Type of the Paper: Article

Holistic analysis of waste copper slag based concrete by means of EIPI method

Wojciech Kubissa [1], Roman Jaskulski [2,*], Damian Gil [3], Iwona Wilińska [4]

[1] Warsaw University of Technology, Faculty of Civil Engineering, Mechanics and Petrochemistry; wojciech.kubissa@pw.edu.pl
[2] Warsaw University of Technology, Faculty of Civil Engineering, Mechanics and Petrochemistry; roman.jaskulski@pw.edu.pl
[3] Lublin University of Technology, Faculty of Civil Engineering and Architecture; Damian Gil gildamian13@gmail.com
[4] Warsaw University of Technology, Faculty of Civil Engineering, Mechanics and Petrochemistry; iwona.wilinska@pw.edu.pl
* Correspondence: roman.jaskulski@pw.edu.pl; Tel.: +48-24-367-2182

Abstract: The aim of the research was a comprehensive evaluation of concrete using the EIPI method. In the evaluation the compressive strength of concrete and its durability properties represented by sorptivity and air permeability were taken into account. Since copper slag waste with increased natural radioactivity was used in the assessed concrete, additional evaluation was carried out taking into account the influence of natural radioactivity within the performance index. Also the reference concrete, which was made without the use of copper slag waste, was evaluated for comparative purposes. In order to make the evaluation as comprehensive as possible, the concrete made with the use of three types of cement was subjected to the assessment: CEM I, CEM II and CEM III. The results show that in both approaches the best result was achieved by concrete with CEM III cement. If natural radioactivity is not taken into account in the evaluation, the best result is obtained by concrete made with copper slag waste, and if radioactivity is considered, the best result is obtained with concrete without addition of the waste. It follows from the above that although natural radioactivity has a significant impact on the EIPI evaluation result, the decisive factor is still the type of cement.

Keywords: concrete performance, concrete durability, EIPI method, copper slag waste, natural radioactivity

1. Introduction

The currently dominant model of goods production in the economy is linear. It assumes the acquisition of raw materials, the production of specific goods associated with the simultaneous production of waste, and then the goods produced after their consumption also become waste. This linear, unidirectional model begins to reach its limits due to the limited amount of natural resources. Another disadvantage is the production of large amounts of waste, which are deposited in landfills. Such landfills not only occupy a place, but can also be a source of emissions of harmful substances or radiation.

In order to be able to develop further harmoniously, we must follow the example of nature, which continually performs recycling processes [1,2]. Thanks to decay processes, which are an important part of its internal cycle, nature is an ideal example of a zero-waste economy. Trying to get at least a little closer to this model, it is worth making attempts to reuse post-production waste, treating it not as waste, but as raw materials of a new era. This is the basic premise of a circular economy, which is currently gaining more and more interest.

The cement and building materials industries offer great opportunities for using different mineral by-products. Materials such as: fly ash, silica fume and blast furnace slag are commonly used as supplementary cementitious materials (SCMs) [3], which introduction into cement composite gives possibility to reduce the amount of cement usage and, consequently, reduction of adverse impact of cement production on the environment. On the other hand, reduction of the amount of landfilled waste is possible. However, the introduction of SCMs into the concrete changes its chemical composition and rheological properties. In effect modifying the properties of the final composite are modified depending on the kind of SCM used, its quantity and physicochemical properties. Therefore, obtaining hardened material with the required properties needs investigation and analysis of physicochemical processes occurring over time in the system. For this purpose, the starting material may requires an additional treatment and modification procedure (e.g. chemical or physical activation) [4–7], and the composition of the mix should be optimized. It is also important that the final material does not adversely affect its user, so it is necessary to study e.g. natural radioactivity.

One of such raw materials, currently not often used in cement composite contrary to the SCMs mentioned above, is copper slag which is a by-product from the process of copper extraction by smelting. The residues from the copper smelting process in the form of hot liquid are taken to landfills where they are cooled and then ground. The copper slag thus obtained contains a significant amount of SiO_2 and if it is cooled down quickly enough, this compound takes an amorphous form and exhibits a pozzolanic activity (ability to react with $Ca(OH)_2$ in the presence of water to produce hydrated silicate and aluminate phases similar to those that are formed during Portland cement hydration). Besides, its physical properties are similar to natural sand [8]. Pure copper slag obtained directly from smelters is a valued abrasive material used in surface blast-cleaning process. Due to the morphology of grains, it is more effective than sand.

Although the ground slag is in large part (in Poland practically entirely) used as an abradant. After such use some of the material is treated and reused, but most of it is considered to be a waste which is in major part disposed in landfills or stockpiles. It contains a small amount of corrosion products and corrosion protection coatings [9] and after the blast cleaning process its granulation is smoother . The fraction content of 0 - 0.125 mm and 0.125 - 0.25 mm is much higher than in the initial material. To distinguish between copper slag and the waste material from blast cleaning procedure, the latter is referred to in the article as waste copper slag.

However, it can be utilised again, and its potential applications are described, amongst others, in [10,11]. Due to its composition and physical form, copper slag can be used in the production of concrete as a partial or total substitute for sand [12–15] even in lightweight concrete [16]. In contrast to e.g. fine fractions of recycled concrete aggregate, the material is also suitable for the production of high-quality concrete, without compromising its quality, and some properties even improves in comparison with concrete manufactured with sand [17,18]. Copper slag used instead of sand significantly improves the consistency of the mixture without changing the amount of mixing water which results in increase in compressive strength [13,17,19]. It is also possible to reduce the water content by about 20% while maintaining the same consistency, thus increasing the compression strength by up to 20%. The material used in the cleaning process does not have these particular advantages, as it deteriorates the consistency of the concrete due to its finer grain size, but it is still very useful in concrete technology. In paper [20] the use of blast-cleaning waste as a substitute for sand in concrete with dosage of cements 300 kg/m^3 and w/c = 0.6 was tested and described. Shrinkage testing of concrete with copper slag as a substitute for sand has shown that such replacement does not have negative consequences of increased shrinkage [12].

An important aspect of using waste materials in the production of concrete is their potential harmful impact on the natural environment. In [21] the authors suggested, that the copper slag is non-toxic and pose no environmental hazard. The slag can be safely considered for use in Portland cement and concrete manufacturing. It should be noted, however, that this material is one of the most intense sources of ionizing radiation among the materials used in construction due to its high content of natural radionuclides [22–25]. Of these, particular attention is paid to the content of radium isotope ^{226}Ra. As a result of its decomposition radon ^{222}Ra is produced, which is a radioactive gas and can be absorbed into the human organism by breathing. There it undergoes further radioactive decay, resulting in radioactive isotopes of lead and bismuth, which as solids accumulate in the body and act as mutagens on its cells [26]. The use of such material as a concrete aggregate requires carrying out tests of the natural radioactivity of the concrete produced from it.

Studies on the radioactivity of building materials and waste used in their production are becoming more and more common [27–30]. So far, there is not a lot of data about radon exhalation rate in building materials containing NORM residues [30]. For example in database [31] there is only 1100 data of 14 European Countries on radon emanation/exhalation rate. The COST Action TU1301 project is being run: "NORM for Building materials (NORM4BUILDING)" with a view to promoting research into the reuse of waste containing increased concentrations of natural radionuclides (NORM) in customised building materials in the construction sector, while taking into account the impact on both external exposure of building users to gamma radiation and indoor air quality. Models are being developed to better simulate the behaviour of NORM residues in different types of building materials.

In the paper the use of waste copper slag obtained from blast-cleaning as a substitute for part of the sand in concrete with 360 kg/m^3 of 42.5 class cements and w/c = 0.45 was tested and described. Some researchers pay attention to the large impact of packing density on many concrete properties [32–35], therefore the concrete mixtures were prepared in two variants which differed from each other in consistency and workability. For each cement type two mixtures with CS were made. In one, the same dosage of superplasticizer as in the reference series was used. In the second, the amount of superplasticizer was experimentally determined in order to obtain consistency similar to the reference series. It was 420±30 mm in table flow test (near the limit between F2 and F3 class).

According to the requirements of the Polish law the tests of natural radioactivity of copper slag waste and the concrete were performed. From the results the coefficients f_1 and f_2 were calculated and compared to the limit values which can be found in the relevant regulations. Leachability of hazardous elements (mainly heavy metals) was also assessed.

Optimization of the manufacturing process, the purpose of which is to obtain a material with required properties, needs consideration of many variables, including knowledge of physicochemical processes occurring during the production process, as well as impact of raw and final materials on the natural environment and on the user. In this work, the main emphasis was placed on evaluation of the composition of the concrete, taking into account its potential natural radioactivity. To evaluate the concrete studied, the method of multi-criteria EIPI assessment presented in [36] was applied, in which as the criteria were used: compressive strength, air permeability and sorptivity as parameters determining the durability of concrete, as well as radioactive activity indices f_1 and f_2 used for the evaluation of building materials. Concrete made of traditional fine aggregate (quartz sand) and concrete, in which waste copper slag characterized by higher values of indices f_1 and f_2, was used as fine aggregate, were evaluated. Due to the co-existence of both positive (improvement of durability and mechanical properties of concrete) and negative (increase in the intensity of ionizing radiation of the material) effects of the use of waste copper slag, the valuation of the applied material solution encounters objective difficulties. The EIPI method allows this judgement to be reduced to a comparison of the value of one indicator, which significantly simplifies the evaluation.

2. Materials and Methods

2.1 Materials

Portland cement CEM I 42.5R, Blast-furnace cement CEM III/A 42.5N from Górażdże Cement Plant and Portland-composite cement CEM II/B-V 42.5N from Lafarge Cement Plant as per PN-EN 197 were used. Basic physical and chemical properties presented by the cement manufacturer are shown in Table 1.

Table 1. Basic physical and chemical properties of the cement

Cement type	setting time		compr.	Specific surface area	specific gravity	SO_3	Cl	Na_2O_{eq}
	start	end	strength	(Blaine)				
	[min]	[min]	[MPa]	[cm^2/g]	[g/cm^3]	[%]	[%]	[%]
CEM I 42.5R	176	231	57.9	3538	3.10	2.52	0.063	0.60
CEM II/B-V 42.5N	203	294	50.6	4888	2.82	2.66	0.063	1.12
CEM III/A 42.5N - LH/HSR/NA	201	306	58.3	4165	2.91	2.30	0.055	0.70

All concrete mixes contained 360 kg/m^3 of cement by 0.45 w/c ratio. Fractions of river sand 0 – 2 mm and granite from Strzegom stone mine fractions of 2 – 8 mm and 8 – 16 mm were used. Aggregates were at laboratory air-dry condition. Copper slag waste from blast cleaning was used as a partial replacement of sand. The ratio of substitution was 66% of sand amount by volume. This amount of waste allowed for the aggregate grading curves both in the reference concrete mixture and in the concrete mixture containing waste, fit between the boundary curves. Superplasticizer Chryso Optima 100 according to PN-EN 934-2 was used. Regular tap water was used as mixing water.

Table 2. Proportions of concrete mixtures [kg/m^3].

Mixture ID Material	CI0	CI66	CI66F	CII0	CII66	CII66F	CIII0	CIII66	CIII66F
CEM I 42.5R	360	360	360	0	0	0	0	0	0
CEM II/B-V 42.5N	0	0	0	360	360	360	0	0	0
CEM III/A 42.5N	0	0	0	0	0	0	360	360	360
natural sand 0-2 mm	598	199	198	587	196	195	591	197	196
granite aggregate 2-8 mm	621	621	618	610	610	608	614	614	612
granite aggregate 8-16 mm	659	659	655	659	647	645	651	651	649
copper slag	0	449	447	0	441	440	0	444	443
water	162	162	162	162	162	162	162	162	162
SP Optima Fluid 100 % m.c.	0.65	0.65	1.65	0.70	0.70	1.30	0.80	0.80	1.50
W/C	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
W+Sp/C	0.457	0.457	0.467	0.457	0.457	0.463	0.458	0.458	0.465

Nine concrete mixtures were prepared. Mix IDs and proportions are presented in Table 2. The consistency of fresh concrete was measured by slump test, in accordance with PN-EN 12350-2.

Specimens were prepared and cured as per PN-EN 12390-2. They were cast in plastic moulds and compacted by double vibration (half and full) on a vibrating table. After one day they were stripped and then water cured in the laboratory for 28 days.

2.2 Performed tests

The compressive strength test was conducted on 100 mm cube specimens on the 28 day of hardening. The test were carried out in accordance with PN-EN 12390-3. The strength tests were performed by using a ToniTechnik instrument of 3000 kN compression force capacity. The rate of loading was maintained at 0.5 MPa/s.

Sorptivity test was conducted on the halves of cubic specimens of 100 mm edge by means of mass method described in [37]. Prior to the sorptivity test, the specimens had been oven-dried to the stable mass at a temperature of 105°C. The measurements were conducted at the temperature of approximately 20°C. The specimens were weighed and arranged in a water containing vessel. Then they were immersed up to the height of 3 mm.

Air permeability test of concrete was performer by means of Torrent method with use of Proceq equipment. Test was conducted on two 150 mm cube specimens, which were cured in water for 28 days and then were stored in air-dry laboratory conditions (temperature t=20±2°C and RH of air equal 55±10%) until they reached age of 90 days. Moisture content was measured, before conducting the air permeability test, using Tramex CMEX II, which is recommended by Swiss Standard SIA 262/1 Annex E and by [38]. Tests procedure is described in [39].

Tests for the content of hazardous substances released from waste copper slag (i.e. leaching tests) were carried out in accordance with the applicable standards and regulations by the Laboratory of Solid Waste Analysis at the Central Environmental Monitoring Department of the Mining Institute in Katowice in accordance with Annex 3 to the Ordinance of the Minister of Economy of 16 July 2015 on the approval of waste for storage at landfills (Journal of Laws of 2015, item 1277).

The PI-MAZAR01 meter was used to perform tests of natural radioactivity. It is designed to determine the concentration of natural radioactive elements such as radium, potassium or thorium. The measuring part is located in a lead shielding cabin, which includes: a scintillation probe type SSU-70-2 with a NaI(Tl) (thallium-doped sodium iodide) crystal, a preamplifier and a high voltage power supply as well as a calibration isotope source Cs 137 used to stabilize the measuring path. In the reading part there is a microprocessor controller. The analyser is adapted to work with a PC, so that it is possible to visualize the spectrometric spectrum and save the measurement results on a hard disk.

The natural radioactivity measurement procedure begins with the calibration of the analyser according to the instrument manual and the recommendations of the instructions of Building Research Institute (ITB, Poland) [40] which recommends periodical calibration at least once a year and control measurements with the use of standards once a month or as a result of a change in conditions after 24 hours (e.g. change in temperature at the place of measurement). Samples (so-called qualification samples) were prepared for testing, ground to a maximum grain size of 2 mm, then dried to a constant mass at 105˚C and left to cool down under laboratory conditions to reach air-dry state. The prepared material was placed in the Marinelli type containers with a volume of 1700 cm^3. The container and sample were then weighed, secured with adhesive tape and marked accordingly. The weight of the material of each sample was calculated on the basis of the performed weights. Afterwards, the samples were seasoned in containers for 7 days at a significant distance from the measuring house (over 2 m). Before starting the measurements, the background of the samples was calculated on an aluminium mass standard and then the containers with samples were placed in the measuring chamber of the shielding house. During the study, the meter collected the measurement spectrum and then analysed the number of impulses recorded in potassium, radar and thorium windows, which were the basis for calculating concentrations of radioactive elements and qualification coefficients f_1 and f_2.

3. Results

3.1 Mechanical and durability properties

The results of compressive strength, sorptivity and air permeability tests are presented and discussed in detail in the article [39]. Table 3 presents the average values of those of all the obtained results, which were used for calculations in the EIPI analysis.

Table 3. Test results employed in EIPI calculations [39]

ID of mixture **Test**	**CI0**	**CI66**	**CI66F**	**CII0**	**CII66**	**CII66F**	**CIII0**	**CIII66**	**CIII66F**
Flow [mm]	395	315R	410	410	310R	415	410	330R	440
Compressive strength 28d [MPa]	55.03	53.30	60.16	54.56	57.42	60.38	66.44	61.34	62.45
Compressive strength 90d [MPa]	60.78	61.98	68.18	63.00	67.32	70.50	73.67	68.60	71.96
Sorptivity [$cm^3/(cm^2*h^{0.5})$]	0.091	0.076	0.067	0.088	0.085	0.089	0.061	0.063	0.047
RH Tramex dry	0.40	0.54	0.68	0.58	0.89	0.81	1.42	1.39	1.33
Air permeability k_T [$*10^{-16}m^2$]	2.903	1.922	1.022	1.214	0.563	0.377	0.081	0.245	0.066

Flow: R- collapse of the specimen after lifting the cone

Presented above results show that compressive strength of CEM I and CEM II cement concretes containing copper slag increase both after 28th and 90th day of hydration compared to the reference (CI0 or CII0 respectively). Only in the case of CEM III cement concrete, introduction of waste copper slag reduces compressive strength. On the other hand, the presence of the sand replacement results in improvement of tightness of all investigated concrete compositions In summary, the results obtained indicate a predominance of benefits from the use of copper slag waste in concrete.

3.2 Leaching and natural radioactivity tests

Table 4 presents the results of a test of the leaching of hazardous substances from copper slag waste in comparison with the requirements of Polish legal regulations (The Ordinance of the Council of Ministers of 18 November 2014 on the conditions to be met when introducing sewage into water or soil and on the substances particularly harmful to the aquatic environment). The tests showed that the content of hazardous substances identified in the water extract does not exceed the permissible concentrations of these components specified in the applicable regulations.

Table 4. Hazardous substances released to water extract from waste copper slag.

Identified ingredient or parameter	Content in the water extract [mg/l]	Allowable concentration [mg/l]
Cd	< 0.001	0.2
Cr	<0.005	0.5
Cr(VI)	<0.01	0.1
Cu	0.052	0.5
Ni	<0.005	0.5
Pb	0.009	0.5
Zn	<0.05	2.0
Ba	<0.03	2.0
Sb	<0.005	0.3
As	0.026	0.1
Mo	0.011	1.0
Hg	<0.001	0.1
Se	<0.01	1.0
chlorides	<5	1000
flourides	<0.1	25.0
sulphates	3.6	500
DOC*	1.9	30
soluble matter	33.2	---
pH of water extract	9.9	---

*) Dissolved Organic Carbon

The allowable content of natural radioactive isotopes in raw materials, building materials and waste used in construction is regulated by the Ordinance of the Council of Ministers of 2 January 2007 on requirements concerning the content of natural radioactive isotopes of potassium K-40, radium Ra-226 and thorium Th-228 in raw materials and materials used in buildings intended for human habitation and livestock, as well as in industrial waste used in construction, and control of the content of these isotopes. This Ordinance also applies to waste used for the production of cement and concrete (such as fly ash, slag including copper slag used as an abrasive). Raw materials and building materials are qualified on the basis of two activity indicators f_1 and f_2.

The first of the above mentioned indicators, f_1, identifies the exposure to radiation emitted by natural radionuclides (i.e. the nuclei of radioactive atoms): potassium (K), radium (Ra) and thorium

(Th). This indicator takes into account the different activities of individual radioisotopes and is calculated using the formula (1):

$$f_1 = \frac{C_K}{3000\ Bq/kg} + \frac{C_{Ra}}{300\ Bq/kg} + \frac{C_{Th}}{200\ Bq/kg} \tag{1}$$

where: C_K, C_{Ra}, C_{Th} are concentration values of potassium ^{40}K, radium ^{226}Ra and thorium ^{228}Th in Bq/kg.

The f_2 indicator, calculated according to Equation (2) indicates the radium (Ra) content and indirectly the α radiation intensity emitted by radon (Rn) and products of its radioactive decay present in building materials.

$$f_2 = C_{Ra} \tag{2}$$

The results of tests of natural radioactivity of waste copper slag and coarse aggregate, i.e. granite, carried out using the method described above, are presented in Tables 5 and 6.

Table 5. Results of natural radioactivity tests of waste copper slag.

radionuclide	**radioactivity [Bq/kg]**
^{226}Ra	400±12
^{228}Th	40.1±3.1
^{40}K	749±51

which translates into indicator values f_1 and f_2: $f_1 = 1.78±0.05$; $f_2 = 400±12$.

Table 6. Results of natural radioactivity tests of granite

radionuclide	**radioactivity [Bq/kg]**
^{226}Ra	35.4±6.1
^{228}Th	43.6±4.4
^{40}K	1019±69

which translates into indicator values f_1 and f_2: $f_1 = 0.67±0.05$; $f_2 = 35.4±6.1$.

According to the abovementioned Ordinance, the activity rates f_1 and f_2 must not exceed by more than 20% the limit values of $f_1 = 2$ and $f_2 = 400$ Bq/kg for industrial waste used in the construction of ground structures built on built-up areas or intended to be built on in a local zoning plan and for the levelling of such areas. This means that the tested waste may be used in the production of concrete for the above mentioned applications. Apart from testing the natural radioactivity of selected concrete components, samples of the concrete itself were also tested. The results of these tests in the case of concrete without and with waste copper slag are presented in Table 7.

Table 7. Results of natural radioactivity tests of concrete

Concrete ID	**radionuclide activity [Bq/kg]**			**indicator value**	
	^{226}Ra	**^{228}Th**	**^{40}K**	**f_1**	**f_2**
CI0	16.1±5.1	34.5±4.0	594±48	0.42±0.04	16.1±5.1
CII0	60.8±3.7	47.8±3.5	758±60	0.68±0.03	60.8±3.7
CIII0	16.0±5.4	37.0±4.2	612±50	0.44±0.04	16.0±5.4
CI66F	101±10	44.1±2.9	759±57	0.81±0.05	101±10
CII66F	127±10	53.6±3.5	855±57	0.98±0.05	127±10
CIII66F	115±10	45.3±3.1	781±58	0.87±0.05	115±10

The results presented in Table 7 allow to conclude that despite a relatively high level of values of indicators f_1 and f_2 obtained in the case of copper slag waste, concrete made with this material has a moderate level of radioactivity, although it is significantly higher than in the case of concrete made without the use of copper slag waste. Another important conclusion is the noticeably higher level of radioactivity of concrete, in which CEM II/B-V cement was used, compared to the series made with other cements and the same type of aggregate. The increased radioactivity of these concrete series should be linked to the presence of fly ash in the cement, which is a material with an increased radioactivity level. [27,28,41,42]. Relative and absolute differences in the values of indicators f1 and f2 in the case of CEM II/B-V cement concrete are significantly smaller when copper slag waste is used, which indicates the dominant influence of this component on the radioactivity of the obtained concrete. However, the impact of cement is not negligible and should be taken into account when designing the composition of concrete mix.

4. Discussion

4.1 Assumptions and calculation method

Optimization of the composition of the concrete mix requires taking into account not only the properties of the final composite, but also the need to limit its broadly understood impact on the environment.

In the calculations using EIPI method, emissions, consumption of raw materials and rarity of their occurrence were assumed according to the data presented in the article [36]. The value of PI is evaluated on the basis of the sum of normalized values of selected concrete properties. The compressive strength and sorptivity tested after 28 days were used for calculations. The reference values were adopted at the same level as in [36], i.e. $f_{cm} = 60$ MPa i S = 0.120 cm/h$^{0.5}$. As another concrete property, the air permeability k_T measured with Torrent apparatus on specimens dried at 65°C was included in the evaluation. As a reference value, the limit used for exposure classes XC4, XD1, XD2a, XF1, XF2 in Swiss Standard SIA 262 (SIA 262/1 Annex E) [38], i.e. 2.0·10-16 m^2, was used.

Equation (3), which contains the above mentioned concrete parameters, was used to calculate PI without taking into account radioactivity. The relevant quotients from normalization are multiplied by the respective weighting coefficients, whose values were taken as: $w_{fcm} = 0.4$, $w_{kT} = 0.3$ and $w_S = 0.3$ in the present study. The sum of weighting coefficients should be equal to unity so that a concrete mix with reference values of selected properties will give a PI value of 1.

$$PI = \frac{fcm}{60\ MPa} \times w_{fcm} + \frac{0.120\ cm/h^{0.5}}{S} \times w_S + \frac{2.0*10^{-16} m^2}{kT} * w_{kT} \tag{3}$$

In the further concrete assessment, the values of indicators f_1 and f_2 were taken into account in the PI calculations. In their case, the reference values were adopted according to the Ordinance mentioned above, i.e. $f_1 = 2$ and $f_2 = 400$ Bq/kg. To calculate so extended PI values Equation (4) was used.

$$PI = \frac{fcm}{60\ MPa} \times w_{fcm} + \frac{0.120\ cm/h^{0.5}}{S} \times w_S + \frac{2.0*10^{-16} m^2}{kT} * w_{kT} + \frac{2}{f_1} * w_{f1} + \frac{400}{f_2} * w_{f2} \tag{4}$$

The higher values of PI achieves analysed concrete, the more desirable engineering properties it possesses. The weighting coefficients in Equation (4), were assumed in a few variants which are presented and described in the next subsection.

The value of EI is calculated according to Equation (5) as the square root of the sum of normalized total emission of CO_2 and normalized total raw materials usage both multiplied by weights that sum to one.

$$EI = \sqrt{\frac{EM}{490\ kg/m^3} \times w_{EM} + \frac{RM}{2000\ kg/m^3} \times w_{RM}} \tag{5}$$

To normalize the values of total emission of CO_2 (EM) and usage of raw materials (RM), which have to be calculated first, they are divided by reference values. The reference values in this study were assumed as in [36] and equal approximately 490 kg of CO_2 emission and 2000 kg/m^3 of raw materials usage per cubic metre of concrete. The weighting coefficients were assumed as: $w_{EM} = 0.5$ and $w_{RM} = 0.5$.

A lower EI value means that analysed concrete is more environmentally friendly. Results of calculations the EI for analysed concrete mixtures are presented in Table 8 and repeatedly in Table 9.

A comprehensive evaluation of concrete, taking into account both its ecological impact (EI) and engineering performance (PI), is expressed by Gross Ecological and Performance Indicator (GEPI), which is calculated using Equation (6):

$$GEPI = \sqrt{EI^2 + \frac{1}{PI^2}} \tag{6}$$

When designing a concrete mix in practice, a low GEPI is aimed for concrete with favourable concurrent EI and PI, while a high GEPI should be avoid.

It should be stressed very clearly here that the comparison of different variants of the designed concrete mixtures using the EIPI method in engineering practice will be only reasonable, if all the technical parameters of the concrete obtained from the designed concrete mixtures, taken into account in the PI calculations, meet the specified limit requirements defined by the construction designer or the relevant regulations or standards.

4.2 Results analysis and discution

The results of calculations conducted without taking into account the influence of radioactive nuclide content on the PI value are presented in Figure 1. The PI and EI values calculated under this assumption are presented in Table 8 together with the GEPI values calculated on their basis. Series with CEM III cement are characterized by the most favourable EI value due to lower clinker content than in other cements, resulting in lower consumption of natural resources and lower carbon dioxide emission. The highest PI values were achieved by the CI66F and CIII66F series. This is mainly due to higher tightness than in other series, which consists of the lowest values of sorptivity and one of the lowest values of air permeability. The overall assessment based on GEPI values indicates as the best series CIII66F (GEPI=0.897) and CIII66 (GEPI=1.001). The CI0 series (GEPI=1.480) and CI66 series (GEPI=1.314) were the least favourable from the point of view of the complete score.

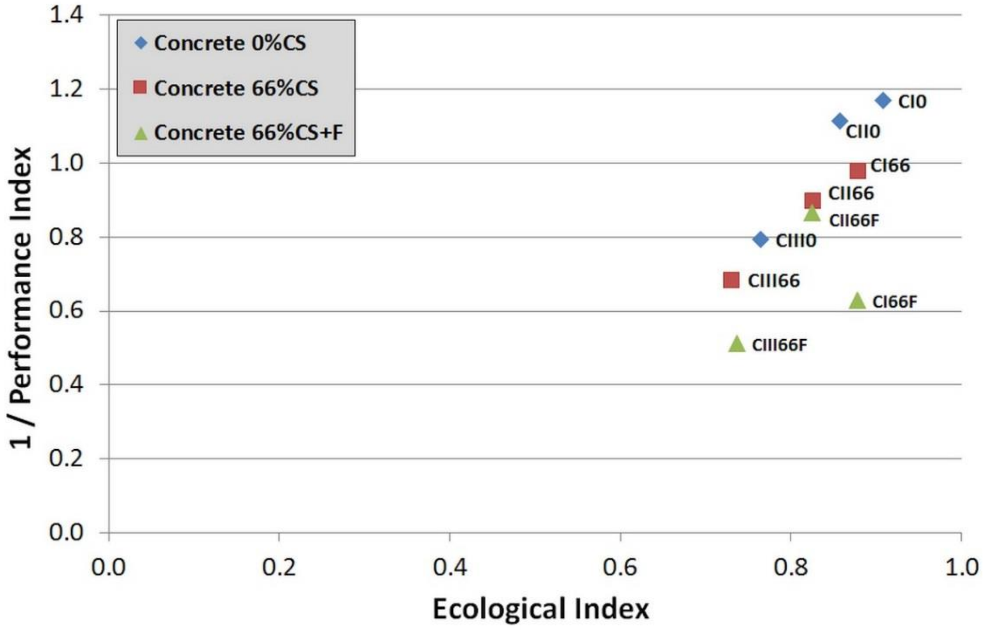

Figure 1. Ecological Index plotted against reciprocal of Performance Index in variant 0.

In the next stage of the assessment, the impact of the radioactive nuclides contained in the concrete was also taken into account. This was done by using formula 4 in the calculations of PI values. Four variants differing in the values of weights for the components of the formula taking into account indicators f_1 and f_2 were used in the calculations. Their influence on PI value was differentiated by assigning to them in the calculations a sum of weights equal to 0.3 (variants S) or 0.7 (variants B). Additional differentiation was based on taking equal weights values (variants S1 and B1) and assigning about twice as much weight to f_2 indicator in relation to f_1 indicator (variants S2 and B2). The list of adopted values of weights is presented in Table 9 and the obtained GEPI results are presented in Table 11.

Table 8. EI, PI and GEPI values without taking into account natural radiation.

	Concrete ID								
	CI0	CI66	CI66F	CII0	CII66	CII66F	CIII0	CIII66	CIII66F
EI	0.908	0.879	0.878	0.858	0.826	0.825	0.764	0.731	0.737
PI	0.856	1.024	1.592	0.898	1.114	1.156	1.262	1.463	1.956
GEPI	1.480	1.314	1.080	1.405	1.220	1.195	1.101	1.001	0.897

Table 9. Variants of weight values

weighting coefficient	weight values in variant:				
	0	S1	S2	B1	B2
w_{fcm}	0.40	0.28	0.28	0.12	0.12
w_{S}	0.30	0.21	0.21	0.09	0.09
w_{kT}	0.30	0.21	0.21	0.09	0.09
w_{f1}	0.00	0.15	0.10	0.35	0.24
w_{f2}	0.00	0.15	0.20	0.35	0.46

Table 10. Results of GEPI calculations

Concrete ID	**GEPI values in variant:**					**max.**	**min.**
	0	**S1**	**S2**	**B1**	**B2**		
CI0	1.480	0.929	0.923	0.913	0.911	0.929	0.911
CII0	1.405	0.986	0.967	0.901	0.893	0.986	0.893
CIII0	1.101	0.787	0.781	0.770	0.768	0.787	0.768
CI66	1.314	1.062	1.048	0.962	0.953	1.062	0.953
CII66	1.220	1.046	1.033	0.948	0.936	1.046	0.936
CIII66	1.001	0.902	0.893	0.836	0.826	0.902	0.826
CI66F	1.080	1.001	0.993	0.952	0.944	1.001	0.944
CII66F	1.195	1.038	1.025	0.946	0.934	1.038	0.934
CIII66F	0.897	0.862	0.856	0.830	0.822	0.862	0.822

The analysis of the obtained results showed a clear but small variation in the calculated PI values obtained in the individual variants. Regardless of the adopted variant, the mutual proportions of GEPI values obtained in the case of individual series remained very close to each other. Therefore, it was found pointless to present in detail the results of EI and PI calculations of all variants and to visualize them on the figures. Only the results of calculations obtained in variant B2 were selected, in which the influence of natural radioactivity of concrete on the result of PI calculations was the greatest. The results obtained in this variant are presented in Table 11 and Figure 2.

Table 11. EI, PI and GEPI values taking into account the natural radiation - variant B2.

	Concrete ID								
	CI0	CI66	CI66F	CII0	CII66	CII66F	CIII0	CIII66	CIII66F
EI	0.908	0.879	0.878	0.858	0.826	0.825	0.764	0.731	0.737
PI	12.828	2.722	2.892	4.002	2.273	2.286	12.969	2.591	2.738
GEPI	0.911	0.953	0.944	0.893	0.936	0.934	0.768	0.826	0.822

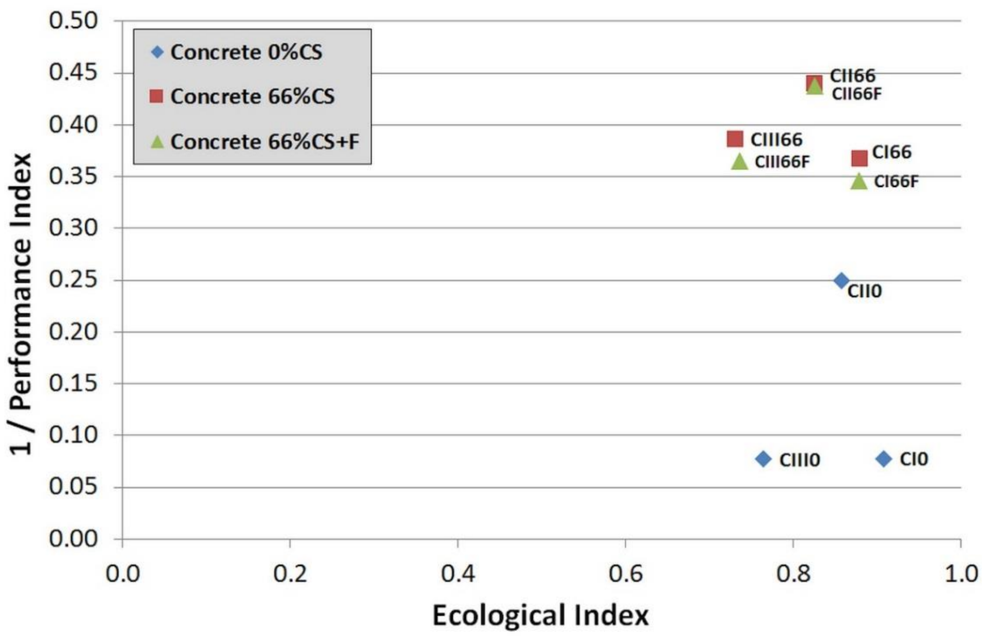

Figure 2. Ecological Index plotted against reciprocal of Performance Index in variant B2.

As can be seen, the weight variation in the adopted variants had the greatest impact on the GEPI values for CEM II cement concrete, regardless of the type of fine aggregate and plasticiser usage, and for copper slag waste, regardless of the type of cement. However, this variation, understood as the difference between the highest and the lowest GEPI value, reaches a maximum of less than 12%.

The significantly lower natural radioactivity of concrete with CEM I and CEM III without the use of copper slag waste caused PI in these two series to be high, several times higher than in series with the same type of cement and waste. It is also about three times higher than that of CII0 series, in which cement with increased natural radioactivity due to fly ash content is used. CIII0 concrete (GEPI=0.768) proved to be the best with such established assessment criteria. Despite increased natural radioactivity, mixtures with the waste and blast furnace slag cement were ranked on the next two places (GEPI=0.822 and GEPI=0.826). The worst results were obtained in case of series with CEM I cement and copper slag waste (GEPI=0.953 and GEPI=0.944). This allows to state that the use of copper slag waste improves the performance of concrete so much that it reduces the negative impact of increased radioactivity in the assessment performed by the EIPI method.

It should be taken into account that when PI is calculated on the basis of other parameters (selected properties, reference values, weights), it is not possible to directly compare PI and GEPI results obtained in the calculation of the different variants. The comparisons make sense between the different concrete mixes assessed on the basis of the criteria adopted for the specific variant and adapted to the requirements of the specific conditions of concrete exploitation and, for example, the limitations related to natural radioactivity. The variant calculations of the impact of natural radioactivity of concrete on the PI value presented in the paper were aimed at analysing various variants of differentiation of weights and their impact on the final assessment of concrete.

5. Conclusions

Results of the performed research allowed to formulate following conclusions:

- Replacing in concrete mixture a part of sand with waste copper slag does not aggravate any of the tested properties of concrete. The use of a plasticiser also allows to obtain the same consistency as in reference series made with sand only.
- Concrete with the addition of copper slag waste is tighter than reference concrete. This effect is particularly noticeable in the case of concrete of the same consistency as the reference concrete.
- Despite the high natural radioactivity of copper slag waste, it is possible to obtain concrete with radioactivity indices much lower than the maximum permitted values. The f_1 values of CI66F

and CIII66F series of concrete are higher than those obtained with CII0 concrete without copper slag waste by 19% and 28% respectively.

- Excluding in the assessment the natural radioactivity of concrete, the highest GEPI rating was obtained by the series CEM III66F with copper slag waste.
- In applications where the natural radioactivity of concrete is of greater importance, the series with CEM III0 without copper slag waste obtained the most favourable result.
- The EIPI method allows for a comprehensive assessment of concrete properties, including among others natural radioactivity. Such an extended assessment may be useful in applications where increased natural radioactivity is not recommended, e.g. indoor areas for permanent human habitation.
- The EIPI evaluation showed that CEM III cement concrete is the best choice, regardless of whether natural radioactivity is considered or not. Omitting it in the evaluation leads to the conclusion that the best concrete is the one with the use of copper slag waste. However, taking into account natural radioactivity, the concrete without the addition of copper slag waste is moved to the leading edge of the CEM III series of concrete. This means that although the type of cement is the dominant factor in the EIPI evaluation, the level of natural radioactivity is also important.
- Taking into account mechanical properties of the composite, parameters relating to tightness of hardened structure as well as environmental impact of cement concrete (including CO2 emission, radioactivity and consumption of natural resources), cement concrete made of CEM III is beneficial.

Author Contributions: W.K. planned and organized the experimental study, made the selection of materials and the mix design, wrote part of the article text. R.J. conducted an analysis of the results using the EIPI method, wrote part of the article text, edited the text. D.G. performed tests of natural radioactivity and developed the results of the tests. I.W. co-edited the text, participated in analysing the results and formulating conclusions. All authors read and agreed with the final version of this manuscript.

Acknowledgments: The work has been supported by the City of Płock through the Mayor's Research Grants Programme "Collaboration with Universities".

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Murray, A.; Skene, K.; Haynes, K. The Circular Economy: An Interdisciplinary Exploration of the Concept and Application in a Global Context. *J. Bus. Ethics* **2017**, *140*, 369–380, doi:10.1007/s10551-015-2693-2.
2. Zaman, A. A Strategic Framework for Working toward Zero Waste Societies Based on Perceptions Surveys. *Recycling* **2017**, *2*, 1–15, doi:10.3390/recycling2010001.
3. Lothenbach, B.; Scrivener, K.; Hooton, R. D. Supplementary cementitious materials. *Cem. Concr. Res.* 2011, *41*, 1244–1256.
4. Hela, R.; Orsakova, D. The mechanical activation of fly ash. *Procedia Eng.* **2013**, *65*, 87–93, doi:10.1016/j.proeng.2013.09.016.
5. Garcia-Lodeiro, I.; Donatello, S.; Fernández-Jiménez, A.; Palomo, Á. Hydration of hybrid alkaline cement containing a very large proportion of fly ash: A descriptive model. *Materials (Basel).* **2016**, *9*, 1–16, doi:10.3390/MA9070605.
6. Wilińska, I.; Pacewska, B. Influence of selected activating methods on hydration processes of mixtures containing high and very high amount of fly ash: A review. *J. Therm. Anal. Calorim.* **2018**, *133*, 823–843, doi:10.1007/s10973-017-6915-y.
7. Wilińska, I.; Pacewska, B.; Ostrowski, A. Investigation of different ways of activation of fly ash–cement mixtures: Part 1. Chemical activation by Na2SO4 and Ca(OH)2. *J. Therm. Anal. Calorim.* **2019**,

doi:10.1007/s10973-019-08485-1.

8. Meenakshi Sudarvizhi, S.; Ilangovan, R. Performance of Copper slag and ferrous slag as partial replacement of sand in Concrete. *Int. J. Civ. Struct. Eng.* **2011**, *1*, 918–927.
9. Rzechuła, J. Gospodarcze wykorzystanie odpadowego ścierniwa z żużla pomiedziowego. In *Fizykochemiczne Problemy Mineralurgii, zeszyt 28*; Łuszczkiewicz, A., Ed.; Politechnika Wrocławska: Wrocław, 1994; pp. 207–218.
10. Gorai, B.; Jana, R. K.; Premchand Characteristics and utilisation of copper slag - A review. *Resour. Conserv. Recycl.* **2003**, *39*, 299–313, doi:10.1016/S0921-3449(02)00171-4.
11. Dhir, R. K.; de Brito, J.; Mangabhai, R.; Lye, C. Q. *Sustainable Construction Materials-Copper Slag*; Woodhead Publishing: Cambridge, 2017;
12. Ayano, T.; Sakata, K. Durability of concrete with copper slag fine aggregate. *Spec. Publ.* **2000**, *192*, 141–158.
13. Al-Jabri, K. S.; Al-Saidy, A. H.; Taha, R. Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete. *Constr. Build. Mater.* **2011**, *25*, 933–938, doi:10.1016/j.conbuildmat.2010.06.090.
14. Alp, I.; Deveci, H.; Süngün, H. Utilization of flotation wastes of copper slag as raw material in cement production. *J. Hazard. Mater.* **2008**, *159*, 390–395, doi:10.1016/j.jhazmat.2008.02.056.
15. Kubissa, W.; Jaskulski, R.; Ng, P.-L.; Chen, J. Utilisation of Copper Slag Waste and Heavy-weight Aggregates for Production of Pre-cast shielding Concrete Elements. *J. Sustain. Archit. Civ. Eng.* **2018**, *22*, 39–47, doi:10.5755/j01.sace.22.1.20006.
16. Jaskulski, R.; Kubissa, W. Lightweight concrete with copper slag waste as sand substitution. In *MATEC Web of Conferences*; 2018; Vol. 163.
17. Al-jabri, K. S.; Hisada, M.; Al-saidy, A. H.; Al-oraimi, S. K. Performance of high strength concrete made with copper slag as a fine aggregate. *Constr. Build. Mater.* **2009**, *23*, 2132–2140, doi:10.1016/j.conbuildmat.2008.12.013.
18. Ambily, P. S.; Umarani, C.; Ravisankar, K.; Ranjan, P.; Bharatkumar, B. H.; Iyer, N. R. Studies on ultra high performance concrete incorporating copper slag as fine aggregate. *Constr. Build. Mater.* **2015**, *77*, 233–240, doi:10.1016/j.conbuildmat.2014.12.092.
19. Wu, W.; Zhang, W.; Ma, G. Optimum content of copper slag as a fine aggregate in high strength concrete. *Mater. Des.* **2010**, *31*, 2878–2883, doi:10.1016/j.matdes.2009.12.037.
20. Kubissa, W.; Jaskulski, R.; Simon, T. Surface blast-cleaning waste as a replacement of fine aggregate in concrete. *Archit. Civ. Eng. Environ.* **2017**, *3*, 89–94.
21. Shanmuganathan, P.; Lakshmipathiraj, P.; Srikanth, S.; Nachiappan, A. L.; Sumathy, A. Toxicity characterization and long-term stability studies on copper slag from the ISASMELT process. *Resour. Conserv. Recycl.* **2008**, *52*, 601–611, doi:10.1016/j.resconrec.2007.08.001.
22. Zapotoczna-Sytek, G.; Mamont-Cieśla, K.; Rybarczyk, T. Naturalna promieniotwórczość wyrobów budowlanych, w tym autoklawizowanego betonu komórkowego (ABK). *Przegląd Bud.* **2012**, *83*, 39–42.
23. Keller, G.; Hoffmann, B.; Feigenspan, T. Radon permeability and radon exhalation of building materials. *Sci. Total Environ.* **2001**, *272*, 85–89, doi:10.1016/S0048-9697(01)00669-6.
24. Skowronek, J.; Michalik, B.; Dulewski, J. NORM in Polish industry. *Proc. an Int. Conf. held Szczyrk, Poland, 17–21 May 2004* **2004**, 1–9.
25. Cooper, M. B. Naturally Occurring Radioactive Materials (NORM) in Australian Industries - Review of Current Inventories and Future Generation. *EnviroRad Serv. Pty. Ltd.* **2005**.

26. Clavensjö, B.; Åkerblom, G. The Radon Book. *J. Radiol. Prot.* **1996**, *16*, doi:10.1088/0952-4746/16/3/020.
27. Kovler, K. Radiological constraints of using building materials and industrial by-products in construction. *Constr. Build. Mater.* **2009**, *23*, 246–253, doi:10.1016/j.conbuildmat.2007.12.010.
28. Nuccetelli, C.; Pontikes, Y.; Leonardi, F.; Trevisi, R. New perspectives and issues arising from the introduction of (NORM) residues in building materials: A critical assessment on the radiological behaviour. *Constr. Build. Mater.* **2015**, *82*, 323–331, doi:10.1016/j.conbuildmat.2015.01.069.
29. Campos, M. P.; Costa, L. J. P.; Nisti, M. B.; Mazzilli, B. P. Phosphogypsum recycling in the building materials industry: assessment of the radon exhalation rate. *J. Environ. Radioact.* **2017**, *172*, 232–236, doi:10.1016/j.jenvrad.2017.04.002.
30. Leonardi, F.; Bonczyk, M.; Nuccetelli, C.; Wysocka, M.; Michalik, B.; Ampollini, M.; Tonnarini, S.; Rubin, J.; Niedbalska, K.; Trevisi, R. A study on natural radioactivity and radon exhalation rate in building materials containing norm residues: preliminary results. *Constr. Build. Mater.* **2018**, *173*, 172–179, doi:10.1016/j.conbuildmat.2018.03.254.
31. Trevisi, R.; Leonardi, F.; Risica, S.; Nuccetelli, C. Updated database on natural radioactivity in building materials in Europe. *J. Environ. Radioact.* **2018**, *187*, 90–105, doi:10.1016/j.jenvrad.2018.01.024.
32. Wong, H. H. C.; Kwan, A. K. H. Packing density of cementitious materials: Part 1-measurement using a wet packing method. *Mater. Struct.* **2008**, *41*, 689–701, doi:10.1617/s11527-007-9274-5.
33. Kwan, A. K. H.; Wong, H. H. C. Packing density of cementitious materials: Part 2-packing and flow of OPC + PFA + CSF. *Mater. Struct.* **2008**, *41*, 773–784, doi:10.1617/s11527-007-9281-6.
34. Li, L. G.; Kwan, A. K. H. Packing density of concrete mix under dry and wet conditions. *Powder Technol.* **2014**, *253*, 514–521, doi:10.1016/j.powtec.2013.12.020.
35. Li, L. G.; Lin, C. J.; Chen, G. M.; Kwan, A. K. H.; Jiang, T. Effects of packing on compressive behaviour of recycled aggregate concrete. *Constr. Build. Mater.* **2017**, *157*, 757–777, doi:10.1016/j.conbuildmat.2017.09.097.
36. Kubissa, W.; Jaskulski, R.; Chen, J.; Ng, P.-L.; Godlewska, W.; Reiterman, P. Evaluation of Ecological Concrete Using Multi-Criteria Ecological Index and Performance Index Approach. *Archit. Civ. Eng. Environ.* **2019**, *12*, 97–107, doi:10.21307/acee-2019-009.
37. Kubissa, W.; Jaskulski, R. Measuring and Time Variability of The Sorptivity of Concrete. *Procedia Eng.* **2013**, *57*, 634–641, doi:10.1016/j.proeng.2013.04.080.
38. Jacobs, F.; Leemann, A.; Teruzzi, T.; Torrent, R.; Denarie, E. Specification and site control of the permeability of the cover concrete : The Swiss approach Dedicated to Professor Dr . Bernhard Elsener on the occasion of his 60th birthday. *Mater. Corros.* **2012**, *63*, 1127–1133, doi:10.1002/maco.201206710.
39. Kubissa, W.; Jaskulski, R. Improving of concrete tightness by using surface blast-cleaning waste as a partial replacement of fine aggregate. *Period. Polytech. Civ. Eng.* **2019**, *(In press)*.
40. Brunarski, L.; Dohojda, M. *Badania promieniotwórczości naturalnej wyrobów budowlanych. Poradnik [Natural radioactivity testing of construction products. Guidebook]*; ITB: Warsaw, 2010;
41. Hasani, F.; Shala, F.; Xhixha, G.; Xhixha, M. K.; Hodolli, G.; Kadiri, S.; Bylyku, E.; Cfarku, F. Naturally occurring radioactive materials (NORMs) generated from lignite-fired power plants in Kosovo. *J. Environ. Radioact.* **2014**, *138*, 156–161, doi:10.1016/j.jenvrad.2014.08.015.
42. European Commission *Radiological protection principles concerning the natural radioactivity of building materials (Radiation Protection Report RP-112)*; Luxembourg, 1999;