J Radioanal Nucl Chem (2010) 284:73–77
DOI 10.1007/s10967-009-0431-x

Radionuclides in steel slag intended for road construction

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Received: 8 December 2009 / Published online: 24 December 2009

Abstract The objective of this study was to describe the radiochemical characteristics of electric arc furnace (EAF) slag from Croatian EAF black steel slags, generated from carbon steel production process in CMC Sisak d.o.o., and steel mill in Split in order to enhance the understanding of possibilities for their use in road construction. This article presents the results of radionuclide in electric arc furnace steel slag. The presence of natural isotopes ^{40}K, ^{232}Th (^{228}Ra), ^{226}Ra and ^{238}U was established. The measured activity in slag natural isotopes lies within the Croatian legally permitted limits.

Keywords Metallurgical by-products · Radionuclide distribution · Steel · Slag

Introduction

In extractive metallurgical operations phases are generated, formed mainly from the addition of mixtures of oxides and fluxes, and is also composed of reaction products like those resulting from the oxidation of charge materials and the dissolution of refractories. Steel slag, a by-product of steelmaking, is produced during the separation of the molten steel from impurities in steel-making furnaces and occurs as a molten liquid melt. This kind of steel slag is a complex solution of silicates and oxides that solidifies upon cooling.

The main slags are classified in three types: ferrous slag, including iron slag generated in blast-furnace process and steel slags, non-ferrous slag generated by production of non-ferrous metals (Cu, Zn, Pb, Ni,..) and incineration slags generated by combustion of solid waste.

Slags from different metallurgical processes contain many useful components (metals and oxides) used for various industrial and construction purposes. The properties of slag including mineralogical composition play important roles in determining specific applications.

Steel-making processes produce significant volumes of waste, which is a problem both from the economical and environmental point of view. Steel-making operations, such as Basic Oxygen Furnace Process (BOF), Electric Arc Furnace (EAF) process and nowdays rare Open Hearth Furnace (OHR) produce slags of different compositions.

Of the total amount of all types of waste produced in the EAF process of steel production, steel slag is definitely the most significant in amount, for its amount ranges from 60 to 263 kg t^{-1} of raw steel [1]. Even though electric arc furnace steel slag has been classified as non-hazardous waste by its physical and chemical characteristics, and is possible to be disposed of at provided disposal sites without danger to the environment, this is rarely applied, because the permanent disposal of steel slag is highly expensive and requires a great area, and the valuable ingredients of steel slag are lost forever. Therefore, it is indispensable to consider the electric arc furnace slag (EAFS) as a by-product and not classify it as metallurgic waste, but to examine it in detail and, in accordance to final results, apply it as a valuable raw material in other

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industries. In order to find solutions for exploitation of steel slag, as well as due to increasingly demanding legal regulations in environment protection, physical, chemical and radiochemical properties of this material are more and more frequently subjected to systematic research.

Metallurgical slags from different processes, including blast furnace, steel-making and non-ferrous slags contain many useful components and could be used as a low-cost substitute in many metallurgical processes and also as a secondary source of iron. The properties of slag, including mineralogical, chemical and radiochemical composition play important roles in determining specific applications.

The history of the use of iron and steel slag dates back a long way and in 2006 European Slag Association noted that the earliest reports [2] on the use of slag refer to Aristotle, who used slag as a medicament as early as 350 B.C. Throughout history, the use of slag has ranged from the novel to the usual including: cast canon balls in Germany (1589), wharf buildings in England (1652), slag cement in Germany (1852), slag wool in Wales (1840), reinforced concrete in Germany (1892), and slag bricks made from granulated slag and lime in Japan (1901) (according to Iron and Steel [3] and Mihok et al. [4]). Blast-furnace slag has been utilized in concrete masonry for many years. The blast-furnace slag can impart many desirable properties to the masonry units such as lighter weight and increased fire resistance. Blast-furnace slag products have been used successfully in virtually all phases of bridge construction. According to studies that date as far back as 1927 by Penn State University, Ohio State University, U.S. Department of Agriculture, Auburn University, and Canadian research [5], agricultural slag applications have been equivalent to limestone and dolomite in increasing crop yields at equal levels of fineness.

The physical and chemical properties of mineral wool insulation, also known as slag wool [6], are major factors in their utility as residential and commercial insulation, pipe and process insulation, insulation for ships, mobile homes, domestic kitchen appliances, and a wide variety of other applications.

The non-ferrous slag generated in smelting often contains residual metal, which, in most cases inhibits their use without further processing.

The application of steel slag from steel mills was not very popular until the late 1990s, for there were vast amounts of blast-furnace steel slag available, while the steel slag from steel mills was used for the manufacture of chemical fertilizers, where only the so-called Thomas steel slag, a by-product of steel production from phosphorous raw iron, was used.

Nowadays, due to a relatively high stake of electric-furnace steel in the total amount of steel produced throughout the world, thus also the growth of available amounts of this type of waste i.e. reduced production of iron in blast furnaces, steel slag is becoming increasingly important, while the application of steel slag is also rapidly growing in the developed countries. Through awareness of environmental considerations and more recently the concept of sustainable development, extensive research and development has moved slag from industrial waste into modern industrial product which is effectively and profitably used.

Over the past 100 years, slag has been used for many industrial purposes, especially as raw material in cement production, landfill cover material, and the numerous construction and agricultural applications [7]. Slags can also be used in the lower layers of the pavement structure as granular base, in subbase and even in embankments.

This paper presents the results of radiochemical testing of steel slag with the purpose of its characterization as the type of waste, i.e. by-product of electric-furnace processes intended for recycling in other industries. Special attention has been directed at investigating the possibilities of it being used as substitute for natural mineral aggregates in road construction.

Experimental

The testing has been conducted on steel slag created during the production of EAF low carbon steel in the Steel Mill of CMC Sisak, Croatia and steel mill in Split. The analysis by γ-spectrometry is applied to determine the presence of radionuclides and their activity in the steel slag.

Sampling

Liquid steel slag was, after being poured out of the electric furnace, cooled with air and water, after which it was subjected to the following procedures: grinding, magnetic separation in order to remove leftover particles of the cooled steel melt, fragmentation and sieving. In this way an average specimen of steel slag was created, as well as specimens of granulometric fractions (0/4 mm, 4/8 mm, 8/16 mm and 16/32 mm).

Steel slag generated in steel mill in Split was taken from deposition pile as random sample of raw material.

The samples of investigated slags for γ-ray spectrometry analysis were crushed in a ring mill to the grain size below 1 mm, homogenised, and quartered to the quantity of 1.00 kg. They were dried at 378 K for 24 h, transferred to glass bottles with ground cap, and marked.

Quantitative determination

The aliquot of prepared samples were transferred to standard counting vessels of 125 cm^3 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 a 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 a 8192-channel CANBERRA analyser. 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 analysed 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 1,460.7 keV peak, activities of ^{137}Cs were calculated from the 661.6 keV peak, and activities of ^{60}Co from the 1,173 keV peak. Activities of ^{238}U were calculated from the ^{235}U activities assuming the ^{235}U/^{238}U activity ratio [8] 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 [9, 10] 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 [11]. From LD, a lower limit of determination (LLD) was estimated at the base of know efficiency, counting time, energy intensity and sample mass.

Results and discussion

Data from previous works [12–23] indicate the appearance of radionuclides in the waste from steel production processes, and the most common radionuclides are the following: ^{137}Cs, ^{60}Co, ^{226}Ra, ^{192}Ir, ^{241}Am, ^{232}Th and ^{90}Sr, which are distributed among the melt, slag and electric-furnace dust during the technological process of steel production, depending on their chemical and physical properties [12, 13]. In line with the said, and according to valid regulations [24], in order for the electric-furnace slag to be used as supplement in the production of construction material, it is essential to be familiar with the composition and amount of radionuclides in such a material, which is exactly why it was exposed to a γ-spectrometric analysis.

When radionuclides are present in slag, this slag 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. From this point of view, long-lived artificial and natural radionuclides deserve special attention. Just as the before mentioned slag and is by-product or waste in steel-making process, and in order to define possibilities for further use, radionuclides' distribution and potential radiation risk in steel-making process was examined. In this manner, the presence of natural isotopes ^{40}K, ^{232}Th (^{228}Ra), ^{226}Ra and ^{238}U was determined in the specimens of electric-furnace slag and obtained results are shown as presented in Tables 1 and 2.

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.

In Table 1 results of radionuclides determination in slag granulometric fractions are shown. As it was expected, the electric arc furnace 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 <8.4 Bq kg^{-1} (sample 4/8 mm) to 36.9 ± 4.8 Bq kg^{-1} (sample A); ^{232}Th from 6.7 ± 1.9 Bq kg^{-1} (sample B) to 14.4 ± 0.9 Bq kg^{-1} (sample 0/4 mm); ^{226}Ra from 13.4 ± 1.9 Bq kg^{-1} (sample 4/8 mm) to 24.0 ± 0.8 Bq kg^{-1} (sample 0/4 mm); and ^{238}U from 9.0 ± 3.7 Bq kg^{-1} (sample 4/8 mm) to 24.1 ± 2.8 Bq kg^{-1} (sample 0/4 mm).

In either group of samples, the presence of artificial radionuclides was not detected. For the purpose of testing the possible origin of the identified radionuclides in electric-furnace slag specimens, previous research [22] conducted a determination of the composition of the radionuclides in the materials added into the electric arc furnace as non-metal additives, graphite electrodes, as well as in ferroalloys and other materials used in the process itself, as presented in Table 3.

In detail, in order for the electric-furnace slag to be used as supplement in the production of construction materials it is essential to fulfill the prescribed values of maximum limit radioactive pollution of construction material [24], which should not exceed the following concentration of activities:

Table 1 Results of γ-spectrometric analysis of the slag granulometric fractions from CMC Sisak steel mill

EAF slag sample (fraction)	radionuclide	Measured activity concentration ± measurement uncertainty (Bq kg^{-1})	LLD[a] (Bq kg^{-1})
(0/4 mm)	^{40}K	22.0 ± 2.8	8.4
	^{226}Ra	24.0 ± 0.8	0.8
	^{232}Th (^{228}Ra)	14.4 ± 0.9	0.7
	^{238}U	24.1 ± 2.8	4.1
(4/8 mm)	^{40}K	<LLD	8.4
	^{226}Ra	13.4 ± 1.9	0.8
	^{232}Th (^{228}Ra)	11.0 ± 2.1	0.7
	^{238}U	9.0 ± 3.7	4.1
(8/16 mm)	^{40}K	14.2 ± 6.2	8.4
	^{226}Ra	16.9 ± 2.2	0.8
	^{232}Th (^{228}Ra)	9.7 ± 2.1	0.7
	^{238}U	13.2 ± 4.4	4.1
(16/32 mm)	^{40}K	14.1 ± 6.8	9.3
	^{226}Ra	14.8 ± 2.0	0.9
	^{232}Th (^{228}Ra)	10.2 ± 2.1	0.8
	^{238}U	13.3 ± 4.5	4.5

[a] *LLD* lower limit of determination

Table 2 Results of γ-spectrometric analysis of the slag taken from deposition pile as bulk material in steel mill in Split

Slag sample	Radionuclide	Measured activity concentration ± measurement uncertainty (Bq kg^{-1})	LLD[a] (Bq kg^{-1})
A	^{40}K	36.9 ± 4.8	8.1
	^{226}Ra	17.1 ± 1.9	0.8
	^{232}Th (^{228}Ra)	9.8 ± 1.4	0.7
	^{238}U	17.3 ± 3.8	3.9
B	^{40}K	15.3 ± 6.1	8.4
	^{226}Ra	17.7 ± 2.1	0.8
	^{232}Th (^{228}Ra)	6.7 ± 1.9	0.7
	^{238}U	15.6 ± 4.3	4.0
C	^{40}K	25.7 ± 5.6	8.3
	^{226}Ra	14.6 ± 2.3	0.8
	^{232}Th (^{228}Ra)	13.1 ± 2.2	0.7
	^{238}U	14.6 ± 3.9	4.0

[a] *LLD* lower limit of determination

300 Bq kg^{-1}for ^{226}Ra

200 Bq kg^{-1} for ^{232}Th

3,000 Bq kg^{-1}for ^{40}K

So that this condition is met: $(C_{Ra}/300) + (C_{Th}/200) + (C_K/3,000) \leq 1$ (1)

Where: C_{Ra}, C_{Th} and C_K are the concentrations of appropriate radio nuclides in Bq kg^{-1}.

Table 4 presents the calculated values of radioactive pollution in the specimen of the analyzed electric-furnace slag.

From the data listed in Table 4 we reach the conclusion that the analyzed slag can be used as supplement in the production of construction materials, because the calculated index values of present radionuclides are significantly lower than the maximum allowed limit.

Conclusion

In this article the results of radionuclide in electric arc furnace steel slag are presented i.e. the presence of natural isotopes ^{40}K, ^{232}Th (^{228}Ra), ^{226}Ra and ^{238}U was established and the activity in slag natural isotopes was measured.

Table 3 Results of γ-spectrometric analysis of materials used in the EAF process [22]

Specimen	Activity (Bq kg^{-1})			
	^{40}K	^{232}Th (^{228}Ra)	^{226}Ra	^{238}U
SiMn	<LLD[a]	<LLD[a]	<LLD[a]	<LLD[a]
FeSi	10.0 ± 2.0	<LLD[a]	2.2 ± 0.6	2.2 ± 0.6
Boxite	34.2 ± 7.2	147.2 ± 4.1	59.6 ± 1.9	58.9 ± 6.3
Fluorite	10.0 ± 2.0	2.7 ± 1.1	123.8 ± 2.3	118.5 ± 7.5
Lime	<LLD[a]	<LLD[a]	<LLD[a]	<LLD[a]
Coke	10 ± 1.1	<LLD[a]	2.0 ± 0.5	2.0 ± 0.4
Graphite electrode	46.4 ± 8.7	<LLD[a]	2.5 ± 0.5	2.5 ± 0.6
Refractory material	22.2 ± 6.0	2.5 ± 0.7	9.1 ± 0.9	8.7 ± 3.1

[a] *LLD* lower limit of determination

Table 4 Index values of radioactive pollution in the electric-furnace slag

Slag	Activity (Bq kg^{-1})			Index value
	^{40}K	^{232}Th (^{228}Ra)	^{226}Ra	
Fraction (0/4 mm)	22	14.4	24	0.16
Fraction (4/8 mm)	<LLD[a]	11.0	13.4	<0.11
Fraction (8/16 mm)	14.2	9.7	16.9	0.11
Fraction (16/32 mm)	14.1	10.2	14.8	0.11
Sample A	36.9	9.8	17.1	0.12
Sample B	15.3	6.7	17.7	0.10
Sample C	25.7	13.1	14.6	0.12
Allowed value	3000	200	300	1.00

[a] *LLD* lower limit of determination

In addition, the 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.

Activity of natural isotopes can be considered normal, as they are found in raw materials in minor quantities. The measured activities of naturally occurring radionuclides in investigated electric arc furnace slags are significantly lower than the maximum Croatian allowed limit so that slags, in terms of the radionuclides present, may be applied as raw materials and/or additives in the production of various construction materials, especially in road construction.

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