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Low-activation Concrete-using limestone aggregate

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Abstract

As a result of investigating factors causing activation of component materials with regard to the phenomenon of activation of concrete, it was ascertained that the contents of sodium and other activation-inducing constituents were extremely low compared with non-limestone aggregates. It was also learned that there was a trend for long-lived radionuclides-producing elements like europium and cobalt to be contained to a high degree in coal fly ash, blast-furnace slag, etc. On performing activation of concrete is reduced in accordance with the quantity of limestone aggregate used due to less ^{24}Na produced. The amount of ^{24}Na production originating from magnesium was also studied.

Keyword : low activation, concrete, limestone, accelerator, Na, Mg, Eu, Co

1. Introduction

Shielding concrete is used in large quantities at constructions requiring shielding from radiation such as by neutrons, gamma rays, and X-rays, for example, nuclear reactor, accelerator, uranium processing, and radioisotope strange facilities, medical irradiation room, etc., so that radiation will not leak outside of controlled areas[1]. However, at nuclear reactor and accelerator installations, activation of shielding concrete can subject workers to radiation exposure while carrying out maintenance operations and cause problems of radioactive waste management when decommissioning a facility.

Since the only measures that can be taken against these problems are basically to hold down the amount of radio-nuclides produced in the concrete and to await attenuation, taking precautionary steps to prevent nuclear reaction is of particular importance. The authors will call these prior measures "low activation". It is expected that usage of the term "low activation" will differ depending on the user. The need will be great for the two point below to be focused on.

A. Measures against radiation exposure of workers during maintenance: the main cause of radiation exposure during maintenance of nuclear reactor and accelerator facilities is emission of gamma rays from short-lived radionuclides (^{24}Na) produced in shielding ^{24}Na concrete by thermal neutrons[2], and reduction in ^{24}Na production quantity is to be aimed for.

B. Reduction in production of radioactive waste; the main long-lived radionuclides produced in shielding concrete of nuclear reactor and reactor and accelerator installations are ^{3}H, ^{22}Na, ^{152}Eu, ^{60}Co, etc. Of these radionuclides, ^{152}Eu will pose the greatest problem in demolition of facilities, and reduction in ^{152}Eu production is to be aimed for.

With regard to adioactive waste management among these problems, numerous studies have been made of production processes utilizing experimental reactors. And it has been reported that the use of limestone aggregates is effective for achieving "low activation" of concrete[3].

On the other hand, activation of shielding concrete of accelerators is due to not only to thermal neutrons, but also fast neutrons, so that a comprehensive study is required. Studies on concrete for accelerators reported up till now have been those such as the ascertainment of low activation of accelerator concrete using limestone aggregate carried out by CERN(1971)[4], estimation of the proportions of elements producing ^{24}Na through irradiation experiments with a 6.2-GeV accelerator by Gilbert et al.(1969)[5], and analysis of 14 kinds of radionuclides produced in shielding concrete walls of the 12-GeV proton synchrotron accelerator of KEK(High Energy Accelerator Research Organization) by Miura et al(2000)[6]. However studies such as of what degree of "low activation" can be aimed for by control to what kinds of elements had been made.

The authors therefore carried out systematic investigations of activation-causing constituents of concrete materials inducing "low activation" of accelerator shielding concrete, and investigative tests of activation phenomena by accelerator, which will be reported below.

2. Testing Samples

2.1 Investigation of Concrete Materials

Samples were cement (ordinary, moderate heat, low heat, type B blast-furnace slag) manufactured in Japan according to Japanese Industrial Standards, mineral admixtures (ground granulated blast-furnace slag, coal fly ash, silica fume, limestone powder), and ordinary aggregates. Considerations were not given to to whether samples were representative of their sources when obtaining them.

2.2 Accelerator Irradiation Tests

The objects of tests were three type of cement and 15 varieties of aggregates selected according to 2.1 above, and three kinds of concrete using these as materials.

Concrete specimens were stripped from molds at the age of 7 days, then air-cured at 20℃ for 21 days, upon which they were pulverized and homogeneous materials obtained as samples. The mixture proportions of the concretes and their physical properties at 28 days.

3. Details of Investigations and Tests

3.1 Constituent Investigations of Concrete Ingredient Materials

The objects of investigations were the content amounts of Na, Mg, Al, and Si (quantification results given in terms of oxides) the parents elements of ^{24}Na,and Eu and Co, the parent element of ^{152}Eu and ^{60}Co.

In examining compositions, semi -quantitative analyses were first carried out followed by quantification of necessary constituents, and their distributions were investigated. For Eu and Co in particular, activation analyses were performed as they were of minute quantities.

(1) Sample preparation

Preprocessing was done according to the procedure below giving through attention to A: representativeness, B: uniformity, C: contamination of the constituent being investigated. Approximately 100g of material was obtained through sample reduction and, after pulverizing down to under 100 μm size using an agate mortar, this was thoroughly mixed and made the evaluation sample.

(2) Semiquantitative Analyses of Cement and Admixtures

Mass spectrometry was performed by ICP-MASS to ascertain the orders of elements contained in cements and mineral admixtures (fly ash, slag). The testing solutions used were those preprocessed (acid-base extraction) in accordance with the Japan Cement Association Method.

(3) Constituent Investigations of Aggregates

The losses on ignition(975℃) of powered samples were measured, along with which rapid quantitative analyses were obtained by atomic absorption analyses.

(4)Constituent Investigations of Eu and Co in Concrete Materials

Activation analyses of dried samples in 0.2g amounts were carried out using the JRR4 reactor of Japan Atomic Energy Research Institute. Thermal neutron irradiation (flux density 4.7113 $\times 10^{13}$ (n/cm^2·sec) は, irradation time 20 (min), consisted of short time (5days) cooling, long time (61days) cooling followed by γ-ray spectrometry, calculating concentrations of analysis object elements in samples based on the enumerated values obtained and measurements of standard substances irradiated simultaneously.

3.2 Neutron Irradiation Experiments by Accelerator

Forty to 50g of powdered samples were placed at location 2m to sides of targets at the EP1 and EP2 beam line tunnels of the 12GeV proton synchrotron accelerator of KEK (High Energy Accelerator Research Organization) with activation achieved by secondary neutron irradiation. Short time irradiation (5 days) and long time irradiation (50 days) were carried out. Of various γ radionuclides produced, ^{7}Be, ^{22}Na, ^{24}Na, ^{46}Sc, ^{51}Cr, ^{54}Mn, ^{56}Mn, ^{59}Fe, ^{58}Co, ^{60}Co, ^{65}Zn, ^{134}Cs, ^{152}Eu, and ^{154}Eu were measured by Ge semiconductor detector. The differences between neutron simultaneously irradiating gold leaf and aluminum foil, calculated from gold corresponded to 1×10^7 (n/cm^2·sec), and the fast neutron flux calculated from aluminum to 1×10^5 (n/cm^2·sec).

Furthermore, reagents $NaHCO_3$, MgO and Al_2O_3 were similarly subjected to irradiation tests and the influences of these constituents on ^{24}Na production were investigated.

4. Results and Comments

4.1 Analyses Results of Cement and Admixtures

A part of the results of analyses by ICP-MASS is given in Table 1. Of constituents involved in activation, the content of Co was the orders of 10^{-6}, and that of Eu 10^{-7}. These minute quantity constituents were of concentrations not possible to detect with the anlysis precision in ordinary quality control of cement, and it was necessary for measures such as activation analysis for quantification to be taken.

Table 1. Example Result of Analysis by ICP-MASS for cement

100mg/kg over	Na,Mg,Al,Si,P,S,K,Ca,Ti,Mn,Cu,Zn,Sr,Ba
1-100mg/kg	V,Cr,Co,Ni,Ga,Ge,As,Rb,Y,Zr,Cd,Ce,Pb
1mg/kg under	Sc,Pd,Ag,Eu,Au,Th,U

4.2 Results of Investigations of Aggregates

The distributions of Na_2O and MgO in Fig.1. It can be seen that limestone as a whole is low in content of constituents other than MgO and that it is an aggregate effective for inhibiting production of ^{24}Na. However, with regard to MgO, it can be comprehended from Fig.1 that there are aggregates with high content of this constituent. This is because the MgO content of limestone aggregate varies greatly according to the source, and there are even some limestones having intercalations of dolomite and magnesite.

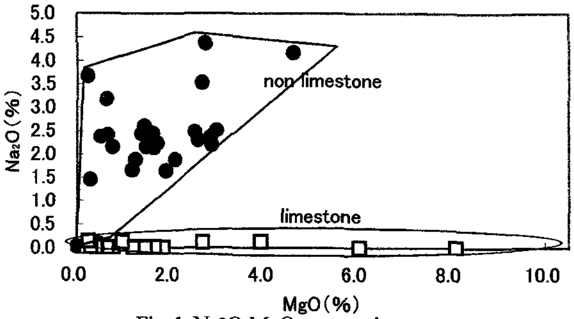


Fig. 1. Na2O-MgO contents in aggregates

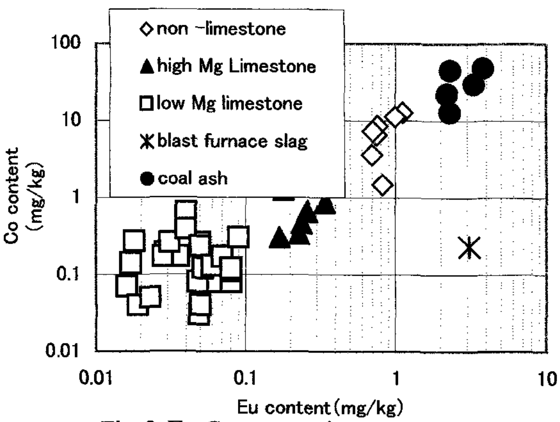


Fig. 2. Eu-Co contents in aggregates

Talbe 2 Eu-Co contents in cement-admixtues

	Eu(mg/kg)	Co(mg/kg)
Oridinary Portland Cement	0.60	11.90
Low heat Portland Cement	0.38	16.50
Blast furnance slag Cement B	1.65	6.30
Fly Ash Cement B	1.10	15.90
Blast furnace slag admixture	2.70	0.90
JIS Fly Ash for admixture	2.60	28.10
Silica fume	1.47	1.70
Limestone powder	0.08	0.10

4.3 Activation Analysis Results

A part of the results obtained in analyses of cement-admixtues is shown in Table2. Prominent characteristics were not grasped regarding Co contents, whereas compared with fly ash and blast-furnace slag were high in Eu contents. It is thought much Eu came to be contained in coal fly ash because Eu is constituent which becomes concentrated on the flux side accompanying heat treatment of silicate (the rise in Eu concentration in the phase equilibrium of Si-Al isconsidered an abnormal phenomenon of Eu in geochemistry)[7].

As coal is used as a feul in manufacture of Portland cement it is thought unavoidable for around 0.3-0.8 mg/kg of Eu to be contained. With blended cements, there are Eu concentrations due to admixtures, and blast-furnace slag and fly ash cements thus have higher Eu concentrations than Portland cements.

Fig.2 shows results of Eu and Co contents measurements on various aggregates where all limestone aggregates had extremely low Eu concentrations compared with non-limestone aggregates had extremely low Eu concentrations compared with non-limestone aggregates. This is thought to have been because limestone is not an igneous rock, but originates from organisms, with its purity maintained provided it is not subjected to metamorphism through such causes as contact with igneous rocks.

Limestone is one of the richest natural resources in which Japan is self-sufficient and limestone of extremely high Ca purity is widely produced. Aggregates conforming to JIS standards have been supplied in large quantities and there have been many cases in Japan where concretes having limestone as aggregate have been used[8]. It is looked forward to that production of long-lived ^{60}Co and ^{152}Eu radionuclides in such limestone concretes will be held down and there will be less radioactive wastes to be coped with when decommissioning installations.

Table 3. Result of Irradiation test by 12GeV accelerator(slag)

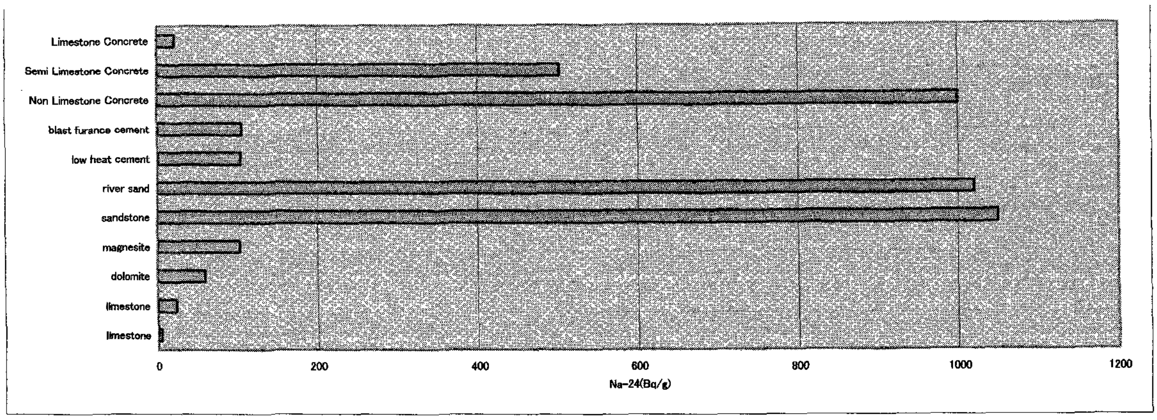
	After 5 hours	After 26.5 hour	After 60.5 hour	After 155.0 hour
Be-7	14.30	14.10	13.90	13.20
Na-22	1.37	1.37	1.37	1.37
Na-24	100.00	39.00	7.91	0.10
Sc-46	13.40	13.30	13.20	12.90
Cr-51	6.31	6.12	3.99	3.41
Mn-54	1.78	1.78	1.73	1.73
Mn-56	388.00	1.31	0.00	0.00
Fe-59	2.19	2.18	2.12	1.95
Co-58	0.08	0.08	0.08	0.08
Co-60	0.39	0.39	0.39	0.35
Zn-65	1.53	1.53	1.52	1.50
Cs-134	1.44	1.44	1.43	1.43
Eu-152	1.08	1.08	1.08	1.08
Eu-154	0.23	0.23	0.23	0.23

4.4 Results of Irradiations Experiments with Accelerator

Examples of the constituents of samples used irradiation tests by 12 GeV accelerator are given to examples of time-dependent changes in radiation intensities (blast-furnace slag cements) in Table3,. According to the examples of blast-furnace slag cement in Table3, short-lived radionuclides such as ^{56}Mn(half-life 2.6hours) and ^{24}Na(half-life 15hours) which existed in large quantities immediately after ceasing irradiation are greatly attenuated at about 60 hours. However, long-lived radionuclides such as the likes of ^{152}Eu (half-life 13.5years) and ^{60}Co (half-life 5.3years) which are though will remain at the time of decommissioning and demolition of a facility are practically unattenuated after elapse of 155 hours. This was a trend with all component materials of concrete even though there may have been differences in concentrations.

The ^{24}Na radiation intensities of various irradiated samples are shown in Fig.3, even with magnesite having MgO content of approximately 42%, ^{24}Na concentration was 1/10 compared with river sand, while with dolomite and limestone aggregates having lower MgO contents, concentration of ^{24}Na produced were all less than 1/10. Cements, irrespective of variety, produced less ^{24}Na than non-limestone aggregates, but more than limestone aggregates. The result leads one to judge that for lower activation of concrete in Japan, it will be effective as a first step to bring about a switch to limestone aggregate.

According to Gilbert(1969), the ^{24}Na productions per



unit mass of the elements Na, Mg, Al and Si are as given by Eq.(1).

Na:Mg:Al:Si=1:0.02:0.01:0.002————(1)

From Eq.(1), that limestone aggregate depended greately on low production of ^{24}Na due to its low content of Na_2O[3] ,but that Under conditions of fast neutron influence, the MgO constituent will also contribute to ^{24}Na production was of concern. Therefore, it was necessary to reconsider the appropriateness of limestone of high MgO content for achieving "low activation"of concrete. It was for this reason that an examination was also made of the influence of MgO.

Upon evaluation was also made of the influence of various constituents on ^{24}Na production by ^{24}Na concentration ration per unit weight, Eq.(2) was deduced and the result obtained was that the degree of contribution of Mg to activation was lower than Gilbert's (1969) result (Na:Ma:Al=1:0.02:0.01) obtained with 6.2 GeV apparatus.

Na:Mg:Al:Si=1:0.02:0.01:0.002————(2)

The results of trial calculations of ^{24}Na inhibiting effect of concrete with limestone aggregate applying Eq.(2) are given in Table 6. Although contribution by MgO can be seen, it was trial-calculated that when limestone aggregates are used the ratio of concentration of ^{24}Na produced are about 1/15 to 1/45 of those in cases of using non-limestone aggregates. It should be noted that in Japan any aggregate with MgO content exceeding 10.5% percent is classified as dolomite [8] .

Although there are still matters needing study and explanation such as improvement in precisions of analysis methods, measures to deal with scatter in quality, anisotropy in non-pulverized concrete samples, and influence of the amount of ^{3}H (tritium) that remain, it has been shown in the present examination that concrete containing a large proportion of limestone is "low activation concrete" of low ^{24}Na production.

5. Conclusions

(1) When contemplating low activation of concrete in Japan, it is most effective in design of "low-activation" concrete to realize conversion of aggregate to limestone.

(2) To effect reduction in radiation exposure of workers during maintenance operations it will be advantageous to choose materials low in Na and Mg contents. In irradiation experiments by accelerator, ^{24}Na production with limestone was about 1/45of that with river sand. Cements were lower in ^{24}Na production than non-limestone aggregates, but higher than limestone aggregates.

(3) The degree of influence of individual constituents on ^{24}Na production according to the results of neutron irradiation experiments using a 12 GeV proton synchrotron accelerator indicated in terms of ^{24}Na concentration ration per unit mass were : Na_2O:MgO:Al_2O_3= 1 :1/100:1/100.

This is a result where the degree of contribution of Mg to activation is lower than the result (Na:Ma:Al=1:0.02:0.01) in irradiation by the 6.2 GeV apparatus of Gilbert(1969).

(4) It is necessary to select materials low in Eu and Co contents to reduce radioactive waste production when discarding concrete subjected to radiation. That means "selecting materials such as limestone aggregate" or "not using materials such as blast-furnace slag and coal fly-ash". Concrete used in accelerator facilities and nuclear reactor facilities is mostly mass concrete. Thus, in the study reported here concrete using "low heat Portland cement" and not blast-furnace slag cement or fly-ash cement is evaluated positively in selection of cement from the view point of inhibiting thermal cracking.

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