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Low-Activation Reinforced Concrete Design Methodology (5)
- Low-Activation Material Development Support System-

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ABSTRACT

Radiation shielding wall and biological shielding wall in a typical light water reactor become low-level radioactive wastes by thermal neutron irradiation after reactor decommissioning. Since volume of the concrete waste after reactor decommissioning is very large, to control the radioactivity level of the material below clearance level leads to reduce remarkably the amount of radioactive waste of the nuclear plant. It will contribute to safety of reactor disassemble work and reduce disposal cost of radioactive waste. Raw material selection of steel reinforced concrete is considered to be the possible key to solve this issue. To show the guideline for the low-activation design, low-activation material development support system (LAMDS) was prepared.

INTRODUCTION

A few study carried out to obtain basic data for development of low-activation concrete (for example, Kinno et al. [1] and Suzuki et al. [2]). The major long-lived radionuclides in reinforced concrete material were found to be Cobalt-60 (^{60}Co), Europium-152 (^{152}Eu) and Europium-154 (^{154}Eu) generated by ^{59}Co (n, γ) ^{60}Co, ^{151}Eu (n, γ) ^{152}Eu and ^{153}Eu (n, γ) ^{154}Eu reactions, therefore, it is important to select the low-Co and low-Eu containing raw materials to develop the low-activation reinforced concrete. The radioactivities of other typical radionuclides (Scandium-46 (^{46}Sc), Iron-59 (^{59}Fe), Cesium-134 (^{134}Cs)) are very low level compared to the clearance level. In this paper, these elements are called “target elements”.

In this study, (1) many kinds of raw materials are collected from all over Japan and overseas, determined the chemical composition, especially Co and Eu, and then the materials database of reinforced concrete raw materials is constructed. In addition, (2) the support system “Low-Activation Materials Development Support System” (LAMDS) is developed for manufacturing of low-activation reinforced concrete as economically as possible.

METHOD

In order to determine the content of trace elements in raw materials of concrete and reinforced steel bars, instrumental neutron activation analysis (INAA) was applied. About 350 samples of concrete materials and reinforced steel bar materials were collected from all over Japan. Table 1 shows the samples for INAA.

All samples were ground with the agate mortar and dried at 100^{o}C for 1h, weigh about 50 ~ 100 mg, and sealed with the polyethylene film or the quartz tube. Neutron irradiation was performed in the Pn-2 (Pneumatic Tube-2) of irradiation facility of Kyoto University Reactor (KUR) and the hydraulic rabbit capsule irradiation facility of Japan Material Testing Reactor (JMTR). Thermal neutron fluxes in KUR and JMTR were 2.79×10^{13} n/cm^2/s and 7.16×10^{13} n/cm^2/s, respectively. The samples in KUR and JMTR were irradiated for 40 min and 15 min. After the irradiation, these sample were cooled about 1 ~ 6 month. Residual radioactivity measurements were carried out with a coaxial germanium detector (Canberra GX1020) and a multichannel analyzer (Aptec MCA Application Multichannel Analyzer) in Tohoku University Radioisotope Laboratory. In order to determine the concentration of target elements and input the chemical composition data to the materials database, the calculation and data input support software was developed. The geochemical reference samples (JA-1 (Andesite), JB-1 (Basalt), JG-1 (Granodiorite), JP-1 (Peridotite), JR-1 (Rhyolite), JLs-1 (Limestone), JCFA-1 (Coal fly ash)) for INAA were also irradiated with other samples to calibrate the concentration. Table 2 shows five nuclides detected with INAA in this work.

On the other hand, the content of major elements in raw materials are also needed for materials selection of cement. X-ray Fluorescence (XRF) was adopted for determining the concentrations of CaO, SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, SO_3, P_2O_5, MgO and Cl. Powdered samples were prepared and dried at 100 ^{o}C for 1h.

Table 1. Samples

Concrete aggregate	Feldspar 5, Hornfels 6, Limestone 19, Electro fused alumina (Alumina cement aggregate) 5
Cement	Alumina cement 2, Eco cement 3, High flow cement 1, White portland cement 3, Ordinary portland cement 25, Portland blast furnace cement 3, Low heat cement 3, Moderate heat portland cement 16, High early strength cement 4, Overseas cement 9
Cement middle product	Coarse mixing 2, Cement clinker 10, Other 3
Cement materials	Silica fume 6, Silica Rock 6, Bauxite 4, Expansive material (admixture) 2, Limestone 19, Gypsum 24, Coal (fuel) 2, Fly ash 55, Iron ore 16, Clay 14, Sand 12, Pyrophyllite 7, Iron blast furnace slag 2, Revolving furnace slag 2, Alumina 5, Other Rock 6
Reinforcing bar	Electric furnace reinforcing bar 35
Steel material	Coke 1, Iron ore 16, Pellet 3, Sinter 1, Pig iron 2

Table 2. Radionuclide and γ-ray energy for measurement

Radionuclide	Half-life (yr)	γ-ray energy (keV)
^{46}Sc	0.229	889.26
^{59}Fe	0.122	1099.22
^{60}Co	5.270	1332.51
^{134}Cs	2.062	795.84
^{152}Eu	13.300	1408.08

RESULTS AND DISCUSSION

Table 3 to 5 show the concentrations of Co and Eu in the samples. To compare the activation characteristics of each sample, ΣD/C was calculated (ΣD/C is the sum of the residual radioisotopes's ratio to the clearance level of shielding reinforced concrete in the light water reactor. When the If ΣD/C of waste is less than 1, the waste can be treated as non-radioactive waste). Most of the clearance levels in Japan are almost the same as the values suggested by IAEA [5]. The calculation condition is 2.0×10^5 n/cm^2/s of thermal neutron flux, 40 yr of sequential neutron irradiation, and 6.0 yr of cooling time, respectively, at the inner surface of the biological shielding concrete of a 1,100 MW boiling water reactor [6]. The ΣD/C was calculated by the following formulas:

$$\Sigma_i (D_i / C_i) = \Sigma_A \{ [\Phi_{th} N_{A'} \sigma_{A'} \{1 - \exp(-\lambda_A T_{irrad})\} \exp(-\lambda_A T_{cool})] / CL_A \} \qquad (1)$$

where Φ_{th} : Thermal neutron flux ($n \cdot cm^{-2} \cdot s^{-1}$)

A' : Radionuclide

A : Target element

$N_{A'}$: Atomic densities of radionuclide " A' " (g^{-1})

$\sigma_{A'}$: Reaction cross section of A (n,γ) A' (cm^2)

T_{irrad} : Irradiation time (s)

T_{cool} : Cooling time (s)

$CL_{A'}$: Clearance level of radionuclide " A' " ($Bq \cdot g^{-1}$)

λ_A : $1 / T_{1/2}$ (s^{-1})

In this calculation, the reactions adopted are: ^{39}K(n,α)^{36}Cl, ^{40}Ca(n,γ)^{41}Ca, ^{45}Sc(n,γ)^{46}Sc, ^{54}Fe(n,γ)^{55}Fe, ^{58}Fe(n,γ)^{59}Fe, ^{59}Co(n,γ)^{60}Co, ^{58}Ni(n,γ)^{59}Ni, ^{62}Ni(n,γ)^{63}Ni, ^{93}Nb(n,γ)^{94}Nb, ^{133}Cs(n,γ)^{134}Cs, ^{132}Ba(n,γ)^{133}Ba, ^{151}Eu(n,γ)^{152}Eu,^{153}Eu(n,γ)^{154}Eu. The thermal neutron capture cross sections adopted are from JENDL 3.3.

Table 3. The concentrations of target elements in concrete aggregates and cements (n.d. = not detected)

Material	Number of samples	Eu [ppm]	Co [ppm]	ΣD/C
		average (min.-max.)	average (min.-max.)	average (min.-max.)
Concrete Aggregate				
Feldspar	5	1.2 (0.080 – 3.0)	9.2 (0.75 – 28)	30 (2.1 - 80)
Hornfels	6	1.0 (0.82 – 1.2)	8.1 (1.5 – 12)	26 (20 - 32)
Limestone	19	0.098 (0.0056 – 0.29)	4.5 (0.096 – 68)	3.8 (0.16 – 30)
Electro fused alumina (Alumina cement aggregate)	5	0.55 (n.d. - 0.55)	240 (18 – 380)	94 (19 -140)
Cement				
Alumina cement	2	0.73 (0.077 – 1.4)	0.74 (0.38 – 1.2)	17 (1.9 – 33)
Portland cement (Ordinary, Moderate, Low heat, High early strength)	54	0.58 (0.19 – 1.4)	12 (1.8 - 24)	18 (5.0 - 41)
White cement	3	0.28 (0.25 – 0.30)	1.6 (1.4 – 1.7)	7.0 (6.3 - 7.5)
Overseas cement	9	0.62 (0.26 – 0.83)	8.5 (2.5 – 11)	17 (6.9 – 23)

Table 4. Concentrations of target elements in cement materials (n.d. = not detected)

Material	Number of samples	Eu [ppm]	Co [ppm]	ΣD/C
		average (min.-max.)	average (min.-max.)	average (min.-max.)
CaO Source				
Limestone	19	0.098 (0.0056 – 0.29)	4.5 (0.096 – 68)	3.8 (0.16 – 30)
$SiO_2 – Al_2O_3$ Source				
Silica Rock	6	0.19 (n.d. – 0.37)	1.6 (0.044 – 3.8)	5.0 (0.019 - 9.9)
Bauxite	4	1.6 (0.45 – 3.4)	26 (1.5 – 51)	47 (11 - 96)
Fly ash	55	2.7 (1.5 – 4.9)	41 (15 – 99)	77 (40 - 150)
Clay	14	0.91 (0.48 – 1.3)	4.1 (0.27 – 6.2)	23 (12 - 33)
Sand	12	0.63 (0.068 – 1.2)	7.9 (1.3 – 38)	17 (2.0 - 41)
Pyrophyllite	7	0.80 (0.14 – 1.7)	0.15 (n.d. – 0.58)	19 (3.3 - 40)
Fe_2O_3 Source				
Iron ore	16	0.34 (n.d. – 1.3)	54 (n.d. – 620)	26 (0.022 – 240)
Gypsum				
Gypsum	24	0.16 (n.d. – 0.64)	1.3 (0.083 – 15)	4.1 (0.038 - 20)

Table 5. Concentrations of target elements in reinforced steel bar materials (n.d. = not detected)

Material	Number of samples	Eu [ppm]	Co [ppm]	ΣD/C
		average (min.-max.)	average (min.-max.)	average (min.-max.)
Reinforced bar (Electric furnace)	35	n.d.	78 (22 – 130)	27 (7.6 – 45)
Steel material				
Coke	1	0.48	5.1	13
Pellet	3	0.32 (0.30 – 0.36)	12 (3.1 –19)	12 (8.0 – 15)
Sinter	1	0.40	9.6	13
Pig iron	2	n.d.	27 (18 – 37)	9.5 (6.2 – 13)
Iron ore	16	0.34 (n.d. – 1.3)	54 (0.098 – 620)	26 (0.64 – 240)

Figure 1 shows the ΣD/C average of each sample. Limestones, silica rocks, and gypsums are very low activation materials. Clays, fly ashes, and sands, which are used as SiO_2-Al_2O_3 source of the cement materials, have higher concentration of Eu. Therefore more careful selection or substitutive materials will be required. On the other hand, Eu content of reinforced steel bars was not detected because the metal / slag distribution ratio of Eu in the molten iron in the furnace was very low. Thus the key element of development of the low activation reinforced bar is not Eu but Co [7]. Co in the steel material seems mainly originated from iron ore and scrap iron. The recycled steel is high content of Co because Co accumulates further as the steel is subsequently recycled. To reduce target elements in the reinforced bar, the amount of iron scraps used in steel making process should be as lower possible.

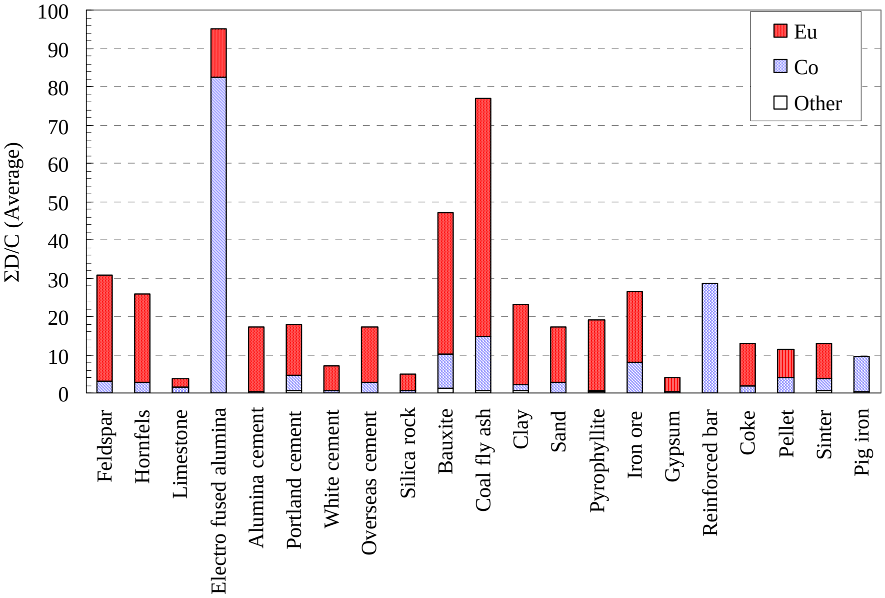
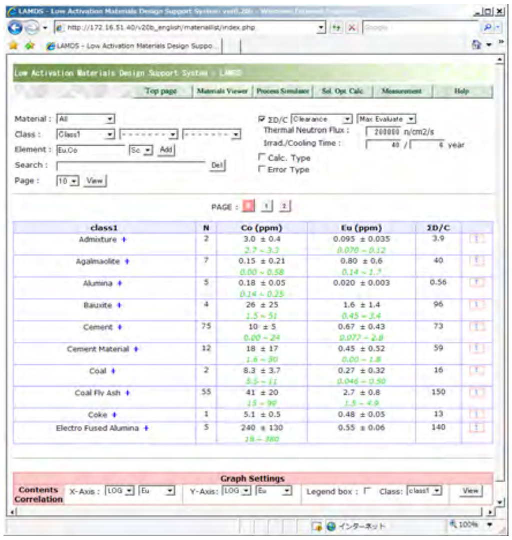


Figure 1. ΣD/C average of each sample (after 40 years of operation and 6 years of cooling)

DATABASE SYSTEM

Low-activation material design support system (LAMDS) was developed for practicably using materials database made in this study. LAMDS has three functions as follows: materials viewer, process simulator, and optimization calculator. LAMDS structure is Apache + PHP + MySQL because LAMDS will available by way of Web services. Figure 2 shows the snapshot of LAMDS.



Material : All
Class : Class1
Element : Eu,Co
Search :
Page : 10
☑ ΣD/C Clearance Max Evaluate
Thermal Neutron Flux : 200000 n/cm2/s
Irrad./Cooling Time : 40 / 6 year
☐ Calc. Type
☐ Error Type

class1	N	Co (ppm)	Eu (ppm)	ΣD/C
Admixture	2	3.0 ± 0.4 2.7 ~ 3.3	0.095 ± 0.035 0.070 ~ 0.12	3.9
Agalmaolite	7	0.15 ± 0.21 0.00 ~ 0.58	0.80 ± 0.6 0.14 ~ 1.7	40
Alumina	5	0.18 ± 0.05 0.14 ~ 0.25	0.020 ± 0.003	0.56
Bauxite	4	26 ± 25 1.5 ~ 51	1.6 ± 1.4 0.45 ~ 3.4	96
Cement	75	10 ± 5 0.00 ~ 24	0.67 ± 0.43 0.077 ~ 2.8	73
Cement Material	12	18 ± 17 1.6 ~ 50	0.45 ± 0.52 0.00 ~ 1.8	59
Coal	2	8.3 ± 3.7 5.5 ~ 11	0.27 ± 0.32 0.046 ~ 0.50	16
Coal Fly Ash	55	41 ± 20 15 ~ 99	2.7 ± 0.8 1.5 ~ 4.9	150
Coke	1	5.1 ± 0.5	0.48 ± 0.05	13
Electro Fused Alumina	5	240 ± 130 18 ~ 380	0.55 ± 0.06	140

Contents Correlation X-Axis : LOG Eu Y-Axis : LOG Eu Legend box : ☐ Class: class1

Figure 2. The snapshot of materials viewer on LAMDS

1. Materials Viewer

The Materials database stores the country of origin, production vendor, chemical composition, and measurement method of the composition. LAMDS can show this information by required materials database, draw graphs, and calculate ΣD/C by Eqs. (1).

2. Process Simulator

This function shows the chemical composition of the product by calculated summation of the composition of raw materials. The output / input ratios of each element in the making process can be also adopted. This function allows to easily estimate the low activation performance when the new materials will be developed. The chemical composition of the product is calculated by Eqs.(2). In addition to estimation of the chemical composition, ΣD/C is calculated by Eqs.(1).

$$X_i = \Sigma_j (D_{ij} \times P_i \times 100) \qquad (2)$$

where X_i : concentration of the element ' i ' (mass / mass)

D_{ij} : concentration of the element ' i ' in the raw material ' j ' (mass / mass)

P_i : output / input ratio of the element ' i ' in production process (%)

3. Selection Optimization Calculator

User input the target chemical composition of the product, ΣD/C, category of raw materials, and cost of raw materials, then some raw materials combinations to fulfill the required conditions is proposed by this function. This function is applied the simulated annealing method [8,9] because calculation time is shorter than other method (e.g. genetic algorithms [10]).

LAMDS has above three functions. For instance, Table 6 shows the result of cement raw materials on the current materials database. In cement production process, chemical composition of product may be summation of raw materials. That is, the P_i of Eqs(2) is 100% for all element. According to Table 6, the best mix selected using the current materials database is a pure limestone (CaO source), silica rock and clay or pyrophyllite (Al_2O_3-SiO_2 source), hematite (Fe_2O_3 source), and gypsum. The ΣD/C of the mixture will be about 1/10 of the mean value of normal portland cements. Thus user is able to concrete selection put together on target by LAMDS.

Table 6. The best mix of cement raw materials on the current materials database

Reduction rate[*1] (%)	CaO		SiO_2-Al_2O_3		Fe_2O_3		Gypsum	
	Material	%	Material	%	Material	%	Material	%
91.0	Limestone C	78.6	Clay B Silica B	6.0 9.1	Hematite B	3.0	Gypsum B	3.2
89.9	Limestone C	77.8	Pyrophyllite D Silica B	10.4 6.2	Hematite B	3.1	Gypsum B	2.5
89.6	Limestone C	78.6	Clay B Silica B	5.7 8.6	Hematite C	3.0	Gypsum B	3.2

*1 ΣD/C compared to the average of ΣD/C of normal portland cements in Japan.

SUMMARY

(1) The concentrations of trace elements in the raw materials and products for low-activation reinforcing bar and concrete were determined by INAA. The concentrations of Co and Eu in limestone are very low. On the other hand, $Al_2O_3 – SiO_2$ source of cement materials include 2 ~ 7 ppm of Co and 0.4 ~ 1 ppm of Eu, which are about 10 times larger than that of limestone. The concentrations of Co and Eu in coal fly ash are about 10 - 20 times larger than that of limestone. As a result of this measurement, the raw materials that are the key of development of the low-activation materials became clear. Especially, $Al_2O_3 – SiO_2$ source of cement raw material is comparatively high Eu content. These data are stored in the materials database. And it will be available for development of the low-activation reinforced concrete by using LAMDS.

(2) The raw materials selection support tool “LAMDS” for development of low-activation reinforced concrete were developed. LAMDS has three functions as follows: materials data viewer, process simulator and raw material mixing optimization calculator. By using the current materials database, it was estimated that the 1/10 low activation cement could be developed. LAMDS shows the candidate of the raw materials mixture to meet the low activation level of user’s target. In addition to input the costs data of each material by user, the low activation materials considered to the cost-effectiveness can be developed. To reduce the calculation load, the radioactivation level is calculated by Eqs. (1) instead of the detail neutron transportation calculation and activation calculation. More precise calculation to estimate the amount of radioactive wastes and disposal costs after reactor operation is available by using “Classification System” [11].

In future work, LAMDS will be uploaded and opened to the public. The arrangement of the materials database, preparation of WWW server and web site are under construction.

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