CHARACTERIZATION OF METALLURGICAL SLAGS USING LOW-LEVEL GAMMA-RAY SPECTROMETRY AND NEUTRON ACTIVATION ANALYSIS*

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Slags are final by-products involved in the iron and steelmaking process and could be used as building materials if they present appropriate physico-chemical characteristics and low natural radioactivity. The impurities contents of metallurgical slag have to be evaluated by accurate analytical techniques because they present an environmental hazard in the vicinity of slag dumps from the steel works areas. In this paper high resolution low-level gamma-ray spectrometry and instrumental neutron activation analysis (INAA) were applied at "Horia Hulubei" National Institute of Physics and Nuclear Engineering (IFIN-HH) at Magurele, Romania, to perform radioactivity measurement and elemental characterization of slag. The obtained concentration levels of U, Th and K natural radioactive elements in slag could be correlated with the limestone and dolomite used as fluxes in the iron metallurgy. They were compared with the permitted levels (OMS no. 51/1983) for steel slag and iron slag. By applying INAA in two irradiation steps the following major, minor and trace elements were determined in the metallurgical slag samples: Al, As, Au, Ba, Ca, Ce, Co, Cr, Cu, Fe, Hf, K, La, Mn, Mo, Na, Rb, Sb, Sc, Sm, V, W and Zn. Their concentrations were compared with previous results reported for furnace slag used as a component of binder materials for ceramic blocks.

Key words: low level gamma spectrometry, natural radioactivity, INAA, slag, trace elements.

1. INTRODUCTION

Slag is one of the main by-products of almost all metallurgical processes. It is a non-metallic material which is produced together with the metallic products of these processes. This product is largely employed in road building waterway

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stabilization, agriculture and in many other sectors [1-7]. The using of these alternative materials helps to minimize the extractive quarrying of primary aggregates thereby protecting more of natural resources and landscape. Air-cooling of metallurgical slag produces a crystalline structured mass which, after crushing and screening, provides an eminently suitable material for use as a construction aggregate in bound or unbound form, like any natural rock.

Blast-furnace and steel slag have certain advantages compared to natural stone: the high raw density coupled with the high abrasion resistance, the rough surface and the cubic shaped grain [1, 3, 7]. Steel slag that is used for hydraulic structures has to ensure - like natural aggregates - environmental compatibility, sufficient volume stability and frost resistance as well as a high compressive strength.

Nowadays, there is a tendency to obtain new building materials having good isolation properties and low density by using cheap and practically inexhaustible solid waste products like furnace slag, fly coal ash and phosphogypsum, without combustion. The Romanian furnace slag can be used alone or mixed with fly ash to obtain some binder materials with mechanical resistance comparable to the Portland cement. From the furnace slag and fly coal ash, in the presence of sulphatic activating additives like gypsum, phosphogypsum and/or lime, one can obtain the ceramic blocks that can substitute the usual bricks. The concentration levels of U, Th and K radioactive elements in slag are correlated with the limestone and dolomite used as fluxes in the iron metallurgy [8].

Possible concentration of radioactivity in iron and steel process involves the necessity of radiometric measurements to identify and quantify the natural and/or artificial radioisotopes in iron and steel raw materials, intermediate and finite products [5, 8-12]. Gamma-ray spectrometry is a powerful non-destructive analytical tool for the qualitative and quantitative determination of the gamma emitters [8, 12-14].

The increased requirements for knowledge of toxic emissions, along with the increasing use of new sources of raw materials (new deposits, industrial by-products, wastes) are making it necessary to carefully analyze the distribution of impurity elements between the main products and by-products of ferrous metallurgical processes [15-19]. Trace elements may present an environmental hazard in the vicinity of industrial activities related to ironmaking and steelmaking, with implications in the environmental pollution – contamination of soils and waters in the vicinity of a steel plant [20]. The situation in the region of an industrial centre should be seriously considered both from the standpoint of ecology and of the existence of a technogenic deposit of elements. Instrumental Neutron Activation Analysis (INAA) is a suitable multi-elemental analytical technique for the non-destructive investigation of solid samples requiring minimum preparation, having high sensitivity and good accuracy.

The aim of this study was to investigate, by low background gamma-ray spectrometry, the radioactivity level of slag from Arcelor-Mittal Iron and Steel Works of Galati, as well as by Instrumental Neutron Activation (INAA) the major, minor and trace element content of metallurgical slag, as a completion to earlier INAA application on various metallurgical samples [17-19].

2. EXPERIMENTAL

2.1. RADIOACTIVITY ANALYSIS

The low-background high resolution gamma-ray spectrometry technique was applied at GamaSpec laboratory of "Horia Hulubei" National Institute of Physics and Nuclear Engineering (IFIN-HH) in Magurele to determine the natural radioactivity of a steel slag material resulted from the metallurgical industry at Galati. The spectrometric chain was equipped with a HPGe (EG&G Ortec) detector of 2.0 keV resolution at 1332 keV of ^{60}Co, and 30% detection efficiency relative to 3"x 3" NaI (Tl) standard, coupled to a PC based multichannel analyzer (Maestro-32 MCA Ortec). GAMMAW software program was used for the spectra processing. The dried and homogenized metallurgical slag sample was measured in 72-mm diameter and 40-mm height plastic beaker placed on the detector end cap, after 21 days of keeping sealed in the measuring box, for a counting time of 24.14 h. The system was calibrated for the detection efficiency using relatively high-activity ^{152}Eu, ^{137}Cs, and ^{241}Am water equivalent volume standard sources, as well as IAEA reference materials of similar density and volume with those of measured sample (IAEA135 sediment, IAEA Soil-6, IAEA S-18 uranium ore), placed into identical beakers (the same measuring geometry).

For a low-level background counting of samples, shielding of the detector to reduce ambient background radiation is an essential request. For environmental application covering the energy range from zero to 2000 keV, 10 cm of lead is sufficient. This thickness of low background virgin lead for bulk shield together with a 0.5 mm cadmium and 1.5 mm copper graded liner is needed [10,13]. Similarly, in the GamaSpec laboratory of IFIN-HH, a lead shield of 10 cm thickness, coated with Sn and Cu foils of 1 mm, and 1.5 mm thickness, respectively, were used. The integral background rate for the gamma-ray energy range of 20 - 2760 keV and 24-h counting time was of 1.76 cps, a value comparable to the accepted value of 1 cps for well-shielded spectrometers in the energy range of 50-1500 keV [21].

The natural background gamma-ray spectrum is mainly due to the gamma-emitting radionuclides of the uranium-radium (^{238}U-^{226}Ra) and thorium (^{232}Th) radioactive series, as well as ^{40}K radionuclide. The aleatory temporal variation of the radon's activity in the natural background of the laboratory requires an

alternately counting of the sample and natural background, especially for low level radioactivity samples.

To determine radium radioactivity, the samples are sealed and measured after 3-4 weeks in order to establish the radioactive equilibrium between ^{226}Ra and its gaseous radioactive descendant ^{222}Rn (radon). ^{214}Pb and ^{214}Bi radon's decay progenies are being measured by gamma-ray spectrometry. U, Th and K concentrations can be determined by measuring uranium (^{238}U), thorium (^{232}Th) and potassium (^{40}K) radioactivity in the sample.

2.2. NEUTRON ACTIVATION ANALYSIS

For a quantitative determination of the elemental contents in steel slag by INAA, the samples were simultaneously irradiated together with appropriate standards, such as cast iron and steel British Chemical Standards (BCS) (Nos. 303, 320, 402/1, 220-2 and 173-1), Eurostandard ECSC-CECA-EGKS No. 482-1, and EURONORM CRM No. 085-1, available from Chemical Laboratory of Romanian Iron and Steel Works at Galati, as well as EOP coal ash standard prepared and certified by the Institute of Radioecology and Nuclear Techniques Kosice, Czechoslovakia. In addition, metallic gold acid solution, KCl and Al_2O_3 have been used as comparator standards.

Neutron irradiation was carried out at the VVR-S Nuclear Reactor of IFIN-HH, at a neutron fluence rate of 10^{12} $n.cm^{-2}\cdot s^{-1}$, during 15 s for short-lived radionuclides, as well as for 30 min, and 2 h for long - lived ones. In order to determine radionuclides of various half-lives, decay time between 2 and 8 min for short-lived nuclides, and ranging from 1 to 4 d for long-lived nuclides were chosen. The gamma spectrometric system for the measurement of the induced radioactivity in samples and standards consisted of a 130 cm^3 volume Ge(Li) ORTEC detector (2.1 keV energy resolution at 1.33 MeV of ^{60}Co, and 30 % relative efficiency), coupled with a 4096 multichannel analyzer CANBERRA based on PC.

3. RESULTS AND DISCUSSION

Table 1 presents the activity concentration values (Λ) of ^{238}U (by ^{234}Th decay daughter), ^{226}Ra (by ^{214}Pb and ^{214}Bi decay products), ^{232}Th (by ^{212}Pb, ^{208}Tl and ^{228}Ac decay products), ^{235}U, and ^{40}K, determined by gamma-ray spectrometry in a slag material from the metallurgical factory at Galati, Romania (expressed in Bq/kg). The analytical uncertainties were calculated from the statistical counting uncertainty and detection efficiency uncertainty for each measured radionuclide. This table also contains the characteristic gamma-rays taken into account and their absolute emission probabilities (ORTEC MCA software catalog). The ^{208}Tl gamma-ray emission probability in this table has been corrected for ^{212}Bi α decay branching ratio of 35.94 % [12,22]. Detection limit corresponds to 3σ of the background.

The concentrations of U, Th and K given in Table 1 are calculated taking into account that 1 g natural U yields 12352.5 Bq ^{238}U and 568.8 Bq ^{235}U, 1 g natural Th yields 4057.2 Bq ^{232}Th, and 1 g K yields 31.7 Bq ^{40}K [12]. To calculate U concentration from ^{226}Ra activity, the radioactive equilibrium between ^{226}Ra and ^{238}U series head is necessary to be established.

As can be seen from Table 1, a rather good agreement between the activity values were obtained for the measured decay products of ^{226}Ra and ^{232}Th, respectively, in the investigated sample. Their average activity concentrations were calculated as arithmetic (unweighted) means of the daughters' activities.

Table 2 presents a comparison of the activity concentrations determined by gamma-ray spectrometry on the steel slag sample, in this work, with permitted radioactivity levels given by the Romanian norms for two types of metallurgical slag (steelwork slag and furnace slag) [23], as well as with radioactivity levels previously reported for the furnace slag elaborated by the steel factory at Galati, obtained as an average of a few hundreds of samples [10].

The elements determined by INAA in a steel slag sample from Galati are the following: Al, Mn and V (by short-term neutron irradiation), as well as As, Au, Ba, Ca, Ce, Co, Cr, Cu, Fe, Hf, K, La, Mo, Na, Rb, Sb, Sc, Sm, W and Zn (by long-term neutron irradiation). Their concentration values, in mg/kg, are given in Table 3. Qualitative analysis was only made for Ga, Ni, Ta, and Zr.

For a comparison, Table 3 also contains INAA concentration values previously determined, by long-term neutron irradiation at the VVR-S reactor of IFIN-HH, on furnace slag used in preparing of ceramic blocks that can substitute the usual bricks (irradiation time of 77 h at $1.1 \cdot 10^{11}$ cm^{-2}·s^{-1} thermal neutron flux, and of 1-3 hours at $2.3 \cdot 10^{12}$ cm^{-2}·s^{-1} mixed neutron flux, counting time of 1-2 hours, and decay times of 3-4 d, 6-7 d and 25-30 d, for three runs of measurements, respectively) [8].

Table 1

Radioactivity analysis of a slag sample from Arcelor-Mittal Galati
by low-background gamma-ray spectrometry

Parent nuclide	Decay product	E_γ (keV)	I_γ	Activity concentration Λ (Bq/kg)	σ (Bq/kg)	Element concentration (mg/kg)	σ (mg/kg)
^{238}U	^{234}Th	63.3	0.048	< 14.2		< 1.15	
^{238}U	^{234}Th	92.4+92.8	0.056	13.5	5.17	1.10 (U)	0.42
^{226}Ra	^{214}Pb	295.2	0.185	8.20	0.68		
(^{238}U series)	^{214}Pb	352.0	0.358	9.22	0.53		
	^{214}Bi	609.3	0.448	8.74	0.80		
	^{214}Bi	1120.3	0.148	8.41	1.95		
	^{214}Bi	1764.5	0.1536	8.53	1.64		

Table 1 (continued)

^{226}Ra (average)				8.62	0.56	0.681 (U)	0.044
^{235}U	^{235}U*	185.7	0.572	0.773	0.266	1.36 (U)	0.47
^{232}Th	^{212}Pb	238.6	0.433	3.79	0.51		
	^{208}Tl**	583.1	0.304	3.18	0.79		
	^{228}Ac	911.1	0.29	4.20	0.68		
^{232}Th (average)				3.73	0.39	0.918 (Th)	0.095
^{40}K	^{40}K	1460.8	0.1067	5.14	3.50	162.0 (K)	110

* Corrected for the spectral interference with ^{226}Ra (186.0 keV), which is measured by ^{214}Pb and ^{214}Bi decay products.
** Corrected for ^{212}Bi α decay branching ratio of 35.94 % [12,22].

Table 2

Natural radioactivity of a steel slag sample from Arcelor-Mittal factory in Galati, compared with furnace slag radioactivity previously determined [10] and maximum permissible levels given by the Romanian norms [23], Bq/kg

Parent nuclide	Decay product	Λ (this work)	Λ (furnace slag) [10]	Permitted levels for steelwork slag [23]	Permitted levels for furnace slag [23]
^{226}Ra	^{214}Pb, ^{214}Bi	8.62	113.7	21.4	173.0
^{232}Th	^{212}Pb, ^{208}Tl, ^{228}Ac	3.73	29.4	29.3	46.5
^{40}K	^{40}K	5.14	148	33.4	288.0

Table 3

Elemental concentrations in metallurgical slag determined by INAA at IFIN-HH, mg/kg

Element	Steel slag (this work)	Furnace slag [8]
Al	50 ± 1	nd
As	1.00 ± 0.02	5.6 ± 0.1
Au (μg/kg)	48.2 ± 9.2	5.6 ± 1.1
Ba	535 ± 32	605 ± 36
Br	nd	0.7 ± 0.2
Ca (g/kg)	381.0 ± 11.4	256.0 ± 7.7
Ce	80.0 ± 1.6	95 ± 2
Co	11.1 ± 0.4	5.4 ± 0.2
Cr	85 ± 6	44 ± 3
Cs	nd	3.5 ± 0.3
Cu	100.0 ± 9.6	nd
Eu	nd	2.5 ± 0.2
Fe (g/kg)	10.1 ± 0.2	16.6 ± 0.3
Hf	8.6 ± 0.6	4.7 ± 0.3
K (g/kg)	1.42 ± 0.14	8.0 ± 0.8
La	40.0 ± 0.5	42.0 ± 0.5

Table 2 (continued)

Lu	nd	0.63 ± 0.02
Mn	48.0 ± 4.8	nd
Mo	28.0 ± 4.2	14.4 ± 2.0
Na (g/kg)	1.62 ± 0.16	3.39 ± 0.34
Nd	nd	34 ± 3
Rb	46.0 ± 4.3	32 ± 3
Sb	15.0 ± 0.9	0.80 ± 0.05
Sc	11.0 ± 0.2	12.0 ± 0.2
Sm	6.0 ± 0.9	nd
Sr	nd	646 ± 142
Ta	nd	0.40 ± 0.04
Tb	nd	0.5 ± 0.1
Th	nd	9.3 ± 0.2
U	nd	8.2 ± 0.2
Yb	nd	5.2 ± 0.2
V	355 ± 17	nd
W	3.10 ± 0.35	nd
Zn	72 ± 9	51 ± 6

nd - not determined.

4. CONCLUSIONS

Low-background high resolution gamma-ray spectrometry is a suitable method to study the natural radioactivity in iron and steel materials. Radioactivity levels of metallurgical slag originated from Arcelor Mittal Galati is only due to the radionuclides from the uranium-radium and thorium radioactive series, as well as potassium natural radionuclide. Their values are lower than the maximum permissible levels given by the Romanian norms.

INAA technique was employed to determine the slag composition of major, minor and trace elements (Al, As, Au, Ba, Ca, Ce, Co, Cr, Cu, Fe, Hf, K, La, Mn, Mo, Na, Rb, Sb, Sc, Sm, V, W and Zn).

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