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ARTICLE

Sorption Behavior of Alpha-Ray Emitting Nuclides on Concrete in Contact with Radioactive Contaminated Water

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The contamination of the concrete inside the buildings at the Fukushima Daiichi Nuclear Power Station was caused by the presence of radioactive nuclides, including alpha-ray emitting actinides such as Pu and Am, which were contained in the contaminated water. The behavior of Pu and Am in aqueous solution is complex, and an understanding of the contamination distribution of these nuclides is therefore important. To simulate the contact between construction materials and contaminated water in the reactor buildings, cement pastes, aggregates and carbon steels were immersed in solutions containing Pu and Am. The distribution ratio of Pu and Am was found to be significantly influenced by pH, which was observed to be markedly reduced when the cement paste was in a carbonated condition. It was noted that carbon steel corroded to form rust, and most of Pu and Am were incorporated in the rust during the process of rust formation, rather than sorption on the formed rust.

KEYWORDS: Fukushima Daiichi Nuclear Power Station, concrete, cement paste, aggregate, sorption, plutonium, americium

I. Introduction

The Great East Japan Earthquake of March 2011 caused extensive damage to the Fukushima Daiichi Nuclear Power Station (F1NPS), resulting in the release of radioactive contaminated water. This was caused by fuel damage, which led to the contamination of the concrete comprising the reactor building basement of F1NPS with fission products, activation products and α-ray emitting actinides.

α-ray emitting actinide nuclides such as ^{238}Pu and ^{241}Am, are important in radioactive waste disposal in safety. It has been reported that the contaminated water and waste, including rubble, vegetation and soil, have been contaminated with plutonium (Pu) and americium (Am).[1)] The accumulation of contaminated water has been observed in the basement of the reactor and other buildings. It has been reported that actinides have been detected in this contaminated water, indicating that the actinides are continuously supplied by the damaged fuel through slow dissolution.[2)] However, the transport ratios of ^{238}Pu and ^{241}Am from fuels are an order of magnitude lower than those of their fission products, ^{137}Cs and ^{90}Sr.[3)] ^{137}Cs and ^{90}Sr, the major radioactive nuclides in the F1NPS contamination, are alkaline and alkaline earth elements, respectively.

With regard to their behavior in aqueous solutions, Pu and Am are different from alkali and alkaline earth metals. The targets of this study, Pu and Am, exhibit a range of chemical forms that are influenced by water conditions. In the oxidized species, Pu +VI is stable under strongly oxidizing conditions, whereas +IV is mainly observed in less oxidizing conditions. Am is generally stable to exhibits a +III oxidation state. Given the complex chemical behavior of Pu and Am, it is desirable to obtain data using Pu and Am themselves, rather than alternative elements, in order to understand their migration behavior in water.

In planning the decommissioning work, it is essential to consider the segregation, processing and disposal of a significant quantity of contaminated concrete. Despite the necessity to comprehend the contamination of concrete in advance, the high dose rate and immersion in the contaminated water render sampling challenging. Consequently, investigating the contamination mechanisms has become a crucial aspect in understanding or estimating the state of contamination.[4)]

The building is primarily composed of reinforced concrete, which is comprised of cement paste, aggregate, and reinforcing steel. In the future, these will become waste. By focusing on individual materials, determining the sorption of Pu and Am on each of them will provide insight into the trend of nuclides transferred to the waste. The distribution ratios of Pu and Am migrating into construction materials such as cement paste, aggregate and carbon steel were determined by immersion tests.

II. Experimental

The distribution ratios were obtained from experiments conducted by immersing simulated building structures in solutions simulating the contaminated water. To simulate the contaminated water containing nuclear materials, test

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solutions were prepared by dissolving mixed oxide (MOX) of uranium and Pu, and uranium oxide. The MOX contained the Am isotope of ^{241}Am, which is produced as a progeny nuclide of ^{241}Pu. Two methods were employed to prepare the test solutions. For test solution A, 40 cm^3 of 0.06 mol/dm^3 $NaHCO_3$ solution and 6 cm^3 of 35% H_2O_2 solution were added to 1.24 g of MOX powder and 3.75 g of UO_2 powder, which were then shaken for six hours. Subsequently, this solution was filtered and diluted with deionized water. For test solution B, the MOX powder was dissolved by heating nitric acid solution and the Pu was extracted with TBP/n-dodecane. This solution was diluted with deionized water as is test solution A. The concentrations and pH of the prepared solutions are summarized in **Table 1**.

Ordinary Portland cement (OPC) and fly ash cement (FAC) are utilized as construction materials for on-site concrete in the construction of buildings. Consequently, Portland cement and fly ash cement paste powders were prepared. The cement pastes were subjected to wet curing at a temperature of 313 K for a period of three months. The cement pastes were ground to a particle size of less than 100 µm using an agate mortar. The buildings of F1NPS have been constructed for over 50 years, during which time the concrete has been exposed to the atmosphere, resulting in carbonation. In addition to the sound condition (dried in relative humidity (RH) 11%), a cement paste was prepared with an accelerated carbonation treatment (293K, RH 60%, CO_2 5%) for three days to create a carbonated condition.

Additionally, carbon steel was employed for immersion, as a scenario in which the rebar would be in contact with contaminated water was foreseeable. Two categories of samples were prepared: carbon steel scraps, created by cutting carbon steel STS410 into 2- or 3- mm pieces, and carbon steel rust, produced by soaking carbon steel STS410 in water, collecting the resulting rust, and drying it.

In the sorption test, 10 cm^3 of the test solution A or B was added to a container containing 1 g of cement paste powder or carbon steel scrap and rust. After 10 minutes of mechanical shaking, the solid-liquid mixture was stored for one week. It was then filtered through a 0.45 µm filter to separate the test solutions. Two sets of all samples were run simultaneously under the same conditions (n=2).

Since sorption on aggregates in concrete may not be ignored, immersion tests of aggregates were also conducted. River sand and limestone were employed as fine aggregate (100 grains, average particle diameter 1.35 mm), while river sand was utilized as coarse aggregate (3 grains, average particle diameter 4 mm). The data were normalized by surface area, calculated from diameter, for comparison purposes. Additionally, cubes of carbon steel STS410 as bulk sample were immersed for comparison.

Test solutions for aggregates were prepared by dissolving the MOX powder in a 7 mol/dm^3 nitric acid solution. Solutions were diluted to two different concentrations, 4.2×10^4 Bq/cm^3 $^{239+240}$Pu and 1.7×10^5 Bq/cm^3 ^{238}Pu+^{241}Am for test solution C, and 3.3×10^3 Bq/cm^3 $^{239+240}$Pu and 1.6×10^4 Bq/cm^3 ^{238}Pu+^{241}Am for test solution D. Concentrations and other information are shown in Table 1 with other test solutions.

The specimens were immersed in 20 cm^3 of the test solution C or D for a period of one month, after which they were also filtered in order to separate the solution.

The determination of Pu and Am was conducted through alpha-ray radioactivity analysis. The peaks of ^{239}Pu and ^{240}Pu, ^{238}Pu and ^{241}Am are in proximity, thus necessitating the correction of ^{241}Am determination through the ratio of nuclides. Furthermore, the pH of the test solution was measured by a pH electrode.

The distribution ratios were calculated using the determined concentrations of the test solutions, as outlined follows:

$$\text{Distribution ratio (cm}^3\text{/g)} = (C_0 - C)/C \times V/M \quad (1)$$

In this equation, C_0 represents the initial concentration of radioactivity present in the test solution (Bq/cm^3), C represents the residual concentration of radioactivity in the filtered test solution following immersion (Bq/cm^3), V represents the volume of the test solution (cm^3), and M represents the mass of the cement powder (g). In the case of aggregates or cube of carbon steel, the distribution ratio in unit of (cm^3/mm^2) is normalized by the surface area of the aggregate grain and the cube of carbon steel, calculated as follows:

$$\text{Distribution ratio (cm}^3\text{/mm}^2\text{)} = (C_0 - C)/C \times V/S \quad (2)$$

Where, S represents the surface area of the grain (mm^2), which is calculated from the estimated diameter or dimension.

III. Results and Discussion

Cement paste powder was immersed in test solutions A and B. The distribution ratios of $^{239+240}$Pu and ^{241}Am between OPC and FAC paste powder and test solution A were shown in **Fig. 1**. The results of immersing cement powder in test solution B are not shown in Fig. 1. A comparison of the distribution ratios were not possible, since all concentrations after immersion were below the determination limit. The higher concentrations of Pu and Am after immersion in test solution A than in test solution B are due to the higher initial pH and

Table 1 Concentration and pH of test solutions

Test solution	$^{239+240}$Pu (Bq/cm^3)	^{238}Pu+^{241}Am (Bq/cm^3)	U (μg/cm^3)	pH	Coexistence
A	2.7×10^4	1.2×10^4	58	4.1	CO_3^{2-} 0.5mM
B	2.6×10^6	1.6×10^6	7.9	1.2	NO_3^- 40mM
C	4.2×10^4	1.7×10^5	25	1.9	NO_3^- 3mM
D	3.3×10^3	1.6×10^4	2.4	3.1	NO_3^- 0.3mM

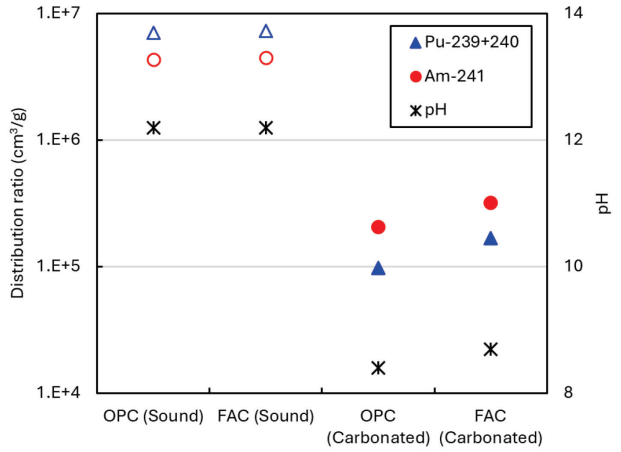

Fig. 1 The distribution ratio of $^{239+240}$Pu and ^{241}Am in the system of OPC and FAC cement paste powder is presented. Those with solution concentrations below the limit of determination had distribution ratios above the plot value and are indicated by open symbols.

smaller pH change due to cement immersion and the higher solubility of Pu and Am due to the presence of carbonate ions.

Cement paste powder with sound conditions had concentrations below the determination limit after immersion even in test solution A. Pu and Am were significantly removed from the solution regardless of cement type. The distribution ratios of Pu and Am in the sound condition are more than one orders of magnitude higher than those in the carbonated condition. The pH of the test solutions immersed with OPC and FAC of the sound condition were both increased to 12.2, while in the carbonated conditions remained at 8.4 for OPC and 8.7 for FAC, respectively, which were lower than in the sound condition. It was found that the distribution ratios of Pu and Am were dependent on the pH, which would be the result from cement degradation. The distribution ratio was found to be affected by the difference in the test solution due to the difference in cement paste state, with no discernible difference observed between OPC and FAC.

A high value of the distribution ratio indicates that both Pu and Am have been sorbed in the cement paste powder or removed from the solution by precipitation. It has been reported that Cs and Sr can be adsorbed onto cement paste through ion exchange, with a distribution ratio of approximately 10.[2,5)] While Cs is univalent and Sr is divalent, the actinides exhibit multiple valences such as Pu^{4+}, PuO_2^{2+}, Am^{3+} in aqueous solution. The distribution ratios of Pu and Am to cement paste that have been reported to date range from 10^2 to 10^6, with all of the ratios being relatively high.6) The reported data sets include the liquid-solid ratio as a parameter,7) experiments conducted under reducing and anoxic conditions,8) and studies investigating the differences among cementitious materials.9) However, the experimental conditions described in the literature vary considerably, which makes a direct comparison of the values presented challenging.

The sound conditions obtained in this study also exhibit a high distribution ratio. However, it is assumed that the actual building is more carbonated, which results in reduced sorption onto the cement paste compared to previous estimates.

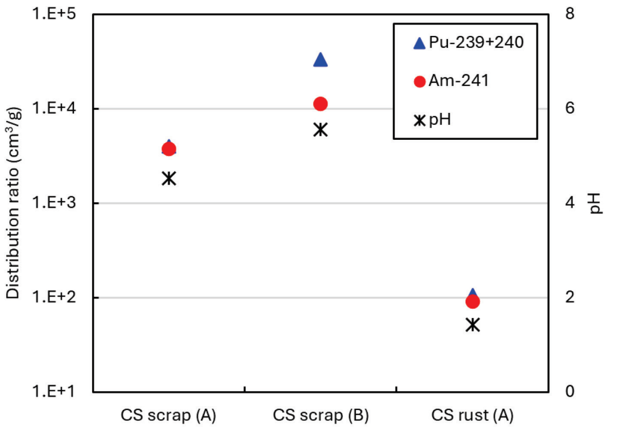

Fig. 2 The distribution ratio of $^{239+240}$Pu and ^{241}Am in the system of carbon steel (CS) scrap and rust. The letters in parentheses indicate whether the test solution was of type A or B.

The pH of the concrete contact surface is neutral due to the fact that the actual pH of the contaminated water is almost neutral and a large amount of water is in circulation. Actinides are more likely to form hydroxides and precipitate when the pH increases, although their effect is also smaller than experimental systems. However, the higher pH of the water inside the concrete makes it difficult for contaminated water to sorb immediately and migrate deeper into the concrete when it penetrates into the interior.

The distribution ratios for carbon steel scrap and carbon steel rust are plotted in **Fig. 2**. In the case of carbon steel scrap, the distribution ratio was approximately 10^4 cm^3/g, which was approximately one order of magnitude higher at higher concentrations of Pu and Am in the test solution B. In contrast, the distribution ratio for carbon steel rust was 10^2 cm^3/g, with the majority of Pu and Am remaining in solution. Carbon steel scrap exhibited a rusty appearance, however, the low distribution ratio of carbon steel rust indicates that Pu and Am do not sorb onto the rust itself. High distribution ratio observed in carbon steel scrap was not attributable to sorption onto the rust coating the steel, but rather to the uptake of Pu and Am during the formation of the rust. The distribution ratio was higher for test solution B due to the lower initial pH, which increased the formation of rust. Rust is an iron hydroxide, Pu and Am were also taken up by co-precipitation as hydroxides.

The analysis of sediments in the on-site accumulated water revealed that Pu and Am are adsorbed on iron particles.10) The sediments collected from Units 2 and 3 at F1NPS demonstrated that the particles containing Pu were mainly composed of iron.11) The particles were composed of Fe oxyhydroxide, which has been indicated to adsorb onto Fe oxyhydroxide particles. This study indicates that Pu and Am was not adsorbed on the rust following the onset of corrosion. Instead, Pu, Am and the rust were deposited together after contact with water containing Pu and Am during the corrosion process.

Distribution ratio for aggregate and carbon steel cube in

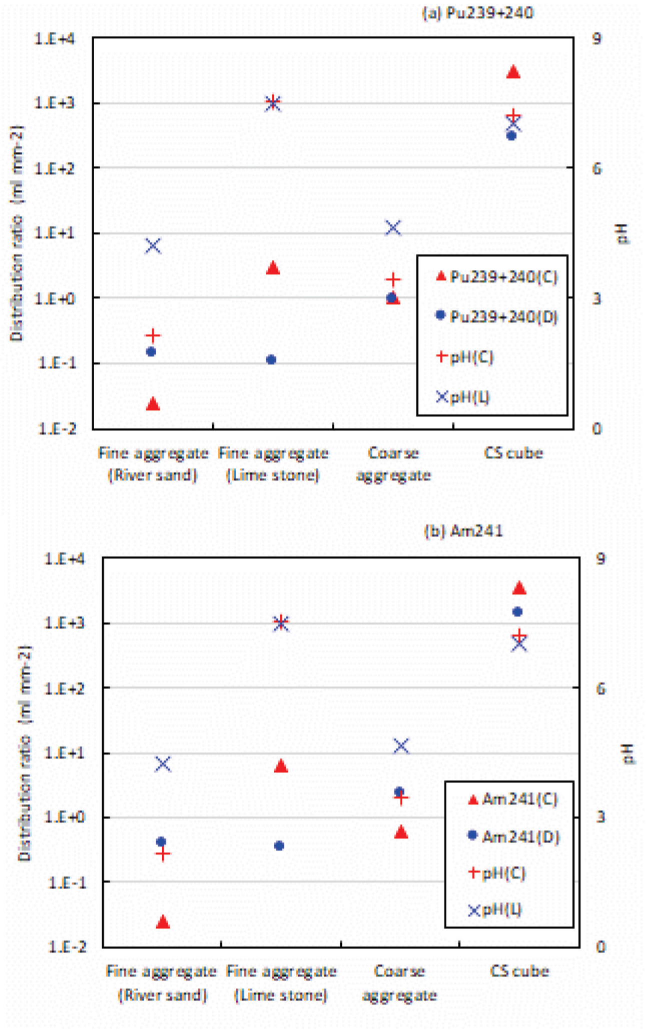

Fig. 3 Distribution ratio in system of aggregate and carbon steel cube. (a) $^{239+240}$Pu, (b) ^{241}Am. The parentheses in the legend show the type of test solutions.

unit of cm^3/mm^2 was shown in **Fig. 3**. For visual clarity, Pu and Am are represented on distinct graphs, designated as (a) and (b), respectively. Due to the different concentrations of the test solutions, river sand had higher distribution ratios and pH in test solution D. The preparation of test solution D results in an high initial pH (pH 3.1 as shown in Table 1) and post-immersion pH, attributable to the higher dilution factor. In contrast, the distribution ratio of limestone was observed to be higher in test solution C. The pH remained consistent across both test solution concentrations, with the concentration after immersion shows minimal variation: 5.1×10^2 Bq/cm^3 in test solution C and 8.3×10^2 Bq/cm^3 in test solution D as ^{241}Am. The solution was nearly saturated, resulting in a higher distribution ratio for test solution C, which contained a greater quantity of material in solution due to the larger decrease in concentration.

The sorption behavior of Pu and Am is dependent on pH, which means that differences in leached components from fine aggregates can alter the pH and sorption performance. The sorption of Pu and Am by limestone, which is high in calcium carbonate, is observed as the pH of the test solution increases when immersed.

The coarse aggregate is composed of river sand, and its pH after immersion was comparable to that of the fine aggregate (river sand). However, the distribution ratio was approximately one order of magnitude higher. The distribution ratio was calculated based on the simple surface area derived from the diameter of the spheres. However, the actual surface area of the coarse aggregate was larger due to the presence of pores. The presence of pores results in high water absorption of the coarse aggregate. This suggests that solutions containing Pu and Am have penetrated into the interior, resulting in an increase in the distribution ratio.

The distribution ratio of carbon steel was found to be markedly elevated in comparison to that of the aggregate, a finding that aligns with the results of the scrap immersion experiment. This suggests that Pu and Am may be incorporated into the rust formation that occurs during immersion. There is a concern that Pu and Am may be concentrated in areas where rebar is exposed in the field and in contact with contaminated water.

A comparison of Pu and Am reveals several instances where the distribution ratio is higher for Am, yet the observed behavior is similar for both. The distribution behavior is largely determined by the oxidation state of the elements, whereas this is not the case for Pu and Am, which are in different oxidation states. The observation of similar distribution behavior suggests that the primary sorption reaction may not be an ion-exchange reaction, but rather precipitation and adsorption of hydroxides generated by hydrolysis.

IV. Conclusion

It is anticipated that a considerable quantity of construction waste containing alpha-ray emitting nuclides will be produced at F1NPS. In order to ascertain the distribution of alpha-ray emitting nuclides migrating into the building structural material, a simulated structural material was immersed in a test solution containing Pu and Am, with a view to determining the distribution ratio. Given the significant influence of pH on the behavior of Pu and Am, the migration of these elements into cement paste is not contingent on the specific cement paste type but is markedly influenced by its carbonation state. The coarse aggregate is more prone to sorption than the fine aggregate due to the presence of pores. When contaminated water contacts concrete in F1NPS, the surface layer is carbonated and the water is neutral, which suppresses the effect of sorption. However, the amount of contaminated water and building concrete is enormous, and the period of contact with contaminated water is over 10 years. As a result, the amount of accumulation will be significant. While rust itself does not sorb much Pu and Am when it comes into contact with contaminated water, a considerable amount of Pu and Am were taken up when the contaminated water came into direct contact with the rebar and rust was generated. Despite the relatively small quantity of rebar in comparison to concrete, it is important to note that rust is a Pu-containing substance due to its tendency to remain and be distributed in a wide range of locations as sediment.

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