org/10.1252/jcej.26.179.
Li, R., Zhao, W., Li, Y., Wang, W., Zhu, X., 2015. Heavy metal removal and speciation transformation through the calcination treatment of phosphorus-enriched sewage sludge ash. J. Hazard. Mater. 283, 423–431. https://doi.org/10.1016/j.jhazmat.2014.09.052.
Lin, W.Y., Ng, W.C., Wong, B.S.E., Teo, S.-L.-M., Sivananthan, G. d/o, Baeg, G.H., Ok, Y. S., Wang, C.-H., 2018. Evaluation of sewage sludge incineration ash as a potential land reclamation material. J. Hazard. Mater. 357, 63–72. https://doi.org/10.1016/j.jhazmat.2018.05.047.
Madruga, M.J., Miró, C., Reis, M., Silva, L., 2019. Radiation exposure from natural radionuclides in building materials. Radiat. Prot. Dosimet. 185, 49–57. https://doi.org/10.1093/rpd/ncy256.
Matsuzuru, H., Moriyama, N., Wadachi, Y., Ito, A., 1977. Leaching behavior of cesium-137 in cement-waste composites. Health Phys. 32, 529–534.
Ogawa, N., Amano, T., Koike, Y., 2021. Elution control of radioactive cesium in MSWI fly ash using water repellent treatment. J. Mater. Cycles Waste Manag. 23, 158–164. https://doi.org/10.1007/s10163-020-01111-5.
Pan, S.-C., Lin, C.-C., Tseng, D.-H., 2003. Reusing sewage sludge ash as adsorbent for copper removal from wastewater. Resour. Conserv. Recycl. 39, 79–90. https://doi.org/10.1016/S0921-3449(02)00122-2.
Papastefanou, C., Stoulos, S., Manolopoulou, M., 2005. The radioactivity of building materials. J. Radioanal. Nucl. Chem. 266, 367–372. https://doi.org/10.1007/s10967-005-0918-z.
Pazos, M., Kirkelund, G.M., Ottosen, L.M., 2010. Electrodialytic treatment for metal removal from sewage sludge ash from fluidized bed combustion. J. Hazard. Mater. 176, 1073–1078. https://doi.org/10.1016/j.jhazmat.2009.11.150.
Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J. Environ. Monit. 1, 57–61. https://doi.org/10.1039/a807854h.
Shacklette, T.H., Goerngen, G.J., 1984. Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States. US Government Printing Office, Washington.
Shyti, M., 2019. Calibration and performance of HPGe detector for environmental radioactivity measurements using LabSOCS. p. 130012. doi: 10.1063/1.5091297.
Smol, M., Adam, C., Anton Kugler, S., 2020. Inventory of Polish municipal sewage sludge ash (SSA) – mass flows, chemical composition, and phosphorus recovery potential. Waste Manag. 116, 31–39. https://doi.org/10.1016/j.wasman.2020.07.042.
Stanić, G., Nikolov, J., Tucaković, I., Mrđa, D., Todorović, N., Grahek, Ž., Coha, I., Vraničar, A., 2019. Angle vs. LabSOCS for HPGe efficiency calibration. Nucl. Instrum. Methods Phys. Res. A 920, 81–87. https://doi.org/10.1016/j.nima.2018.12.059.
Świerczek, L., Cieślik, B.M., Konieczka, P., 2021. Challenges and opportunities related to the use of sewage sludge ash in cement-based building materials – a review. J. Clean Prod. 287, 125054 https://doi.org/10.1016/j.jclepro.2020.125054.
Trevisi, R., Risica, S., D'Alessandro, M., Paradiso, D., Nuccetelli, C., 2012. Natural radioactivity in building materials in the European Union: a database and an estimate of radiological significance. J. Environ. Radioact. 105, 11–20. https://doi.org/10.1016/j.jenvrad.2011.10.001.
Tsushima, I., 2017. Behavior of radioactive materials and safety stock of contaminated sludge. J. Environ. Sci. Health A 52, 158–165. https://doi.org/10.1080/10934529.2016.1240486.
Tsushima, I., Ogoshi, M., Harada, I., 2013. Leachate tests with sewage sludge contaminated by radioactive cesium. J. Environ. Sci. Health A 48, 1717–1722. https://doi.org/10.1080/10934529.2013.815538.
Xiao, Z., Yuan, X., Li, H., Jiang, L., Leng, L., Chen, X., Zeng, G., Li, F., Cao, L., 2015. Chemical speciation, mobility and phyto-accessibility of heavy metals in fly ash and slag from combustion of pelletized municipal sewage sludge. Sci. Total Environ. 536, 774–783. https://doi.org/10.1016/j.scitotenv.2015.07.126.
Xu, H., He, P., Gu, W., Wang, G., Shao, L., 2012. Recovery of phosphorus as struvite from sewage sludge ash. J. Environ. Sci. 24, 1533–1538. https://doi.org/10.1016/S1001-0742(11)60969-8.
Yang, L., Guo, X., Liang, S., Yang, F., Wen, M., Yuan, S., Xiao, K., Yu, W., Hu, J., Hou, H., Yang, J., 2023. A sustainable strategy for recovery of phosphorus as vivianite from sewage sludge via alkali-activated pyrolysis, water leaching and crystallization. Water Res. 233, 119769 https://doi.org/10.1016/j.watres.2023.119769.
Zdeb, T., Tracz, T., Adamczyk, M., 2022. Physical, mechanical properties and durability of cement mortars containing fly ash from the sewage sludge incineration process. J. Clean Prod. 345, 131055 https://doi.org/10.1016/j.jclepro.2022.131055.
Zhang, F.-S., Yamasaki, S., Nanzyo, M., 2002. Waste ashes for use in agricultural production: I. Liming effect, contents of plant nutrients and chemical characteristics of some metals. Sci. Total Environ. 284, 215–225. https://doi.org/10.1016/S0048-9697(01)00887-7.