Monitoring of 137Cs in electric arc furnace steel making process

Sofilić, Tahir; Barišić, Delko; Sofilić, Una

Monitoring of ^{137}Cs in electric arc furnace steel making process

Tahir Sofilić · Delko Barišić · Una Sofilić

Abstract This article presents the results of ^{137}Cs and other radionuclide monitoring in EAF steel-making process in the Croatian CMC Sisak Steel Mill. The presence of ^{137}Cs and natural isotopes ^{40}K, ^{232}Th, ^{226}Ra and ^{238}U was established. Investigations on the occurrence of the isotope cesium, as well as natural isotopes and their distribution in waste from the process of carbon steel production by EAF have been conducted. Detection of artificial isotope cesium in EAF dust indicates that it might originate from steel scrap or from the residue of the material that was used in the technological process, thus deserving special attention.

Keywords Radionuclide distribution · Steel · Slag · Dust

Introduction

Nowadays, one cannot imagine contemporary steel production technology without using steel scrap, which is why steel scrap is considered the basic raw material for steel production. Already during the 1980s the share steel scrap in the metal insert amounted to more than 40%, while it ranges throughout quite broad limits in certain steel production processes, i.e., in Basic Oxygen Furnace Process (BOF) 20–30%, nowadays rarely, Open Hearth Furnace (OHR) 50–60%, and Electric Arc Furnace (EAF) from 95 to 100% of steel scrap.

Nowadays, of the total amount of all types of raw materials used in the EAF process of steel production, steel scrap is definitely the most significant in amount, for its amount ranges from 1039 to 1232 kgt^{-1} of crude steel [1]. In the last 10 years (1999–2008), the level of global crude steel production [2] was between 789 and 1323 million tones/y. If we take on the assumption that there is an average of 1135 kg of steel scrap used per 1000 kg of crude steel, we obtain the consumption of about 300–473 million tones/years of scrap in the observed period. At the same period, the level of crude steel production [2] in the EU (27) was from 182 to 210 million tones/years and consumption of steel scrap was 73.4 to 95.5 million tones/years as well.

Considering the immense significance of steel scrap as raw material in the production processes of steel mill and melting plants, it is vital to be fully acquainted with its disadvantages when it comes to the chemical composition. Alongside the well-known additives, which, during melting or refining, pass to either slag (Al, Si, Ti) or gas (Zn, Cd), i.e., those which only partially turn to slag (Mn, Cr, S, P) or remain fully melted (Cu, Ni, Mo, Sn…), steel scrap can also contain admixtures from the group of radioactive metals.

Some of the contaminant radioactivity is a result of naturally occurring radionuclides. Other radioactivity may be associated with radioactive sources that are contained in industrial or medical devices. In cases where the radionuclide occurs naturally, or is already present in the environment as a result of global fallout, the inadvertent melting of a radioactive source could increase the contaminant concentration above that caused by this background environmental.

T. Sofilić (✉)
CMC Sisak d.o.o., Braće Kavurić 12, 44010 Sisak, Croatia
e-mail: tahir.sofilic@cmc.com

D. Barišić
Rudjer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

U. Sofilić
Tina Ujevića 25, 44010 Sisak, Croatia

Radioactive material may be introduced in steel scrap through three different pathways:

– Discrete radioactive sources may be introduced into the scrap, due to the fact that such radioactive sources may escape from regulatory control because they are abandoned, lost, misplaced, stolen or otherwise transferred without proper authorization.
– Uncontrolled radioactively contaminated material may appear in the scrap stream from the process where the material has been used. The material may have become contaminated after contact with either natural or artificial radionuclides.
– Introduction of material with a very low level of radioactivity, released in accordance with the national regulatory framework.

The problem of radionuclide presence in steel and other scrap is not recent and has been significantly present in work published on the topic through a series of data on occurrences of these unwanted constituents in steel and other metals. The very wide application of many isotopes points to the need for strict control over their usage as well as disposal after usage. To be more precise, today, there is practically no industry that does not use on of the isotopes [3, 4], for instance technical industry (^{241}Am, ^{74}As, ^{82}Br, ^{14}C, ^{144}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{137}Cs, ^{64}Cu, ^{55}Fe, ^{192}Ir, ^{32}P, ^{106}Ru, ^{35}S, ^{124}Sb, ^{182}Ta, ^{204}Tl, ^{170}Tm, ^{65}Zn), medicine and biology (^{241}Am, ^{82}Br, ^{45}Ca, ^{60}Co, ^{51}Cr, ^{137}Cs, ^{55}Fe, ^{22}Na, ^{24}Na, ^{131}J, ^{32}P, ^{89}Sr), and agriculture and food production (^{14}C, ^{45}Ca, ^{60}Co, ^{137}Cs, ^{64}Cu, ^{55}Fe, ^{131}J, ^{99}Mo, ^{32}P, ^{65}Zn).

Data available in published work [5–19] indicate a relatively significant number of recorded cases of the presence of radioactive elements in steel and other metal slag intended for recycling, as well as products created in the steel production process (steel, slag, and dust), and their order, according to element abundance is as follows: ^{137}Cs, ^{60}Co, ^{226}Ra, ^{192}Ir, ^{241}Am, ^{232}Th, and ^{90}Sr. Although today great amount of attention is being paid to the procedures of procurement, usage and disposal of radioactive sources, the number of cases in which they appear in steel and other metal scrap is still to big. Only in the Netherlands in the period from 2003 to 2007, 210–388 scrap loads with increased radiation level have been recorded annually [20].

Many radioactive sources found by recoveries and recyclers originally come from nuclear installations (fission and activation products) as well as from industrial and research irradiator activities (^{137}Cs, ^{60}Co), teletherapy (^{137}Cs, ^{60}Co), industrial radiography (^{60}Co, ^{192}Ir, ^{170}Tm, ^{169}Yb), medical brachytherapy (^{226}Ra, ^{137}Cs, ^{60}Co, ^{192}Ir), humidity gauges (^{241}Am/Be, ^{226}Ra/Be), and density gauges (^{137}Cs), industrial gamma gauges (^{137}Cs, ^{60}Co), and various beta gauging (^{90}Sr), and well logging (^{241}Am/Be, ^{137}Cs, ^{252}Cf). One can also find pipes contaminated with

uranium and thorium and from the potash [21] industries (^{40}K).

Although many of the steel producers have installed equipment for radionuclide monitoring in steel scrap, this equipment cannot provide absolute protection because of the shielding of radioactive emissions that may be provided by uncontaminated scrap metal. If radioactive material is not removed before the melting process, it could contaminate the crude steel and finished metal product, associated dust-recycle process streams, equipment, and the dust generated during the EAF process.

When radionuclides are present in industrial by-product and/or waste, this material can be dangerous for the whole environment. It is clear that in the case of high activity, such materials belong to the radioactive waste but it is not so clear for which purposes such materials can be used when content of radionuclides is low. The disposal options for these materials, specifically the large volumes of material with the lower concentrations of ^{137}Cs, have been limited because of their "hazardous waste" classification and the costs associated with the disposition of large volumes of hazardous or radioactive waste. From this point of view, long-lived artificial and natural radionuclides deserve special attention.

Based on results of earlier studies [3] when the presence of an artificial radionuclide ^{137}Cs was detected in EAF dust, and with the purpose of advancing the existing system of monitoring radionuclides CMC Sisak d.o.o., Croatia, as well as improving the management system of waste from the steel production processes, throughout 2009, studies of occurrence and distribution of present radionuclides in by-products and/or waste from the process of production of non-alloy carbon steel by EAF procedure have been conducted.

Experimental

The testing has been conducted on crude steel produced by EAF and processing by-products, i.e., EAF slag and dust created during the production of low carbon steel in the Steel Mill of CMC Sisak, Croatia. The analysis by γ-spectrometry has been applied to determine the presence of radionuclides and their activity in the by-products and/or wastes.

Sampling

For the purpose of continuous monitoring of artificial isotope ^{137}Cs presence in electric arc furnace dust between January and December 2009, samples were taken (in the middle of the month) at the de-dusting plant outlet (about 5 kg each). The so-called raw sample was obtained after

homogenization by stirring and quartering to the quantity of 1.00 kg. The average samples were dried at 378 K for 24 h, marked with numbers from 1 to 12 and kept in glass bottles with ground cap.

At the same time slag was sampled simultaneously with the melt, cooled in the air, ground in a ring mill to the grain size below 1 mm, homogenized, and quartered to the quantity of 1.00 kg. The sample was dried at 378 K for 24 h, transferred to glass bottles with ground cap, and marked. Sample of molten steel was cast into a copper mould.

Quantitative determination

The prepared samples were transferred to standard counting vessels of 125 cm³ and weighed. The loaded vessels were sealed and stored for at least 4 weeks to allow the in-growth of gaseous ^{222}Rn (3.8 day half-life) and its short-lived decay products to equilibrate with the long-lived ^{226}Ra precursor in the sample.

At the end of the in-growth period, the samples were counted with HPGe multi-channel γ-spectrometer. The activities of ^{40}K, ^{226}Ra, ^{232}Th, ^{238}U and ^{137}Cs were determined by γ-ray spectrometry, using a low background hyper pure germanium semiconductor detector system coupled to 8192-channel CANBERRA analyzer. Detector system was calibrated using standards supplied by both the National Bureau of Standards (USA) and Amersham International (UK).

Depending on sample activity, spectra were recorded for times ranging 100,000–200,000 s, and analyzed using the GENIE 2000 CANBERRA software.

Activities of ^{226}Ra were calculated from the 609.4 keV-peak of its ^{214}Bi progeny. Activities of ^{232}Th were calculated via ^{228}Ra from the 911.1 keV-peak of its ^{228}Ac progeny. Activities of ^{40}K were calculated from the 1460.7 keV-peak, activities of ^{137}Cs were calculated from the 661.6 keV-peak, and activities of ^{60}Co from the 1173 keV-peak. Activities of ^{238}U were calculated from the ^{235}U activities assuming the ^{235}U/^{238}U activity ratio [22] of 0.046. ^{235}U activities were calculated from the 186 keV-peak, after subtraction of the overlapping ^{226}Ra peak, which was previously calculated [23, 24] from ^{214}Bi.

Efficiency of the system was checked during International Atomic Energy Agency inter-comparison runs. Precision and accuracy of the system were checked additionally by simultaneous measurement of IAEA Reference Materials (International Atomic Energy Agency). It should be mentioned that efficiency was calculated as function of energy and geometry at the base of experimental data.

Limit of detection (LD) was determined according to Currie (1968) relation for aired observation and zero blank [25]. From LD, a lower limit of detection (LLD) was estimated at the base of know efficiency, counting time, energy intensity, and sample mass.

Results and discussion

When radioactive sources are melted the three possible outcomes are that the radioactivity partitions mainly to the heat (metal), off-gas dust or the slag. In the technology of steel production by RFA, the most important factor is the slag former, because the partition of radionuclides and the characteristic of steel depend on the composition and basicity of the slag former [26–29]. The partition mechanism and mode of removal radionuclide from scrap to other surrounding media is a complex process that can be influence by numerous chemical and physical factors, including the composition, thermodynamic conditions, solubility of radionuclides in molten steel, melting temperature, and melting practices such as the furnace type and size, melting time and the method of a carbon adjustment, and the physical and chemical properties of radionuclides [29]. Because of their different physical and chemical properties and other factors, during a steel making process, the isotopes were distributed differently in the molten steel and in the by-products, Table 1. The data in Table 1 show some properties of radioactive element found by steel scrap recycling and their entrainment into melt, slag or off gas dust.

The physical and chemical properties, such as boiling temperature and the affinity for oxygen of the radionuclides, influence their distribution into the processing phases. Based on free energy and vapour pressure considerations, cesium would be expected to volatilize from the melt and cesium found both in the slag and in off gas dust. The distribution factors of the main radionuclides expected to enter the steel making process are shown in Table 2.

Just as with the abovementioned EAF by-products or waste in steel making process, and in order to define possibilities for further use, radionuclides' distribution and

Table 1 Some of the properties of radioactive element [3]

Isotope	Occurrence probability	Toxicity class	Spread a risk
^{60}Co	High	Low to moderate	Low
^{226}Ra	High	High	High
^{137}Cs	Moderate	Moderate	High
^{192}Ir	Moderate	Moderate	Low
^{241}Am	Low	High	High
^{232}Th	Low	High	Low
^{90}Sr	Very Low	Very high	High

Table 2 Radionuclide distribution during EAF process into metal, slag, and dust [17, 36]

Isotope characteristic		Distribution factor		
Radionuclide	Half-life	Metal	Slag	Dust
^{54}Mn	312 days	1	0.1	0.05
^{55}Fe	2.70 years	1	0.1	0.05
^{60}Co	5.27 years	1	0.01	0.005
^{63}Ni	96 years	1	0.01	0.001
^{90}Sr	29.10 years	0.1	1	0.1
^{137}Cs	30.00 years	0.001	0.1–0.5	0.5–1
^{192}Ir	74 days	1	0.01	0.001
^{226}Ra	1600 years	0.1	1	0.1
^{232}Th	1.40E10 years	0.1	1	0.01
^{241}Am	432 years	0.1	1	0.001

potential radiation risk in steel making process was examined. In this manner, the presence of natural and particularly artificial isotope ^{137}Cs was determined in the specimens of electric furnace dust, slag and melt, and obtained results are presented in this work.

It should be mentioned that every single sample was counted three times and results in all tables present the average activity value with standard deviation computed from these values and single counting error.

Table 3 shows results of radionuclides determination in EAF dust samples. As it was expected regarding previous research [30], the electric arc furnace dust samples contain natural isotopes ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U and artificial isotope ^{137}Cs. The measured values regarding the presence of individual isotopes and their activity are as follows: ^{40}K from 320 ± 40.9 Bq kg^{-1} (sample D12) to 573 ± 63.2 Bq kg^{-1} (sample D3); ^{232}Th from 3.91 ± 1.78 Bq kg^{-1} (sample D3) to 8.30 ± 2.97 Bq kg^{-1} (sample D11); ^{226}Ra from 5.92 ± 1.47 Bq kg^{-1} (sample D3) to 13.3 ± 2.56 Bq kg^{-1} (sample D12), and ^{238}U from <6.98 Bq kg^{-1} (sample D3) to 21.1 ± 9.98 Bq kg^{-1} (sample D1). The measured values regarding the presence of artificial isotope ^{137}Cs was from 6.83 ± 1.39 Bq kg^{-1} (sample D12) to 20.9 ± 2.79 Bq kg^{-1} (sample D4).

The results of earlier studies point to the distribution of radionuclide during the process of melting steel slag, i.e., production of steel by EAF procedure [31–35], during which ^{60}Co, ^{63}Ni, and ^{192}Ir remain melted, ^{90}Sr, ^{147}Pm, ^{226}Ra, ^{232}Th, ^{238}Pu, ^{241}Am, and ^{244}Cm pass to slag, and the evaporating ^{137}Cs accumulates in the dust, Table 4.

Just as the abovementioned partition mechanism and mode of removal of radionuclides from scrap to melt, slag, and dust is a complex process that can be influenced by the thermodynamic conditions, solubility of radionuclides in molten steel, melting temperature, and melting practices, such as furnace type and size, melting time, the physical

and chemical properties of radionuclides and other phenomena which appear during the steel making process.

To be more precise, it is quite common an occurrence for the slag from the EAF process to contain captured drops of liquid metals in the form of granules, and due to this the distribution ratio of respective radionuclides between slag and melt tends to be smaller than the theoretical values. Furthermore, the occurrence such as the so-called bubble bursting causes minute drops of metal to appear, which, when separated from the melt, are taken to the de-dusting plant by smoke gases and kept in the dust.

According to the data presented in Table 4, it is to be expected for the melt to contain 98–99% of radioactive ^{60}Co, ^{63}Ni, and ^{192}Ir, while the dust contains the majority of all evaporating ^{137}Cs. Slag normally contains 95–99% of ^{90}Sr, ^{147}Pm, ^{226}Ra, ^{232}Th, ^{238}Pu, ^{241}Am, and ^{244}Cm, as well as 1–5% of ^{60}Co, ^{63}Ni, and ^{192}Ir all of which are being captured in the slag in the form of metal granules. That the distribution of radionuclides during melting is a quite complex and complicated process is also demonstrated by the results of Neuschütz et al's [31] study, where during the melting of wastes of low radioactivity the distribution of ^{137}Cs between slag and dust amounted to 60:40, which was above all the consequence of the form in which cesium was used. The cesium distribution was typical for nonchloride Cs compounds. The CsCl was found to volatilize completely and to pass to the EAF dust, while the other Cs compounds (CsOH and Cs$_2$SO$_4$) tend to partition between slag and dust depending on physical and chemical properties of compounds and on slag basicity.

For the purpose of determining the artificial isotope ^{137}Cs presence in electric arc furnace dust and possible distribution between slag and dust, the analysis by γ-spectrometry has been applied to determine the presence of ^{137}Cs and other radionuclides, as well as their activity in the slag and melt, Tables 5 and 6.

In Table 5 results of radionuclide determination in slag samples are shown. As it was expected, the slag samples contain natural isotopes ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U. The measured values regarding the presence of individual isotopes and their activity are as follows: ^{40}K from 45.3 ± 10.3 Bq kg^{-1} (sample S10) to 63.8 ± 12.2 Bq kg^{-1} (sample S12); ^{232}Th from 12.3 ± 3.83 Bq kg^{-1} (sample S11) to 15.4 ± 2.95 Bq kg^{-1} (sample S3); ^{226}Ra from 18.0 ± 2.42 Bq kg^{-1} (sample S4) to 21.6 ± 2.82 Bq kg^{-1} (sample S12), and ^{238}U from 18.9 ± 6.87 Bq kg^{-1} (sample S8) to 32.4 ± 8.47 Bq kg^{-1} (sample S5). The measured values regarding the presence of artificial isotope ^{137}Cs were very low and their activities were from 1.03 ± 0.433 Bq kg^{-1} (sample S2) to 1.57 ± 0.599 Bq kg^{-1} (sample S1).

In Table 6 results of radionuclides determination in melt samples are shown. As it was expected, the melt samples

Table 3 Results of γ-spectrometric analysis of the EAF dust from CMC Sisak steel mil

Sample	Measured activity concentration ± measurement uncertainty (Bq kg^{-1})				
	^{40}K	^{232}Th	^{226}Ra	^{238}U	^{137}Cs
D1	401 ± 50.0	4.02 ± 2.29	6.96 ± 2.04	21.1 ± 9.98	8.84 ± 1.70
D2	516 ± 59.2	4.85 ± 2.21	8.94 ± 1.97	<8.98	11.4 ± 1.81
D3	573 ± 63.2	3.91 ± 1.78	5.92 ± 1.47	<6.98	19.7 ± 2.41
D4	582 ± 66.7	6.07 ± 2.56	9.35 ± 2.22	<10.1	20.9 ± 2.79
D5	457 ± 52.8	5.35 ± 2.28	9.45 ± 1.90	<8.23	18.3 ± 2.43
D6	452 ± 51.8	4.82 ± 2.11	9.11 ± 1.91	<7.78	19.6 ± 2.45
D7	372 ± 43.1	6.03 ± 2.20	8.13 ± 1.66	<7.02	14.3 ± 1.95
D8	378 ± 44.6	4.00 ± 1.95	6.71 ± 1.63	<8.00	16.9 ± 2.21
D9	417 ± 50.4	4.99 ± 2.44	9.88 ± 2.21	<9.87	15.2 ± 2.24
D10	496 ± 59.1	8.08 ± 3.54	10.1 ± 2.34	<10.3	12.4 ± 2.03
D11	470 ± 55.1	8.30 ± 2.97	12.2 ± 2.25	12.2 ±7.21	11.1 ± 1.76
D12	320 ± 40.9	5.05 ± 2.55	13.3 ± 2.56	14.5± 7.82	6.83 ± 1.39

Table 4 The distribution ratios of some radionuclide during steel melting in EAF

Nuclide	Neuschütz et al. [31]			Anigstein et al. [32].		
	Distribution (%)			Distribution (%)		
	Melt	Slag	Dust	Melt	Slag	Dust
^{60}Co	98	1	1	99	–	1
^{63}Ni	98	1	1	99	–	1
^{90}Sr	–	99	1	–	95	5
^{137}Cs	–	<1	>99	–	0–5	95–100
^{147}Pm	–	99	1	–	95	5
^{192}Ir	98	1	1	99	–	1
^{226}Ra	–	99	1	–	95	5
^{232}Th	NA	NA	NA	–	95	5
^{238}Pu/^{239}Pu	–	99	1	–	95	5
^{241}Am	–	99	1	–	95	5
^{244}Cm	–	99	1	–	95	5

NA not available

contain very low activities of natural isotopes ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U. The measured values regarding the presence of individual isotopes and their activity are as follows: ^{40}K all values were less then 5.49 Bq kg^{-1} (sample ST 5); all activities values of ^{232}Th were less then 0.541 Bq kg^{-1} (sample ST 5); all activities values of ^{226}Ra were less then 0.590 Bq kg^{-1} (sample ST 5), except for values in samples ST1, ST10, and ST12 where values were from 0.496 ± 0.337 Bq kg^{-1} (sample ST1) to 0.838 ± 0.345 Bqkg^{-1} (sample ST12). All activities values of ^{238}U were less then 2.74 Bq kg^{-1} (sample ST5) and the measured values regarding the presence of artificial isotope ^{137}Cs were less then 0.009 Bq kg^{-1} (sample ST5).

In order to attempt to determine the source isotope ^{137}Cs in dust and slag, in previous investigations[22] the materials used for the production of one steel melt were tested for the presence of radionuclides. The analysis included the materials added into the electric arc furnace as non-metal additives (Si–Mn, Fe–Si, bauxite, fluorspar, lime, and coke), graphite electrodes and used refractory material. Obtained results are shown in Table 7.

The measured values regarding the presence of individual isotopes and their activities, presented in Table 7, showed very low values or values less then lower limit of detection.

Conclusion

With the purpose of advancing the existing system of monitoring radionuclides, as well as improving the management system of waste from the steel production processes, and on the basis of earlier studies of the presence of isotope ^{137}Cs in the samples of EAF dust, we have conducted a systematic control of this artificial radionuclide in this specific waste material in the period of 1 year. Investigations on the occurrence of the isotope ^{137}Cs, as well as natural isotopes ^{40}K, ^{232}Th, ^{226}Ra, ^{238}U and their distribution in by-products and/or waste from the process of production of non-alloy carbon steel by EAF procedure have been conducted.

It was determined that the electric arc furnace dust samples contain artificial isotope ^{137}Cs and natural isotopes ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U and the measured values regarding the presence of individual isotopes and their activity were for ^{137}Cs from 6.83 ± 1.39 Bq kg^{-1} to 20.9 ± 2.79 Bq kg^{-1}; ^{40}K from 320 ± 40.9 Bq kg^{-1} to 573±63.2 Bq kg^{-1}; ^{232}Th from 3.91 ± 1.78 Bq kg^{-1} to

Table 5 Results of γ-spectrometric analysis of the EAF slag from CMC Sisak steel mil

Sample	Measured activity concentration ± measurement uncertainty (Bq kg^{-1})				
	^{40}K	^{232}Th	^{226}Ra	^{238}U	^{137}Cs
S1	62.9 ± 12.1	15.1 ± 2.81	21.4 ± 2.80	24.3 ± 7.74	1.57 ± 0.599
S2	57.0 ± 11.3	13.3 ± 2.66	19.5 ± 2.57	23.3 ± 7.22	1.03 ± 0.433
S3	54.6 ± 11.3	15.4 ± 2.95	20.8 ± 2.71	21.3 ± 7.27	1.06 ± 0.434
S4	50.3 ± 10.5	14.5 ± 2.86	18.0 ± 2.42	25.0 ± 7.30	1.16 ± 0.499
S5	58.5 ± 11.5	14.5 ± 2.94	20.4 ± 2.67	32.4 ± 8.47	1.34 ± 0.514
S6	52.5 ± 10.8	13.5 ± 2.63	19.1 ± 2.51	29.7 ± 8.06	1.09 ± 0.481
S7	49.1 ± 9.33	13.2 ± 2.41	15.2 ± 2.05	20.6 ± 5.61	1.30 ± 0.466
S8	55.9 ± 11.2	13.0 ± 2.67	19.0 ± 2.52	18.9 ± 6.87	1.11 ± 0.505
S9	57.9 ± 11.5	12.9 ± 2.75	19.7 ± 2.58	24.5 ± 7.44	1.55 ± 0.459
S10	45.3 ± 10.3	14.9 ± 2.99	19.5 ± 2.55	23.6 ± 7.37	1.19 ± 0.496
S11	50.1 ± 11.0	12.3 ± 3.83	18.3 ± 2.51	25.5 ± 7.62	1.08 ± 0.438
S12	63.8 ± 12.2	14.7 ± 2.97	21.6 ± 2.82	26.0 ± 7.61	1.13 ± 0.331

Table 6 Results of γ-spectrometric analysis of the EAF carbon steel from CMC Sisak steel mil

Sample	Measured activity concentration ± measurement uncertainty (Bq kg^{-1})				
	^{40}K	^{232}Th	^{226}Ra	^{238}U	^{137}Cs
ST1	<4.37	<0.431	0.496 ± 0.337	<2.18	<0.007
ST2	<4.10	<0.404	<0.441	<2.05	<0.007
ST3	<4.21	<0.415	<0.453	<2.10	<0.007
ST4	<4.18	<0.413	<0.450	<2.09	<0.007
ST5	<5.49	<0.541	<0.590	<2.74	<0.009
ST6	<4.98	<0.491	<0.535	<2.49	<0.008
ST7	<4.60	<0.453	<0.494	<2.29	<0.008
ST8	<4.19	<0.413	<0.450	<2.09	<0.007
ST9	<4.38	<0.431	<0.470	<2.18	<0.007
ST10	<4.17	<0.411	0.803 ± 0.348	<2.08	<0.007
ST11	<4.25	<0.419	<0.457	<2.12	<0.007
ST12	<4.10	<0.404	0.838 ± 0.345	<2.05	<0.007

Table 7 Results of γ-spectrometric analysis of the materials added into the EAF[22]

Material	Measured activity concentration ± measurement uncertainty (Bq kg^{-1})			
	^{40}K	^{137}Cs	^{226}Ra	^{238}U
SiMn	<LLD	<LLD	<LLD	<LLD
FeSi	10 ± 2.0	<LLD	2.2 ± 0.6	2.2 ± 0.6
Bauxite	34.2 ± 7.2	0.9 ± 0.3	59.6 ± 1.9	58.9 ± 6.3
Fluor spar	10 ± 2.0	<LLD	123.8 ± 2.3	118.5 ± 7.5
Lime	<LLD	<LLD	<LLD	<LLD
Coke	10 ± 1.1	<LLD	2.0 ± 0.5	2.0 ± 0.4
Graphite electrode	46.4 ± 8.7	<LLD	2.5 ± 0.5	2.5 ± 0.6
Refractory material	22.2 ± 6.0	<LLD	9.1 ± 0.9	8.7 ± 3.1

LLD lower limit of detection

8.30 ± 2.97 Bq kg^{-1}; ^{226}Ra from 5.92 ± 1.47 Bq kg^{-1} to 13.3 ± 2.56 Bq kg^{-1} and ^{238}U from <6.98 Bq kg^{-1} to 21.1 ± 9.98 Bq kg^{-1}.

The measured values regarding the presence of artificial isotope ^{137}Cs in slag were very low and their activities were from 1.03 ± 0.433 Bq kg^{-1} to 1.57 ± 0.599

Bq kg^{-1}. The results of natural radionuclide determination in slag samples showed that the slag contained natural isotopes ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U and the measured values regarding the presence of individual isotopes and their activity were for ^{40}K from 45.3 ± 10.3 Bq kg^{-1} to 63.8 ± 12.2 Bq kg^{-1}; ^{232}Th from 12.3 ± 3.83 Bq kg^{-1} to 15.4 ± 2.95 Bq kg^{-1}; ^{226}Ra from 18.0 ± 2.42 Bq kg^{-1} to 21.6 ± 2.82 Bq kg^{-1} and ^{238}U from 18.9 ± 6.87 Bq kg^{-1} to 32.4 ± 8.47 Bq kg^{-1}.

The measurements of radionuclide activities in melt samples showed that all measured values regarding the presence of individual isotopes and their activity were less then their lower limit of determination (LLD) except values of ^{226}Ra in samples ST1, ST10, and ST12 which where were from 0.496 ± 0.337 Bq kg^{-1} to 0.838 ± 0.345 Bq kg^{-1}.

Detection of artificial isotope cesium in electric arc furnace dust indicates that it might originate from steel scrap or from the residue of the material that was used in the technological process, thus deserving special attention.

Activity of natural isotopes in investigated samples can be considered normal, because in previous investigation they are found in raw materials in minor quantities. In addition, presence of natural isotopes can be considered usual and they may appear in raw materials and accessory materials that are used in the steel making process.

Although these measured radioactivity values of artificial isotope ^{137}Cs do not represent significant values from EAF steel making processes, it is important to know the levels of these activities and to try to maintain or even reduce them by improving the existing monitoring system. At the same time, the monitoring of artificial isotope ^{137}Cs in electric arc furnace dust before it leaves the production cycle, does guarantee protection against accidental environment contamination through using dust in other industry or disposal.

References

1. Integrated Pollution Prevention and Control (2008) BAT for the production of iron and steel. EC Directorate—General JRC Joint Research Centre. European IPPC Bureau. 313, 382, 485 pp
2. Worldsteel Association (2009) Steel statistical yearbook 2008. Worldsteel Committee on Economic Studies, Brussels
3. Keck R, Krüger B, Kretschmer R (1994) Stahl u Eisen 1145:69
4. Sofilić T, Rastovčan-Mioč A, Cerjan-Stefanović Š (2001) Strojarstvo 43:203 (in Croatian)
5. Risks from radiation sources. Available from internet <http://www.smsec.com/en/nucl/011.htm>
6. Yu-Tzu C, Radioactive rod found in scrap. Available from internet <http://taipeitimes.com/News/taiwan/archives/2002/03/12/127324>
7. Radiation Safety Control of Steel Mill Owning Smelting Furnaces. Available from internet <http://www.aec.gov.tw/www/english/protection/article.php?n=02>
8. Turner R (2006) Health Phys 91(5):489
9. Truppa WA, Cateriano M (2004) The radioactive sources treated as scrap-regulatory aspects. Control and security, 11th international congress on the international radiation protection association, Madrid, Spain, pp 23–28
10. Lubenau JO, Yusko JG (1995) Health Phys 68(4):440
11. Lubenau JO, Yusko JG (1998) Health Phys 74(3):293
12. Mattia M, Wiener R (1999) International measures needed to protected metal recycling facilities from radioactive materials. Proceedings of the workshop on radioactive contaminated metallurgical scrap. United Nations. Economic Commission for Europe, Prague, Czech Republic, 26–28 May 1999, GE. 99-30636
13. Harvey DS (1999) Experiences within British steel since 1989. Proceedings of the workshop on radioactive contaminated metallurgical scrap. United Nations. Economic Commission for Europe, Prague, Czech Republic, 26–28 May 1999, pp 23–30
14. O'Grady J, Hone C, Turvey FJ (1996) Health Phys 70(4):568
15. Kugeler E, Thierfeldt S (1999) Detection of radioactivity in scrap in Germany. Proceedings of workshop on radioactive contaminated metallurgical scrap. United Nations. Economic Commission for Europe, Prague, Czech Republic, 26–28 May 1999, pp 165–176
16. Hwang JY, Chang JBH, Chang WP (2001) Health Phys 81(6):655
17. Werner Ch (1999) Control of radioactivity at the luxembourg steel—making facilities. Proceedings of the workshop on radioactive contaminated metallurgical scrap. United Nations. Economic Commission for Europe, Prague, Czech Republic, 26–28 May 1999, pp 151–164
18. Bialucha R Radioaktivität von Eisen- und Metallhüttenschlacken, FehS Report des Forschungsinstituts 2/200, p 2
19. Sefzig R, Saha B, Stoppa G (2009) ^{60}Co contaminated stainless steel in Germany—experiences and first steps. International conference and management of inadvertent radioactive material in scrap metal, Tarragona, Spain, 23–27 Feb 2009
20. VROM-Inspectorate South-West Unit Dep. substances and products, p 10. Available from internet <http://www.vrom.nl/get.asp?file=docs/publicaties/W1221.pdf&dn>
21. Légaré JM. Detection of radioactive sources in scrap metal. Available from internet <http://www.sftext.com/…/cuba_detection_radio.html>
22. Murray AS, Aitken MJ (1989) Int J Appl Radiat Isot 39:145
23. Barišić D (1989) The determination of ^{235}U and ^{238}U by gamma-spectrometry method on energies around 186 keV. Proceedings of the XV JDZZ symposium. Priština, p 91
24. Martinez-Lobo A, Palomares J (1991) J Radiat Nucl Chem 147:225
25. Currie LA (1968) Anal Chem 40:586
26. Song PS, Min BY, Choi WK, Jung CH, Oh WZ, Park JH (2006) J Ind Eng Chem 12(2):248
27. Song PS, Min BY, Choi WK, Jung CH, Oh WZ (2008) J Ind Eng Chem 60(2):136
28. Song PS, Min BY, Choi WK, Jung CH, Oh WZ, Kang Y (2008) J Chem Eng Jpn 41(7):602
29. Min BY, Choi WK, Oh WZ, Jung ChH, Lee KW (2009) J Ind Eng Chem 15:31
30. Sofilić T, Barišić D, Grahek Ž, Cerjan-Stefanović Š, Rastovčan-Mioč A, Mioč B (2004) Acta Metall Slovaca 10(1):29
31. Neuschütz D, Spirin D, Quade U, Meier-Kortwig J, Holappa L, Hamalainen M, Heredia Lozano MA, Guio Bonany MJ (2005) ISIJ Int 45(2):288
32. Anigstein R, Thurber WC, Mauro JJ, Marschke SF, Behling UH (2001) Technical Support Document, Potential recycling of scrap metal from nuclear facilities, U.S. Environmental Protection Agency, Office of Radiation and Indoor Air
33. Baldry K, Harvey DS, Bishop A. Accidental melting of radioactive sources. Available from internet <http://irpa11.irpa.net/pdfs/7e3.pdf>

34. Bartley R, Ciani V, Morere Molinero E, Deckers B, Dellatre D, Dodd B, Harvey D, Holmberg N, Ishikawa A, Isakov M, Mattia M, Terashima K, Van der Reijden G (2002) Report on the improvement of the management of radiation protection aspects in the recycling of metal scrap, UN New York and Geneva, EC for Europe, IAEA, Chapter VII, pp 63–67

35. Cheng JJ, Kassas B, Yu C, Le Poire D, Amish J, Dovel ES, Chen SY, Williams WA, Wallo A, Peterson H (2001) RESRAD-recycle: a computer model for analyzing the radiological doses and risks resulting from the recycling of radioactive scrap metal and the reuse of surface-contaminated material and equipment, ANL/EAD-3, Environmental Assessment Division, Argonne National Laboratory, Argonne, Illinois, pp 5–3

36. Ordinance on the limits of exposure to ionising radiation and on the conditions of exposure in special circumstances and in emergency situations (Official Gazette No. 125/06)