Low-Activation Reinforced Concrete Design Methodology (LARC)(6) — Development of Low-Activation Cement —

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ABSTRACT

When nuclear plants will reach to decommission stage, a huge amount of concrete should be disposed as radioactive waste. To reduce the amount of radioactive concrete, the most effective methodology is not to use the materials of high radionuclide content: for example, using limestone aggregate. However, concrete uses Portland cement for hardening, therefore, it is difficult to reduce the amount of radioactive concrete unless radionuclide content in cement is reduced. So in this study, we tried to develop the new type of Low-activation cement by reducing of radionuclide as europium and cobalt. As a result, we could reduce the amount of europium and cobalt in cement significantly, and obtained the result that the new cements can reduce radioactivity to one-third or less against commercially Portland cement in Japan.

EXPERIMENTAL METHODOLOGY

Outline of experiment

In this study, we examined the chemical compositions of cement raw materials, and investigated the cement-manufacturing process, to develop Low-activation cement that contains europium (Eu) and cobalt (Co) as little as possible. Based on these results, we made test production of Low-activation cements using the small-scale rotary kiln.

Examination of cement raw materials

We examined 29 limestones, 5 silicastones, 5 clays, 5 iron raw materials, 6 coal ashes, and 10 additives. They were mainly collected in Japan. Also, several commercially available cements were collected. These raw materials were ground to be under 100 μm fineness using an agate mortar, and we paid utmost care to contamination. The amounts of Eu and Co in them were determined in the following method.

Quantification of Eu and Co was conducted by radioactivation analyses with the JRR4 nuclear reactor of the Japan Atomic Energy Research Institute. Thermal neutron irradiation to raw materials and cements (flux density 4.7113× 1013n/cm^2 sec) were conducted in 20 minutes as irradiation time. After the irradiation, these samples were cooled 5days (short-term) and 61days(long-term), and measured countable number of values by γ ray spectrometer. To calculate concentrations of Eu and Co in the samples, standard substances were also conducted by radioactivation analyses simultaneously.

Investigation of cement-manufacturing process

Cement-manufacturing process is divided broadly into Raw meal process, Clinker burning process, and Clinker grinding process. We focused on ‘grinding’ and ‘burning’, and investigated Co and Eu contamination during these processes.

Compared with Eu that is a rare earth element, Co is used widely in industry as alloy. Since alloys using Co have the characteristics of excelling in wear resistance and corrosion resistance, they are sometimes used in grinding machines. Therefore, we confirmed whether Co had been mixed in or not when a calcium carbonate powder (reagent) was actually ground for 0 to 180 second by a disk-type vibratory grinder. The material of the vessel used in grinding was tungsten carbide containing Co. The amount of Co in the calcium carbonate powder was determined by radioactivation analyses.

Coal is used as fuels in most clinker burning process, and it is incorporated into feed materials after clinker burning process as coal ash. This coal ash changes compound composition of cement product. If coal ash contains Co and Eu, cement products may be high in these elements. Therefore, we made two types of clinker that used the same raw materials to confirm effect of coal. One clinker was manufactured in cement plant using coal, and the other was made by the electric furnace using the silicon carbide heating element. The latter case should not have effect of contamination by coal. The amount of Co and Eu in these clinkers was determined by radioactivation analyses.

Manufacturing of Low-activation cement

Paying attention to selection of raw materials and contamination during manufacturing process, we made test production of Low-activation cement. Designs of the Low-activation cement are shown in Table 1. Raw materials for the Low-activation cement are shown in Table 2. All raw materials were grinding by alumina-ball mill.

Both Low-activation type A and type B was designed so that hydration heat conforms to Low heat cement of Japanese industrial standards because these cements aimed at using to massive radiation shielding concrete. Low-activation type A is approximately the same design of Low heat cement. Low-activation type B is completely novel cement that contains only a small quantity of C_3A and C_4AF.

Low-activation cements were manufactured by the small-scale rotary kiln that has 450mm in diameter and 8340mm in length. Its capacity of production is about 100kg-cement/hr, and heavy oil was used as kiln fuel. Clinker-cooling system is rotary types. Gypsum was added to clinker to be 2% as SO_3 in cement, and these were grinding with alumina-ball mill.

Table 1. Designs of Low-activation cement.

Cement	Mineral composition (%)				Modulus				Hydration heat (J/g)	
	C_3S	C_2S	C_3A	C_4AF	H.M.	S.M.	I.M.	LSF	7day	28day
Low-activation type A	34.8	51.9	1.9	9.2	1.97	4.80	0.87	0.80	≦250	≦290
Low-activation type B	34.8	56.2	5.9	0.9	2.11	10.57	8.06	0.79	≦250	≦290
(Ref.) Low heat cement	33.5	52.8	2.0	9.5	1.95	4.63	0.88	0.79	192	258
(Ref.) White cement	57.4	27.0	12.5	0.9	2.29	4.74	17.39	0.91	350	391

※ Mineral composition was determined by Bogue's equations [1].

Table 2. Raw materials for Low-activation cement.

Raw materials	Chemical composition (%)										
	Ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5
Limestone	43.72	0.13	0.09	0.03	55.35	0.47	0.01	0.00	0.01	0.00	0.01
Pyrophyllite	3.43	80.82	14.55	0.29	0.16	0.00	0.09	0.03	0.15	0.53	0.06
Hematite	18.91	2.04	1.06	55.86	21.11	0.13	0.00	0.00	0.07	0.04	0.18
Activated earth	8.09	89.90	1.26	0.16	0.21	0.11	0.13	0.10	0.06	0.14	0.00
Magnesium carbonate	57.53	0.07	0.01	0.02	0.38	41.75	0.11	0.00	0.00	0.00	0.02

Physical testing of Low-activation cement

Low-activation cements were tested according to JIS R 5201-97[2][3] and JIS R 5203-95[4]. The details for compressing strength test, setting test, and fluidity test[5] are shown in Table 3. Physical properties of Low-activation cements have to meet the requirements of Low heat cement on Japanese Industrial Standard.

Table 3. Mix design of paste and mortar for physical test.

Physical test	W/C (%)	Cement (g)	Water (g)	Fine aggregate (g)	PC (Cement×wt%)
Compressing strength	50	450	225	1350	—
Setting	—	500	Normal consistency	—	—
Fluidity	30	675	203	1350	0.65

PC: Polycarboxylic acid type superplasticizer

RESULTS

Examination of cement raw materials

Examination results of various raw materials are shown in Fig. 1 to 4., the amount of Eu and Co in limestone were extremely low compared with others. This is proof that concrete using limestone aggregate was low radioactivity. Coal ash, recycled iron, blast furnace slag, and silica fume were all high in Eu and Co contents. Many by-products have come to be used as raw materials of cement in recent years[6], but it is presumed that these by-products are not necessarily appropriate as raw materials for Low-activation cement.

Blast furnace slag (Fig. 4) and coal ash (Fig. 2) used especially in large quantities as raw materials of cement were found to have high contents of Eu. Similar trends were recognized in the results of various cements shown in Fig. 5.

From this examination result, to reduce the amount of Eu and Co in cement, we should select natural raw materials, for example limestone, silica stone and iron ore, for Low-activation cement.

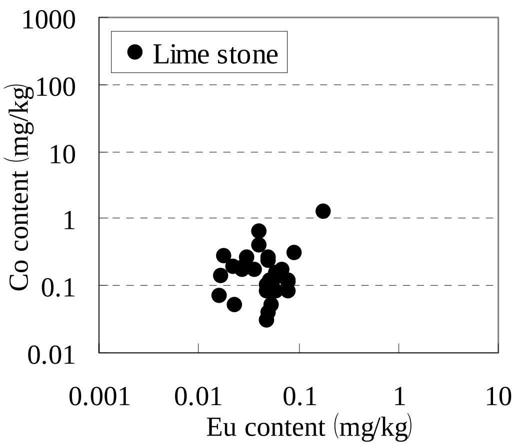

Fig. 1 Amount of Eu and Co in lime stone.

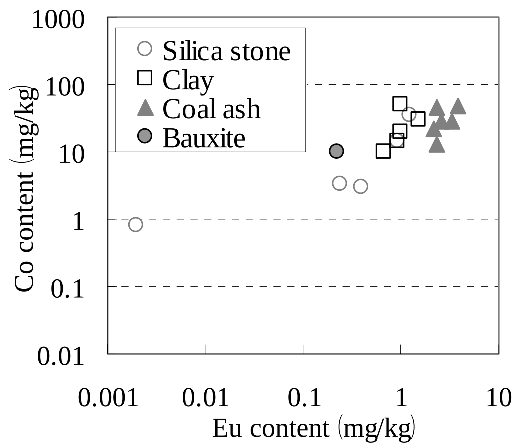

Fig. 2 Amount of Eu and Co in raw materials composed mainly of Al_2O_3 and SiO_2.

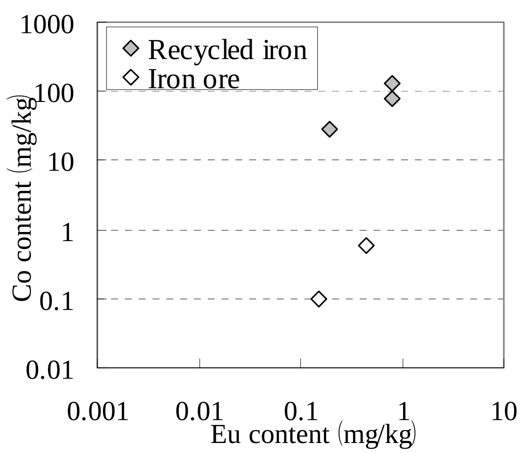

Fig. 3 Amount of Eu and Co in raw materials composed mainly of Fe_2O_3.

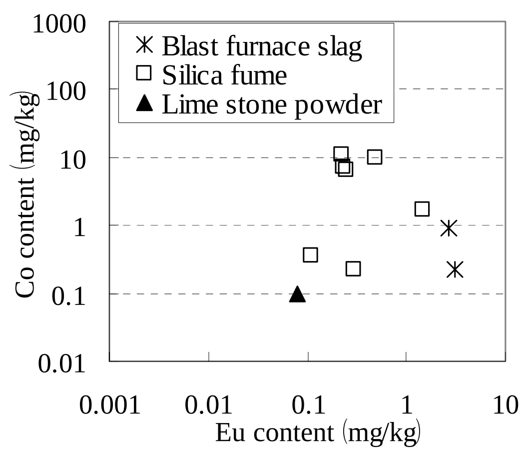

Fig. 4 Amount of Eu and Co in admixture.

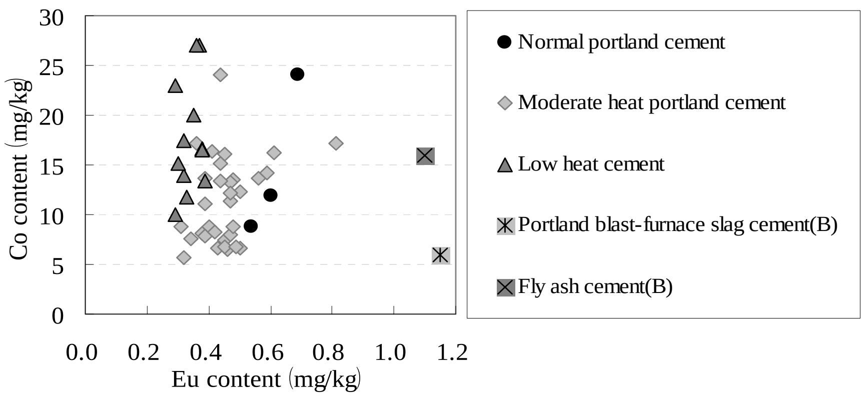

Fig. 5 Amount of Eu and Co in cement.

Investigation of cement-manufacturing process

With regard to Eu content in cements, a trend attributable to raw materials was recognized. But there was much fluctuation of Co content in cements, and it was surmised that there were other factors than raw materials involved.

Influence during grinding process is shown in Fig. 6. It was confirmed that Co is readily mixed to reagent even when grinding for only a short period of time. As other factors, the kind and quantity of fuel used on clinker burning process may affect to Co content in cement. For example, coal ash contains much Co (fig. 2).

Influence during clinker burning process is shown in Fig. 7. The amount of Eu and Co in Portland clinker made by electric furnace was low than Portland clinker manufactured in cement plant. The cause of this difference has roots in coal ash. In fact, if we use coal (Fig. 2) that have 15% ash content during clinker burning process and assume the clinker product to be composed of about 1.5% coal ash, the result of Fig. 7 was considered to be appropriate.

From this investigation result, to prevent the contamination of Eu and Co on cement-manufacturing process, we should grind all raw materials and clinker by alumina-ball mill, and use heavy oil or gas for clinker burning.

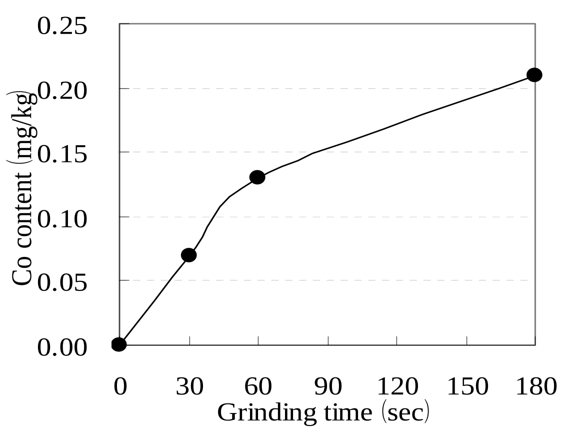

Fig. 6 Amount of Co in calcium carbonate after grinding with disk mill.

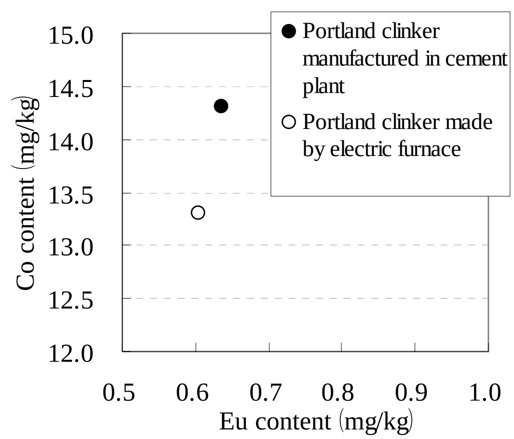

Fig. 7 Amount of Eu and Co in Portland clinker. (Influence of burning process on Eu and Co content)

Manufacturing of Low-activation cement

Based on the result described above, we have carefully selected natural raw materials, and made test production of Low-activation cement by the small-scale rotary kiln. Table. 4 to 6 shows the character of low-activation cements. Low-activation cements met the requirements of Low heat cement on Japanese Industrial Standard. Compressing strength and hydration heat of Low-activation cement type B was higher than type B. This is because Low-activation cement type B had much C_3S, C_2S and C_3A than type B.

Table. 7 show the amount of Eu and Co in Low-activation cements. We could reduce the amount of Eu and Co in cements significantly. Compared to Co, the reduction of Eu in Low-activation cements was small. This is because pyrophyllite and activated earth as raw materials had much Eu content than other row materials. Although a trial calculation, the result was obtained that these Low-activation cements can reduce radioactivity to one-third or less against commercially available Portland cement in Japan. In addition, it was thought that further reducing would be possible through improvements in the selection raw materials and manufacturing process (prevention of contamination during grinding and selection of fuel, etc).

Table 4. Chemical composition of Low-activation cement.

Cement	Ig.loss (%)	f-CaO (%)	Chemical composition (%)									
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5
Low-activation type A	1.16	0.22	26.34	2.49	3.05	62.83	1.39	2.37	0.01	0.02	0.11	0.03
Low-activation type B	1.19	0.68	27.61	2.51	0.41	64.49	1.37	2.07	0.01	0.02	0.11	0.02

Table 5. Character of Low-activation cement.

Cement	Mineral composition (%)				Modulus				Density	Specific surface
	C_3S	C_2S	C_3A	C_4AF	H.M.	S.M.	I.M.	LSF	(g/cm^3)	area (cm^2/g)
Low-activation type A	27.7	54.7	1.4	9.3	1.97	4.75	0.82	0.80	3.21	3280
Low-activation type B	29.3	57.2	6.0	1.2	2.11	9.46	6.12	0.80	3.17	3220

※ Mineral composition was determined by the Bogue's equations [1].

Table 6. Physical properties of Low-activation cement.

Cement	Compressing strength (N/mm^2)			Setting time (min)			Fluidity (mm)		Hydration heat (J/g)	
	7day	28day	91day	Water (%)	Initial	Final	0min	30min	7day	28day
Low-activation type A	14.3	31.8	64.0	25.7	185	310	323	276	201	247
Low-activation type B	18.6	42.8	69.6	29.5	135	220	416	384	231	290
(JIS) Low heat cement	≧7.5	≧22.5	≧42.5	－	≧60	≦600	－	－	≦250	≦290

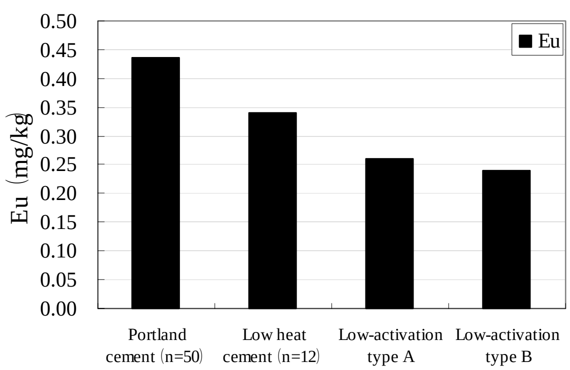

Fig. 7 Amount of Eu in Low-activation cement.

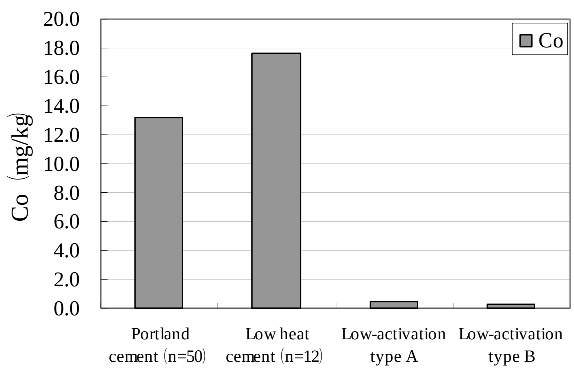

Fig. 8 Amount of Co in Low-activation cement.

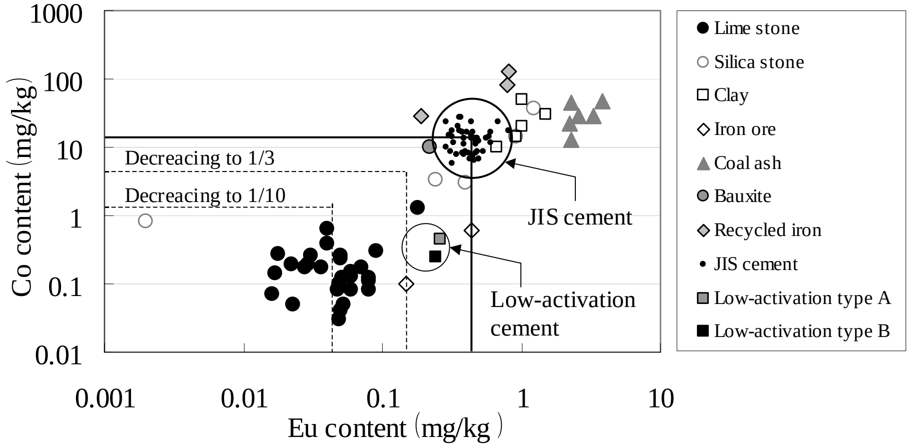

Fig. 9 Possibility of attaining Low-activation of cement.

SUMMARY AND CONCLUSION

We have been developing Low-activation cement to minimize the radio-active concrete. First, this study examined the chemical compositions of cement raw materials, and to reduce the amount of Eu and Co in cement, we confirmed that natural raw materials, for example limestone, silica stone and iron ore were appropriate. Next, we investigated cement-manufacturing process to prevent the contamination of Eu and Co, and confirmed that we should grind all raw materials and clinker by alumina-ball mill on grinding process, and use heavy oil or gas on clinker burning process. Finally, we have carefully selected natural raw materials and grind them by alumina-ball mill, and made test production of the Low-activation cement by the small-scale rotary kiln. As a result, Low-activation cements met the requirements of Low heat cement on Japanese Industrial Standard, and their amount of Eu and Co could be reduced significantly. Also, we obtained the result that the new cements can reduce radioactivity to one-third or less against commercially Portland cement in Japan. In addition, it was thought that further reducing would be possible through improvements in the selection raw materials and manufacturing process (prevention of contamination during grinding and selection of fuel, etc).

ACKNOWLEDGEMENT

This work is supported by a grant-in-aid of Innovative and Viable Nuclear Technology (IVNET) development project of Ministry of Economy, Trade and Industry, Japan. . We thank to all the members listed below who discussed and suggested in the course of performing this study.

Masaharu Kinno, (Fujita Corp.)

Katsumi Hayashi(Hitachi Ltd)

Uematsu Mikio(Toshiba corp)

Mikihiro Nakata(Mitsubishi Heavy Industries)

Ryoetsu Yoshino (Denki Kagaku Kogyo corp)

Mitsuru Sato (Nippon Steel Technoresearch corp)

Shigeru Ito (Tohoku Electric Power corp)

NOMENCLATURE

C_3S (Alite) = $3CaO \cdot SiO_2$

C_2S (Belite) = $2CaO \cdot SiO_2$

C_3A (Aluminate) = $3CaO \cdot Al_2O_3$

C_4AF (Ferrite) = $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

H.M. (Hydraulic modulus) = $CaO/(SiO_2+Al_2O_3+Fe_2O_3)$

S.M. (Silica modulus) = $SiO_2/(Al_2O_3+Fe_2O_3)$

I.M. (Iron modulus) = Al_2O_3/Fe_2O_3

LSF (Lime saturation factor) = $CaO/(2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3)$

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