Low-Activation Reinforced Concrete Design Methodology (10) − Low-Activation Concrete Based on Fused Alumina Aggregates and High Alumina Cement −

Masaharu Kinno[1)], Hirokazu Nishida[1)], Ken-ichi Kimura[1)], Yusuke Fujikura[1)], Norichika Katayose[1)], Ryoetsu Yoshino[2)], Taiichiro Mori[2)] and Akira Hasegawa[3)]

1) Fujita Corporation Technology Development Division
2) Inorganic Material Research Center, Denki Kagaku Kogyo Kabushiki Kaisha, Itoigawa, Japan
3) Tohoku University, Sendai, Japan

ABSTRACT

Screening test using neutron irradiation was performed to select low-activation fused alumina aggregates, low-activation high alumina cement, and other low-activation materials. Manufacturing tests regarding the 1/300-low-activation concrete composed of those were conducted, substituting the quartzite aggregates and silica sand. Here, "1/300-low-activation" concrete denotes that the activity reduction rate to the ordinary concrete is designed to be 1/300. The detailed data regarding the concentrations of Co and Eu in fused alumina aggregates, high alumina cement, quartzite aggregates, silica sand, and B_4C sand and powder were obtained. By admixing with the B_4C of which concentration is from 1 to 2.5 w%, the total residual radioactivity reduction ratio of the 1/300-low-activation concrete to the ordinary concrete, in ΣDi/Ci unit, is estimated to be approximately from 1/1,000 to 1/10,000.

INTRODUCTION

Reutilization after decommissioning of shielding concrete around a reactor−the inner part of the biological shielding wall is classified as radioactive waste in terms of its clearance level as recommended by the International Atomic Energy Agency (IAEA-RS-G 1.7 [1])−is indispensable in the management of radioactive waste disposal operations in the future. We have been developed the 1/300 type of low-activation concrete composed of low-activation fused alumina aggregates and high alumina cement as very useful shielding material in a nuclear facility. Fused alumina aggregates and high alumina cement are known as very low-activation raw material [2]. Other strong points for this concrete are high specific density, i.e. 3.0 g/cm^3, and high heat conductivity. The combination of fused alumina aggregates and high alumina cement is similar to that of refractory brick. However, no systematic study on the manufacture of the 1/300 type of low-activation concrete appears to be published so far. The purpose of this study is to obtain the basic data regarding the concentrations of Co and Eu in fused alumina aggregates, high alumina cement, quartzite aggregates and silica sand, and the B_4C sand and powder, and to develop new types of low-activation concrete by mixing with the low-activation fused alumina aggregates and the high alumina cement, and by substituting the low-activation quartzite aggregates and silica sand. The effectiveness of admixing with the B_4C sand and powder has been also discussed.

EXPERIMENTAL METHODOLOGY

Fused alumina, quartzite and silica sand

Nineteen kinds of fused alumina considering site of factories, 18 kinds of quartzite and silica sand, and B_4C sand and powder were collected and irradiated in the thermal reactor JRR-4 of the Japan Atomic Energy Agency. The radionuclides induced by neutron irradiation in these samples were detected by a Ge detector and a liquid scintillation counter. To determine the Co and Eu contents in the specimen (hereafter designated "Specimen A"), the following formulas were applied by the evaluated geo-standard sample, JG-1:

$$\text{Co (ppm) (Specimen A)} = \{^{60}\text{Co(Specimen A)} / ^{60}\text{Co(JG-1)}\} \cdot \text{Co(ppm)(JG-1)} \quad (1)$$

and

$$\text{Eu (ppm) (Specimen A)} = \{^{152}\text{Eu (Specimen A)} / ^{152}\text{Eu (JG-1)}\} \cdot \text{Eu (ppm) (JG-1)} \quad (2)$$

where

^{60}Co (Specimen A) = Measured specific activity of ^{60}Co (Bq/g) in Specimen A
^{152}Eu(Specimen A) = Measured specific activity of ^{152}Eu (Bq/g) in Specimen A
^{60}Co (JG-1) = Measured specific activity of ^{60}Co (Bq/g) in JG-1,
^{152}Eu (JG-1) = Measured specific activity of ^{152}Eu (Bq/g) in JG-1.

The concentrations of Co and Eu for the fused alumina are obtained by Equations (1) and (2), and plotted in Fig. 1. Those for the quartzite aggregates and silica sand are obtained in the same way, and plotted in Fig. 2. As a guideline for screening, two curved lines are plotted corresponding to the sum of the residual radioisotope's ratio to the clearance level (ΣDi/Ci, Di: concentration of radionuclide i, Ci: clearance level of radionuclide i, cited from IAEA-RS-G-1.7). The boundary line for acquiring the clearance level is ΣDi/Ci = 1.0, assuming the thermal neutron $2\times10^5 n_{th}\cdot cm^{-2}s^{-1}$, 40 yr of operation, and 6 yr of cooling. In this case, the ΣDi/Ci stands for (^{60}Co(Bq/g)/0.1(Bq/g) + ^{152}Eu(Bq/g)/0.1(Bq/g) + ^{154}Eu(Bq/g)/0.1(Bq/g)). The area enclosed by the curve designated "ΣDi/Ci = 1.0" represents the domain in which the material could be disposed of as non-radioactive waste following decommissioning. The curve designated "ΣDi/Ci = 0.1" represents as a reference boundary line for the low-activation manufacturing design.

Fused alumina aggregates are, generally, used for raw material of refractory brick and for abrasive material. The specific density of fused alumina is 3.62 g/cm^3 for bulk density and 3.98 g/cm^3 for true specific gravity. The chemical composition of the low-activation fused alumina is, usually, Al_2O_3 with 99.6 w%, Na_2O with 0.15 w%, SiO_2 with 0.02 w% and Fe_2O_3 with 0.03 w%. The ratio of long-lived radio activities, in ΣDi/Ci unit, of the low-activation fused alumina to that of the ordinary aggregates is approximately 1/1,500[1]. The specific density for both of quartzite aggregates and silica sand is approximately 2.65. The chemical composition of the low-activation silica sand, i.e. the beach sand from Indonesia, is SiO_2 with 99.8 w%, Al_2O_3 with 0.10 w% and Fe_2O_3 with 0.012 w%. The ratio of long-lived radio activities, in ΣDi/Ci unit, of the low-activation quartzite aggregates and silica sand to the andesite aggregates is approximately 1/150 – 1/2,000. Quartzite aggregates and silica sand, however, have a week point of volume change, i.e. at transformation temperature of 573 ℃.

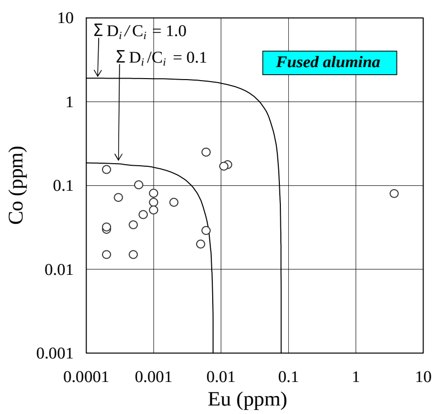

Fig.1 Concentrations of Eu and Co of fused alumina

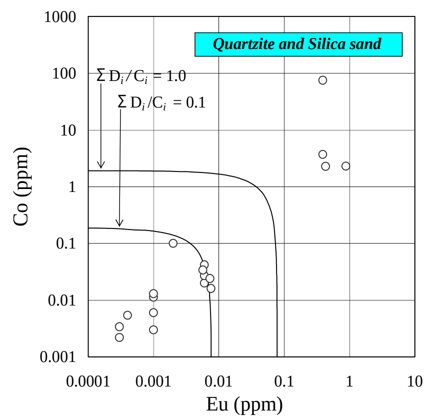

Fig.2 Concentrations of Eu and Co of quartzite and silica sand

High alumina cement

Eleven kinds of high alumina cement, considering with a manufacturing site, were collected and irradiated in the thermal reactor JRR-4. The concentrations of Co and Eu for the high alumina cement are plotted in Fig. 3. High alumina cement (Blaine specific surface area of 2,100-7,900 cm^2/g, usually 4,800 cm^2/g, density of 3.1-3.3 g/cm^3) is, generally, used to manufacture refractory material. The ratio of ^{152}Eu, ^{60}Co and ^{154}Eu activities, in ΣDi/Ci unit, of the low-activation high alumina cement to the ordinary Portland cement is about 1/30. High alumina cement, however, has week points of high heat of cement hydration, poor workability and reduction of long-term strength, comparing to other types of Portland cement. The improvement regarding poor workability and reduction of long-term compressive strength for the high alumina cement are discussed in another paper of "Low-Activation Reinforced Concrete Design Methodology (7)- Application of High Alumina Cement for Low-Activation Mortar- [3].

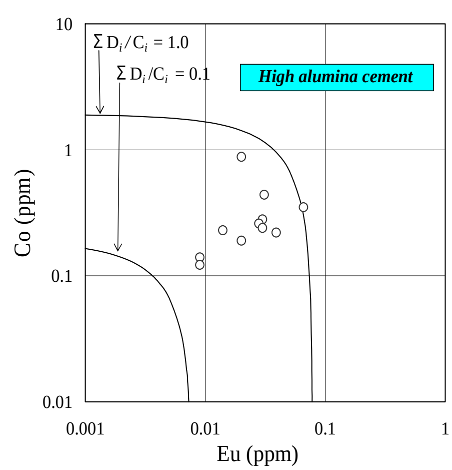

Fig.3 Concentrations of Eu and Co of high-alumina cement

Manufacturing of 1/300- and other types of low-activation concrete

Manufacture of the 1/300-low-activation concrete composed of the high alumina cement (approximately 74 w% of Al_2O_3 and 25 w% of CaO) and the fused alumina was executed by substituting quartzite aggregates, silica sand or limestone aggregates. The mix proportion designs of those are presented in Table 1. The No.1 type is a basic 1/300-low-activation type, and is composed of the fused alumina, and the high alumina cement with a unit weight of 437 kg/m^3. The No.2 type is a mortar, and is admixing with a little of alumina bearing ball in order to reduce water, i.e. W (water) / C (cement) = 0.4. The No.3 type is a less expensive type of low-activation concrete, substituting the quartzite aggregates and the silica sand instead of the fused alumina aggregates. The No.4 type is a less expense type of mortar composed of the beach silica sand. The No.5 type is a very inexpensive type of low-activation concrete, substituting the limestone aggregates and the beach silica sand instead of the fused alumina.

Table 1 Composition of low-activation concrete

No.	Type of concrete	Aggregate			Cement	Admixture	Water
		Coarse	Fine	B_4C sand			
1	Basic type of 1/300-low-activation concrete	Fused alumina 777 kg/m^3	Fused alumina 1,190 kg/m^3	With and without	High alumina cement 437 kg/m^3	Fused alumina powder 149 kg/m^3	272 kg/m^3
2	Fused alumina / alumina ball + High alumina cement	-	Fused alumina / alumina ball 2,000 kg/m^3	With and without	High alumina cement 600 kg/m^3	-	237 kg/m^3
3	Quartzite aggregate / silica sand + High alumina cement	Quartzite aggregate 1,045 kg/m^3	Silica sand 702 kg/m^3	With and without	High alumina cement 400 kg/m^3	-	168 kg/m^3
4	Silica sand + High alumina cement	-	Silica sand 1,548 kg/m^3	With and without	High alumina cement 480 kg/m^3	-	202 kg/m^3
5	Limestone / silica sand + High alumina cement	Limestone 983 kg/m^3	Silica sand 788 kg/m^3	With and without	High alumina cement 400 kg/m^3	-	168 kg/m^3

The principle physical properties are shown in Table 2, where the density, slump, compressive strength and adiabatic temperature are presented. The No.1 type is high density (2.924 g/cm3), but poor workability and high heat of cement hydration (Q_{max} = 60.7 ℃). The No.2 type of mortar is high density and high fluidity of no segregation. The No.3 and No.4 types are similar to the ordinary concrete and mortar. The No.5 type of concrete is also similar to the ordinary concrete.

Table 2 Physical properties of low-activation concrete

No.	Type of concrete	Density (g/cm^3)	Slump (cm)	Compressive strength (28d) (MPa)	Adiabatic temperature rise Q (t)$^{(1)}$
1	Basic type of 1/300-low-activation concrete, without B_4C	2.924	17.5	47.1	Q_{max} = 60.7 ℃, α = 30.0, β = 1.3
2	Fused alumina/alumina ball + High alumina cement, without B_4C	2.980	25.0	77.3	Not measured
3	Quartzite aggregate/silica sand + High alumina cement, without B_4C	2.310	18.0	50.0	Not measured
4	Silica sand + High alumina cement, without B_4C	2.090	10.0	31.9	Not measured
5	Limestone aggregate/silica sand + High alumina cement, without B_4C	2.460	19.0	71.5	Not measured

(1) $Q(t) = Q_{max}\,[1 - \exp(-\alpha t^{\beta})]$

The dominant target elements (Sc, Fe, Co, Cs and Eu) in above concrete obtained by an activation analysis are presented in Table 3, comparing with the calculated values of ΣDi/Ci ratio. The element of Sc is typified as an index of rare earth elements in this study. The elements of Fe and Cs are the target element of $^{54}Fe(n,\gamma)^{55}Fe$ and $^{133}Cs(n,\gamma)^{134}Cs$ reactions. The ΣDi/Ci ratio is normalized by the andesite concrete which is considered to be "ordinary concrete". The ΣDi/Ci ratio of No.1 type is 1/298. The ΣDi/Ci ratio of No.2, 3, 4 and 5 types are 1/133, 1/125, 1/68 and 1/25, respectively.

Table 3 Target element and $\Sigma D_i/C_i$ values of low-activation concrete

No.	Type of concrete	Target element					ΣDi/Ci(1) ratio (Andesite concrete ≡ 1)
		Sc (ng/g)	Fe (μ/g)	Co (ng/g)	Cs (ng/g)	Eu (ng/g)	
1	Basic type of 1/300-low-activation concrete, without B_4C	180 ± 8	260 ± 20	102 ± 8	10 ± 2	3 ± 2	1/298
2	Fused alumina / alumina ball + High alumina cement, without B_4C	111 ± 6	590 ± 30	166 ± 8	9 ± 2	6.5 ± 0.6	1/133
3	Quartzite aggregate / silica sand + High alumina cement, without B_4C	144 ± 7	610 ± 30	142 ± 7	50 ± 10	8 ± 4	1/125
4	Silica sand + High alumina cement, without B_4C	280 ± 10	560 ± 30	340 ± 20	20 ± 10	13 ± 3	1/68
5	Limestone aggregate / silica sand + High alumina cement, without B_4C	230 ± 10	670 ± 30	160 ± 10	50 ± 10	54 ± 4	1/25

(1)∑Di/Ci～Di: concentration of radionuclide i, Ci: clearance level of radionuclide i, cited from IAEA-RS-G1.7, assuming the thermal neutron $2\times10^5 n_{th}\cdot cm^{-2}s^{-1}$, 40 yr of operation, and 6 yr of cooling.

Admixing with B4C sand and powder

Adding boron compound to concrete is, generally, not so efficient for the reduction of the exposure dose, because neutron dose equivalent is depends on mainly fast and epi-thermal neutron flux. It is only efficient for reducing the generation of the secondary gamma rays. As for activation, the adding boron is, however, very efficient to reduce the generation of long-lived radionuclides, in the following reasons,

(1) The long-lived residual radionuclides in concrete are almost generated by thermal neutron reactions.

The dominant residual radionuclides induced in the ordinary concrete are ^{152}Eu, ^{60}Co, ^{154}Eu and ^{3}H, and they occupy over 99 % of induced radioactivity, in ΣDi/Ci unit, among that by all the radionuclides [2]. The reactions of $^{151}Eu(n,\gamma)^{152}Eu$ and $^{6}L(n,\alpha)^{3}H$ are generated almost by thermal neutrons, and the reactions of $^{59}Co(n,\gamma)^{60}Co$ and $^{153}Eu(n,\gamma)^{154}Eu$ is generated mainly by thermal neutrons.

(2) The thermal neutron flux is overwhelmingly dominant in thick concrete.

The calculated neutron spectra in a biological concrete shield at a nuclear power plant are shown in Fig.4. The spectra of inner surface, 10 cm in depth, 100 cm in depth are presented in this figure. The spectrum of inner surface consists of mainly epi-thermal neutrons, partially of thermal neutrons, and a few of fast neutrons. That of 10 cm in depth consists of mainly thermal neutrons and partially epi-thermal neutrons. That of 100 cm in depth consists of almost thermal neutrons.

(3) The reduction of thermal neutron flux in concrete, therefore, causes the similar effect of "low-activation".

Boron is, generally, utilized as "a thermal neutron absorber or a cut-off admixture". The boron containing concrete, denoted as neutron-absorbing concrete, was already introduced by our former

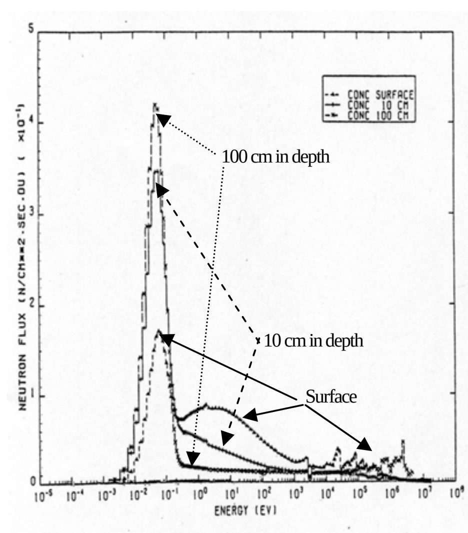

Fig.4 Neutron spectra in concrete of nuclear power plant

report [4]. The neutron-absorbing concrete was composed of columanite aggregate, columanite sand, white cement, water and chemical admixtures. The density in air dry was 2.14 g/cm^3, and the concentration of boron was 9.3 w%. The report suggested that the reduction rates of fast, epi-thermal and thermal neutron flux in the neutron-absorbing concrete, were roughly 1/1, 1/30, and 1/5,000 -1/10,000, respectively, compared to that in the ordinary concrete, under the assumption of 50 cm concrete bulk in thick, as shown Fig.5 and Table4. The neutron attenuation fluxes in the neutron-absorbing concrete and the ordinary concrete were calculated by a one-dimensional discrete ordinate transport code. The reduction rates of the thermal neutron flux in the thick neutron-absorbing concrete to that in the ordinary concrete are, roughly, 1/10,000, 1/1,000, 1/100 and 1/10, corresponding to the boron contents of approximately 10 w%, 5w%, 2 w%, and 0.8 w%. The reactions of ^{133}Cs(n, γ)^{134}Cs and ^{132}Ba(n, γ)^{133}Ba are generated by epi-thermal and thermal neutrons. The reactions of ^{54}Fe (n,p) ^{54}Mn, ^{23}Na (n,2n) ^{22}Na and ^{39}K (n,p) ^{39}Ar are generated by fast neutrons.

Table 4 Neutron flux reduction ratio by admixing with Boron(1)

Neutron energy	Reduction ratio
0.001 – 0.4 eV	1/5,000 – 1/10,000
0.4 – 100 eV	1/300
100 eV – 100 keV	1/30
100 keV – 15 MeV	1/1

(1) 9.3 w% of 2.14 g/cm^3

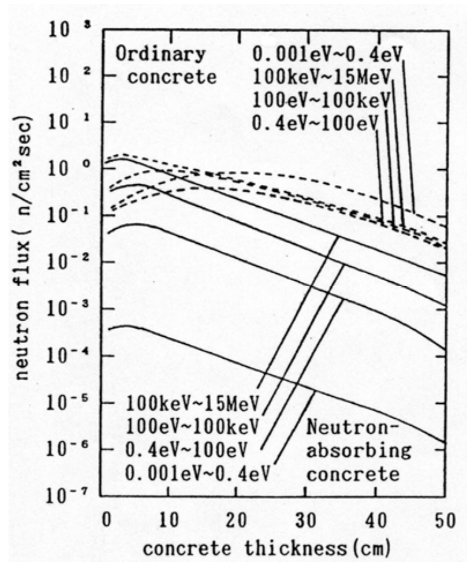

Fig.5 Neutron flux decrease by admixing with boron [4]

The dominant target elements (Sc, Fe, Co, Cs and Eu) in the B_4C sand and powder obtained by an activation analysis are presented in Table 5 with the calculated ratios of ΣDi/Ci for those to the andesite concrete, which are not so small because of high concentrations of Co element compared to the other low-activation raw materials. Although manufacturing the low-activation B_4C is essential, but is considered to be very expensive. The isotopic composition and cross section at 0.00253 eV of boron are indicated in Table 6.

Table 5 Target element and $\sum D_i/C_i$ ratio of B_4C sand and powder

No.	Type of B_4C	Target element					ΣDi/Ci(1) ratio (Andesite concrete ≡ 1)
		Sc (ng/g)	Fe (μ/g)	Co (ng/g)	Cs (ng/g)	Eu (ng/g)	
1	B_4C sand(2)	56 ± 4	710 ± 50	3,100 ± 200	< 40	30 ± 10	1/14
2	B_4C powder(2)	970 ± 50	4,400 ± 200	940 ± 70	100 ± 50	90 ± 20	1/13

(1) ∑Di/Ci～Di: concentration of radionuclide i, Ci: clearance level of radionuclide i, cited from IAEA-RS-G-1.7, assuming the thermal neutron $2\times10^5 n_{th}\cdot cm^{-2}s^{-1}$, 40 yr of operation, and 6 yr of cooling. (2) From Denka Co., Japan.

In summing up, the reduction ratio of radioactivity, in ΣDi/Ci unit, is roughly estimated to be 1/3 to 1/30, by admixing with 0.8－2 w% of boron, taking into consideration of epi-thermal and fast neutrons. The total reduction ratio of radioactivity for the basic type of the 1/300-low-activation concrete to that of the ordinary concrete estimated to be approximately 1/1,000 to 1/10,000, as presented in

Table 6 Isotopic composition and cross section of boron [5]

Item	Isotopic composition	Cross section at 0.0253 eV	Note
^{10}B	19.9 %	(n, α) 3,837 b	$^{10}B + n \rightarrow {}^{7}Li + \alpha$ $\rightarrow {}^{7}Li^{*}$(96 %) $^{7}Li^{*} \rightarrow {}^{7}Li + \gamma$ (0.48 MeV)
^{11}B	80.1 %	(n, γ) 5.075 mb	-

Table 7. As for obtaining the conclusive evidence of the ΣDi/Ci ratio only by calculation is, in principle, very difficult, because the ΣDi/Ci ratio is dominated entirely the error estimation of the trace element measurement. The tests of admixing with the B_4C of which concentration is from 1 to 2.5 w% are now in progress in this project.

Table 7 Total $\sum D_i/C_i$ ratio by admixing with B_4C sand and powder

No.	Type of concrete	Total ΣDi/Ci ratio (Andesite concrete ≡ 1)
1	Basic type of 1/300-low-activation concrete, with B_4C sand and powder (1-2.5 w%)	1/1,000 – 1/10,000
2	Fused alumina / alumina ball + High alumina cement, with B_4C sand and powder (1-2.5 w%)	1/400 – 1/4,000
3	Quartzite aggregate / silica sand + High alumina cement, with B_4C sand and powder (1-2.5 w%)	1/300 – 1/3,000
4	Silica sand + High alumina cement, with B_4C sand and powder (1-2.5 w%)	1/200 – 1/2,000
5	Limestone aggregate / silica sand + High alumina cement, with B_4C sand and powder (1-2.5 w%)	1/75 – 1/750

Chemical composition of basic type of 1/300 low-activation concrete

The chemical compositions of the basic type of 1/300-low-activation concrete without B_4C are presented in Tale 8. The element contents were obtained by activation analysis, ICP-AES, ICP-MS, and other chemical analyses.

Table 8 Chemical compositions of basic type of 1/300 low-activation concrete without B_4C

(density in air dry ρ = 2.890 g/cm^3)

Major element (w%)	H	Si	Ca	Al	Fe	Mg	Na	K
	0.62	1.03	3.52	45.72	0.026	0.0	0.040	0.0
	Ti	Mn	C	S	P	B	O	
	0.01	0.0	0.22	0.01	0.0	0.0	48.80	
Minor element (ppm)	Eu	Co	Li	Cs	Ba	N	Ni	Cl
	0.003	0.10	0.42	0.01	12	12	0.1	10
	Sc	Cr	Zn	Cu	Nb	Sm	Th	U
	0.18	25.9	2	0.10	1.0	0.1	0.098	0.1

CONCLUSIONS

(1) Screening test using neutron irradiation was performed to select low-activation fused alumina aggregates, low-activation high alumina cement, and other low-activation materials.

(2) Manufacturing tests regarding the 1/300-low-activation concrete composed of the above was performed, substituting the quartzite aggregates and silica sand.

(3) The detailed data regarding the concentrations of Co and Eu in fused alumina aggregates, high alumina cement, quartzite aggregates、silica sand, and B_4C were obtained.

(4) By admixing with the B_4C of which concentration is from 1 to 2.5 w%, the total residual radioactivity reduction ratio for the basic type of 1/300-low-activation concrete to the ordinary concrete, in ΣDi/Ci unit, is estimated to be approximately from 1/1,000 to 1/10,000.

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REFERENCES

1. IAEA Safety Standards Series, "Application of the Concept of Exclusion, Exemption and Clearance", No. RS-G-1.7, 2004.

2. Kinno, M., Kimura, K. and Nakamura, T., "Raw Materials for Low-Activation Concrete Neutron Shields," Journal of Nuclear Science and Technology, Vol. 39, No.12, 2002, p.1275.

3. Yoshino R. et al., "Low-Activation Reinforced Concrete Design Methodology (7) - Application of High Alumina Cement for Low-Activation Mortar-", SMiRT 19, [to be published], 2007.

4. Kinno, M., et al., "Neutron activation screening tests of raw materials for developing low-activation concrete shield", Proc. 7 th Int. Conf. on Radiation Shielding, Bournemouth, UK, Vol. 1, 1988, p.48.

5. Shibata, K., et al., "Japanese Evaluated Nuclear Data Library Version 3 Revision-3: JENDL3.3", Journal of Nuclear Science and Technology, Vol. 39, 2002, p.1125.