- Technical Paper -

IMPACT OF CONCRETE CHARACTERISTICS ON THE CS TRANSFER IN CONCRETE

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ABSTRACT

For the decommissioning of the Fukushima-Daiichi Nuclear Power Station and for the safety assessment of concrete facilities for radioactive waste disposal, evaluation of cesium (Cs) transfer in concrete is essential. In this study, several factors affecting Cs transfer, such as Cs concentration, clay, and carbonation, are experimentally evaluated using autoradiography of radioisotope Cs-137 by imaging plate. For the evaluation, mortar specimens were immersed in CsCl solution. The concentration did not affect the transfer profiles for sound mortar. However, carbonation increased the Cs binding and retarded the transfer.

Keywords: cesium, transfer, concentration, binding, carbonation, Fukushima-Daiichi, imaging plate

1. INTRODUCTION

For the decommissioning of nuclear power stations (NPS), especially those that suffered accidents, such as the Fukushima-Daiichi NPS (1F-NPS), details on the distribution of contamination in the concrete are critical. As part of a series of projects known as the "Wisdom projects": the Nuclear Energy Science & Technology and the Human Resources Development Project -through concentrating wisdom-, operated by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), a project from Jan. 2018 to Mar. 2020 on the "Estimation of contamination distribution in concrete members of 1F-NPS buildings based on mechanism-understanding of radionuclides contamination of cement-based materials" has been organized [1]. Of these contaminants, radio-cesium (r-Cs) is a key contaminant; furthermore, the estimation of r-Cs contamination in concrete is important for the disposal facilities made of concrete in off-site.

Cs contamination in concrete has been well studied [2]. Alkali ions such as Cs transfer in concrete by diffusion under the effect of binding. Cs is known to interact with C-S-H of lower C/S, clay minerals but the interaction is interfered by Na and K by competitive adsorption [3]. In the pore solution of concrete, Na and K are in the concentrations of 0.1 M order. However, Cs concentration in cement is 1-10 ppm order and that in pore solution is 10 μ M order. Therefore, Cs binding by C–S–H of low C/S or clay minerals in a cement system is expected to be limited. Another important factor affecting Cs binding is the degradation such as carbonation and Ca leaching of concrete [3]. These degradations generate alumino-silica gel having cation exchanging capacity. However, in such degraded concrete, there is no reported Cs or alkali transfer.

Based on this, this study investigated the effect of concentration, clay minerals, and carbonation as an example of degradation on Cs transfer through autoradiography using the imaging plate (IP) method for Cs-137.

2. EXPERIMENTS

2.1 Materials

It is preferable to use small samples to carry out immersion tests using radioisotopes. Therefore, mortar is used in the present study instead of concrete. The cement used was Ordinary Portland cement (OPC). Two types of sand were used: washed out pure limestone (LS) assumed to have limited Cs adsorbing ability and river sand containing clay (RS, estimated to be used in 1F-NPS [1]). According to petrographic analysis, a small amount (0.1 mass% order) of chlorite was detected. The abbreviations used for the sample denote the cement type-sand-solution. For example, "OPC-LS 100 mM" denotes the OPC and limestone aggregate immersed in 100 mM of CsCl solution.

The water-to-cement ratio was 0.55 and the sand-to-cement ratio was 2.39. After demolding after 24 hours from mixing, samples were cured at 20 °C for one year under a sealed condition. Some samples were carbonated in a chamber at 20 °C, 60% relative humidity (RH), and 5% CO_2 for three months; the carbonated depth was 8 mm.

For both samples without/with carbonation, before immersion, mortar specimens were water saturated under vacuum for 24 hours. Water used for immersion test is ion exchanged water.

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Fig.1 Transfer profile imaging procedure (modified after [4])

2.2 Immersion test

Immersion tests were conducted by using CsCl solution at concentrations 100 mM, 1 mM, or 10 μ M, labeled with Cs-137. The original radioisotope (RI) solution of Cs-137 supplied by the Japan Radioisotope Association was composed of 1 MBq/5 ml of Cs-137 and 0.01 M of Cs-137Cl. From this RI solution, by dilution with water and addition of CsCl reagent, the Cs-137 concentration was controlled at 2500 Bq/mL and the CsCl concentration was controlled at the required concentrations, respectively.

The amount of solution was 10 mL for the 100 mM and 1 mM concentrations and was increased to 100 mL for the 10 µM solution because an increased solid Cs distribution ratio from the solution at lower concentration was expected. For the immersion test, to reduce the amount of RI solution and to avoid carbonation as much as possible, aluminum laminated bags (Al bag) were used. A piece of non-woven fabric was laid at the bottom of the Al bags to facilitate solution contact with the exposed sample surfaces. The solution was poured into 400 and 825 mL Al bags for the 10 mL and 100 mL solutions, respectively, before sample insertion. For the 10 mL solution, only the bottom of the sample was immersed in the solution, while for the 100 mL solution, half of the sample was immersed in the solution.

2.3 Measurements

The transfer profile imaging procedure is based on a previous study [4] and is shown in Fig. 1 (modified after [4]). Samples coated with epoxy resin except for the immersion face were immersed in solutions. The radiation dose rate of the solution and the immersion surface of the mortar were measured by NaI scintillation and GM survey meters (NaI and GM, respectively). Survey meters were placed in lead blocks whose detector surfaces set toward upper and Al bag containing RI solution or sample covered by thin plastic film are placed. The radiation events were counted for 180 s three times and counts per minute were calculated.

Primarily, NaI counts γ -rays and GM counts β -rays. β -rays are attenuated quickly and penetrate only 0.1 mm into concrete or mortar. However, γ -rays penetrate much deeper and 10 cm of concrete decrease the intensity of γ -rays from Cs-137 by only 40%. At

each measurement interval, samples were removed from the bags and wiped with paper. In this step, 0.08 g and 0.55 g of solution were lost for the 10 mL and 100 mL solutions in average, respectively. For the solution, measurements were taken from the bottom side of bags. For the samples, the exposed surface was placed on detectors. The measurement errors of this type of measurement are expected to be $\pm 15\%$ for the bags due to the difficulty in placing them in the same position. The immersion test was continued for 56 days.

After immersion for 56 days, 1.6-mm-thick cross-sections were sliced. These sections were exposed on an imaging plate (GE Healthcare, BAS IP MS) with standard cement paste containing a known concentration of 137Cs (1 MBq/kg). Radiation signals were read by a Typhoon FLA9500 (GE Healthcare) with a spatial resolution of 50 µm and the data were analyzed by the Image Quant. By applying a mesh of 1x100 composed of 15x0.5 mm sized pixels on an IP image, a line profile of r-Cs concentration can be obtained. In order to convert the obtained IP signals (photostimulated luminescence, PSL) into radiation or material concentrations, cement paste containing 1 MBq/kg of Cs-137 was prepared and exposed on IP simultaneously with samples. PSL is proportional to radiation concentration and by comparing PSLs from samples and the standard, it is possible to calculate the radiation concentration of samples. The radiation concentration and stable Cs concentrations in immersion solution are known as 1 MBq/5cc and 0.05 mg/g as CsCl, respectively. Therefore, from the calculated radiation concentration, it is possible to calculate the material concentration also. Then, the distribution ratio of Cs between solid and solution can be calculated as the ratio of Cs concentration in solid (mol/kg) to that in solution (mol/L), giving a unit of L/kg.

3. RESULTS AND DISCUSSION

3.1 Water-saturated no degradation samples (1) Dose rate measurement

The dose rate change during the immersion test of water-saturated no-degradation samples are shown in Fig. 2. The values of the 10 μ M solution are larger than the others as the solution volume and the bottom area of the immersion bag were larger than others. Therefore,



Fig. 2 Dose rate change of immersion solution and sample (water-saturated no-degradation samples)

the values are plotted on a second axis.

The dose rates of the solutions are constant during the immersion period in both NaI and GM There are decreases measurements. in NaI measurements between the original values and the first measurement but there is no decrease in GM measurement. This is contradiction. Sample setting of Al bag for NaI measurement is quite difficult to obtain reproducibility as shown significant fluctuation in other measurements and the decrease observed in the first measurement is assumed to be caused by an error in the measurement of original values. The constant values for all range of immersion period means that the adsorption of Cs is limited compared to the amount in the solution even in the case of clay minerals containing sand.

The NaI measurements indicate the total amounts of transferred Cs in the mortar. The dose rates of the samples measured by NaI show a linear increase against the square root of age, suggesting the accumulation of Cs in the samples. This behavior is judged as simple diffusions. There is no Cs concentration dependence for the OPC-LS series. However, the OPC-RS 100 mM showed 70% higher values, suggesting an increased binding ability of the clay minerals.

The GM measurements indicate the surface concentration of Cs. The dose rates increase in the beginning but were saturated in one week. There are different behaviors depending on the samples and solutions. The highest values were obtained in the lowest concentration solution, 10 μ M. This can be explained by assuming that a small amount of Cs is bound even by pure limestone aggregate. The adsorbed

amount is very limited and no changes are detected in NaI and GM measurements. For the same bound amount, the relative strength of radiation is stronger with lower Cs concentration. For RS, 30% more Cs was bound, suggesting the absorbing ability of Cs by clay minerals.



Fig. 3 IP images of water-saturated no degradation samples. The specimen size is 20x50mm.
From top to bottom, OPC-RS 100 mM, OPC-LS 10 μM, OPC-LS 1 mM, OPC-LS 100 mM, and 1x100 mesh for line profile.



Fig.4 Line profile of radiation concentration (left) and material (Cs) concentration (right) of no-degraded samples



Fig. 5 Dose rate change of immersion solution and sample (water-saturated carbonated samples)

(2) IP analysis

IP images for water-saturated no-degradation samples are shown in Fig. 3. The contrast is enhanced to show the wide range of signal strength. Because of the nature of IP, the measurement results have a wide dynamic range of five orders of magnitude as shown in Fig. 4 left (radiation concentration profiles).

Line profiles of radiation concentration and material concentrations are shown in Fig. 4. The radiation concentration profiles are close for all OPC-LS samples, independent of Cs concentration. Only at the surface do the radiation concentrations differ, following the order of OPC-LS 10 μ M >

OPC-LS 1 mM > OPC-LS 100 mM, and this order is the same with the dose rates given by GM shown in Fig. 2 (right bottom). In an area less than 5 mm, other alkali ions such as Na and K were transferred from the mortar to the immersion solution. Then, the competitive adsorption by K against Cs became weak and the difference in binding might be observed.

From the radiation concentration profiles, the Cs material concentration profiles are calculated and shown in Fig. 4 right. Reflecting the difference in the solution concentration, the concentration profiles are in a different concentration range. The background level is considerably different and can be attributed to the



Fig. 6 Line profile of radiation concentration (top) and material (Cs) concentration (bottom) of carbonated samples

background level of the original IP image. Independent of the Cs concentration in solution, the limit of Cs transfer is the same as 20 mm for OPC-LS series. For OPC-RS 100 mM, the depth was 15 mm, lower than the others. Cs binding by clay may affect the transfer.

3.2 Water-saturated carbonated samples

(1) Dose rate measurement

The results of dose rate measurements of solution and samples are shown in Fig. 5. Different from the water-saturated no-degradation samples, rapid decreases in dose rate are observed for the solution. The lower concentration solution showed a faster decrease. For the 10 μ M solution, the quantity of the solution was 10 times more, reducing the amount of decrease compared to the other concentrations. However, still fastest decreases were observed. Even for the 100 mM solution, the concentration decreased to 1/3 after 56 days of immersion. There is no effect of clay minerals on RS.

For the radiation dose rate of the samples, differences that are more significant are observed. The range of radiation dose rate is much higher compared to no-degraded samples. The difference is one or two orders of magnitude, suggesting strong absorption Cs in carbonated area. OPC-LS 10 μ M showed rapid changes until one week and saturated after that point. However, this is the only saturation of the NaI detector. The radiation dose rate is considered as too high. Except for this sample, OPC-LS 100 mM and OPC-RS 100 mM showed an approximately linear increase with the square root of age; however, the trend slowed at longer ages. OPC-LS 1 mM had an evident slow down and saturation of dose rate increase. This may be caused by the significant uptake of Cs from the solution.

From the GM measurement, all samples showed saturation after one week. The order of saturation corresponds to the results from the NaI detector. The strange behavior of the OPC-LS 10 μ M sample may have been caused by the detection limit of the GM tube. (2) IP analysis

Radiation and Cs material concentration profiles of the water-saturated carbonated samples are shown in Fig. 6. The radiation dose rate levels are one or two orders of magnitude higher than the water-saturated no-degradation samples shown in Fig. 4. This increase was caused by the strong Cs binding at the carbonated sections.

The material concentration shown in Fig. 6 bottom clearly indicates the binding strength of carbonated OPC and clay. The amounts of bound Cs were also one or two orders of magnitude higher.

In the carbonated area, Cs plateaued, and beyond this, it demonstrated some diffusion profiles, although the shape is not clear. More precise IP measurement is required.

The penetration depths are in the range 6-10 mm and less than half of 20 mm in the case of water-saturated no-degradation samples. Strong Cs binding of carbonated areas retards the penetration of Cs.



3.3 Distribution ratio of Cs in solid to solution

At the surface of the samples, the K concentration is assumed to be negligible and the Cs concentration is estimated from the dose rate from the GM tube for solutions at 56 days. The distribution ratios of Cs in solid to solution were calculated and are plotted against the Cs concentration in solution in Fig. 7. In the figure, reported values from [3] are also

plotted. As shown, the distribution ratio demonstrates a negative correlation with Cs concentration and the trend is the same as per previous studies. The absolute values are different by approximately one order of magnitude. For increased accuracy, the concentrations of other alkali ions have to be measured and the selective ion distribution should be considered.

The effect of clay is also clearly indicated. Even at high Cs concentration such as 100 mM, the clay enhances the distribution coefficient by one order of magnitude. The content of clay in this study is limited. When more clay is included, higher retardation by clay will be observed. However, this strong binding is under low K concentrations. It is ambiguous how much the Cs binding of clay minerals is present at large depths in the cement. Selective distribution behavior has to be considered in more detail.

4. CONCLUSIONS

To investigate the radio-Cs transfer in concrete, autoradiograph using the imaging plate technique was carried out for a wide range of Cs concentrations (10 μ M - 100 mM) and the effect of Cs binding by clay minerals in aggregate and carbonated OPC were examined experimentally.

- (1) Pure limestone assumed to have limited binding ability for Cs did not show Cs concentration dependence on Cs transfer. The depth of Cs transfer was 20 mm at 56 days. Through the inclusion of minor clay minerals, the depth was decreased to 15 mm.
- (2) After carbonation of 8 mm of the specimen (thickness), the Cs transfer was decreased to 6–10 mm.
- (3) Cs binding significantly retarded Cs transfer.
- (4) Negative concentration dependency of Cs distribution in solid to solution is confirmed for

carbonated OPC.

(5) The effect of carbonation on Cs binding was confirmed.

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REFERENCES

- [1] Nagoya University, Estimation of contamination distribution in concrete members of Fukushima Daiichi NPS buildings based on mechanism-understanding of radioactive nuclides contamination of cement-based materials (Report MEXT mentioned for project in the acknowledgement), 2019 (in Japanese).
- [2] Atkinson, A. & Nickerson, A.K., Diffusion and Sorption of Cesium, Strontium, and Iodine in Water-Saturated Cement. Nuclear Technology, Vol. 81, pp.100-13, 1988.
- [3] Haga, K., Watanabe, S., Yamada, K., Quantification of interaction between alkali metal ions and C-(A-)S-H/cement paste for a wide range of ion concentrations, Proceedings of 15th Congress on the Chemistry of Cement, 339, 2019.
- [4] Osawa, N., Yamada, K., Igarashi, G., Tomita, S., A trial on the separated determination method between Cs-137 and Sr-90 by Imaging plate (II), JCI Proceedings, 41, 1001, 2019 (in Japanese).