

Fixation of γ -Radionuclides by the PVA-PMAA System

**Hui-Jun Won, Byung-Gil Ahn, Chong-Hun Jung, Gye-Nam Kim,
and Won-Zin Oh**

Korea Atomic Energy Research Institute
150 Dukjin-dong, Yusong-gu, Taejeon 305-353, Korea
nhjwon@kaeri.re.kr

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Abstract

A series of laboratory experiments was conducted to investigate the fixation characteristics of poly(vinylalcohol)-poly(methacrylic acid)(PVA-PMAA) mixed solution on the soluble γ -radionuclides. Using the potentiometric titration technique, it was found out that the PVA and PMAA in a solution form intermacromolecular complex. The mobilized portion of each radionuclide by water from sand surface treated with a fixative was measured by γ -ray spectroscopy. The mobilized portion of minor radionuclides such as ^{241}Am , ^{154}Eu , ^{155}Eu and ^{144}Ce were higher than those of ^{134}Cs and ^{137}Cs . The capability of PVA-PMAA system was better among the candidate solutions for the fixation of total γ -radioactivity. $^{134,137}\text{Cs}$ which is composed of more than 85 % of total γ -radioactivity could be fixed effectively by the PVA-PMAA solution.

Key Words : potentiometric titration, intermacromolecular-complex, radionuclide, fixation

1. Introduction

After a severe nuclear accident in Chernobyl, a great amount of highly radioactive particles were released into the atmosphere. The total mass of the particles emitted from the reactor was estimated as 6-8 tons[1]. During the cleanup of largely contaminated areas, the former USSR sprayed fixatives onto the soil to suppress the resuspension of radioactive particles. The fixatives which efficiently reduced airborne activity were asphalt, lignin, lignosulfonate, oil slime, PVA, siliconate, polyelectrolyte complex and latex[2].

Interpolymer complexation between complementary polymers through hydrogen bonding has attracted an interest. Potentiometric titration and viscometric measurement are among the most frequently used methods for the study of these complexes[3,4,5]. Due to acid-base character of the hydrogen bonding interaction the obtained results are plotted using Henderson-Hasselbach or modified Henderson- Hasselbach equation[6]. The viscometric results are presented usually by plotting either the reduced viscosity or the specific viscosity as a function of the molar ratio[7,8,9].

Manchanda and Mohapatra studied the

complexation of Eu^{3+} and Am^{3+} with ionizable macrocyclic ligands[10]. They explained that larger complex formation constants for Am^{3+} over Eu^{3+} are caused by the better availability of f orbitals for participation in the bonding of the actinide ion. Adeleye et al. studied the sorptive properties and transport of radionuclides with clay minerals as potential backfill materials of repositories[11]. They reported that the uptake of these radionuclides increases in the order $\text{Cs} < \text{Sr} < \text{Eu}$.

The long-term behaviour of highly radioactive particles which may eventually become dissolved in soils, especially with regard to migration and soil-to-plant transfer, will be dominant factors in the feasibility of land reclamation[12]. In a previous study, we investigated the water stability of sand layer treated with PVA-PMAA solution. And, we showed that permeability of sand layer is directly proportional to the PMAA concentration when the [PMAA] is below 0.082 M[13].

The main objective of the present study is to evaluate the fixation capability of the PVA-PMAA system on γ -radionuclides(Cs, Am, Eu, Ce). Explanation of fixation characteristic is attempted, based on the radionuclide mobilization by water. Because ^{137}Cs is a main γ -radionuclide, the control of Cs which is a key function for the middle and long term migration of radionuclides is emphasized.

2. Experimental

PVA(Shinyo Pure Chemical Co. Ltd., average degree of polymerization: 1500) was purified with distilled water, NaOH, acetone and ethyl alcohol. PMAA was prepared by polymerization of methacrylic acid(Junsei Chemical Co.) with H_2O_2 as an initiator. Then the gelled polymer was dissolved in distilled water and precipitated with diethyl ether. Lignin and Na-type liginosulfonate were used as received(Aldrich Co.).

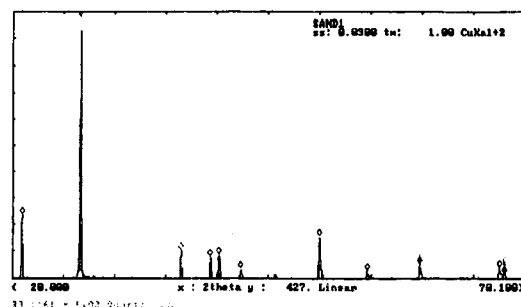


Fig.1. X-ray Diffractogram of Sand

PVA in aqueous solutions of 0.1 M NaNO_3 was titrated with PMAA by 682 Titroprocessor (Metrohm Co.) at 20 °C. IR absorption analysis {FT-IR Spectrophotometer(Digilab Division Co., FTS-80)} on this system was also carried out. The broad band at ca. 3348.4 cm^{-1} was considered to be the hydroxyl stretching mode for pure PVA. The sharp band in the lower region (2939.5 cm^{-1}) was considered to be the methylene stretching mode of PVA. As the content of PMAA was increased, the band of hydroxyl stretching mode is shifted to the higher region.

Sands were collected near the Pripyat River in the Ukraine. X-ray diffraction analysis was carried out to determine the mineralogy of the sands(Rigaku Denki Co., Model; Reigerflex, with CuK radiation). The X-ray diffraction pattern of sand is shown in Fig. 1. It is predominantly quartz with lesser quantities of mica and feldspar. BET {AUTOSORB-1 (Quantachrome Co.)} was used to measure the specific surface area and the average pore radius of sands(Table 1). After the sands were separated carefully from mica and feldspar, they were ground into fine powders(average particle diameter: $16.15\text{ }\mu\text{m}$). The variation of zeta potential of the fine sands (concentration: 0.3 g/L) with pH in aqueous solutions of 0.001 M KNO_3 was investigated at 23 °C by the zeta potential analyzer(Brookhaven Instruments Corp.). The adjustment of the solution pH was made by adding

Table 1. Physical Property of Sands

Size (mm)	Specific Surface Area (m ² /g)	Average Pore Radius(nm)
0.10 - 0.25	0.30	5.65
0.25 - 0.50	0.16	6.48
0.50 - 1.00	0.08	9.30

dilute NaOH and HNO₃ solutions.

Radioactive solution for contamination was obtained by leach contaminated soil with 8M HNO₃ and H₂O mixed solution and filtration. Homogeneously contaminated sands were prepared by dropping the 2ml of the radioactive solution into 10 g of sands, and the sands were cured at room temperature for 3 days[13]. The radioactivity of the sands was determined by γ -ray spectroscopy [Multichannel Analyzer (Canberra, Model 2024) with high purity Ge-detector (Canberra, Model GC 3019)]. The scanning range was 50.23 - 3749.25 KeV. These sands were moved to the Buchner type funnel(Iwaki Glass Co. Model 11 G2), treated with a polymer solution and dried for 3 days. After applying 20 ml of water, 10 ml of effluent flowing down from the system was collected. The radioactivity remained in the sands was also measured. Because the radioactivity of ¹⁰⁶Rh and ¹²⁵Sb in the effluent was low to be detected, they were excluded in the data analysis. Experimental conditions are listed in Table 2. Here, wt% is the weight percent of a pure fixative(solute) in a given volume of a fixative solution. And, the applied quantity(g/cm²) is the weight of solutes applied per unit area of sand surface. As listed in Table 2, the applied quantity of each solute is same.

Lignin, as the chemical property is similar to that of PVA, was used to investigate the effect of solution pH on the fixation characteristics of PVA. The PVA-PMAA system and lignosulfonate were used to evaluate the effect of polyanion on the

Table 2. Experimental Conditions

Fixative	wt %	Applied Quantity (g/cm ²)	pH
PVA	2.2	6.6 X 10 ⁻³	6.9
PVA + PMAA	2.4		4.4
Lignin + KOH	2.2		10.3
Lignosulfonate	2.2		8.8

fixation of γ -radionuclides.

3. Result and Discussion

3.1. Complex Formation Between PVA and PMAA

The dependence of polycarboxylic acid concentration on pH is well described by the following modified Henderson-Hasselbach equation[14].

$$\text{pH} = \frac{1}{m+1} \text{pK} - \frac{m}{m+1} \log[A] \quad (1)$$

where [A] is a concentration of polycarboxylic acid, pK is related to the dissociation constant of polycarboxylic acid and m is a constant which represents a characteristic of polycarboxylic acid. A plot of pH against the log [PMAA] under various initial PVA concentrations is shown in Fig. 2. At a given [PMAA], the elevation of pH occurs as the increase of initial [PVA].

If it is assumed that the pH elevation at a given [PMAA] is caused by the complexation between PVA and PMAA and that pK value does not vary in a solution, the complex concentration at a given pH will be a difference between [PMAA]_P and [PMAA]_w.

$$[\text{complex}] = [\text{PMAA}]_P - [\text{PMAA}]_w = \Delta C \quad (2)$$

where, [PMAA]_P is a concentration of PMAA in

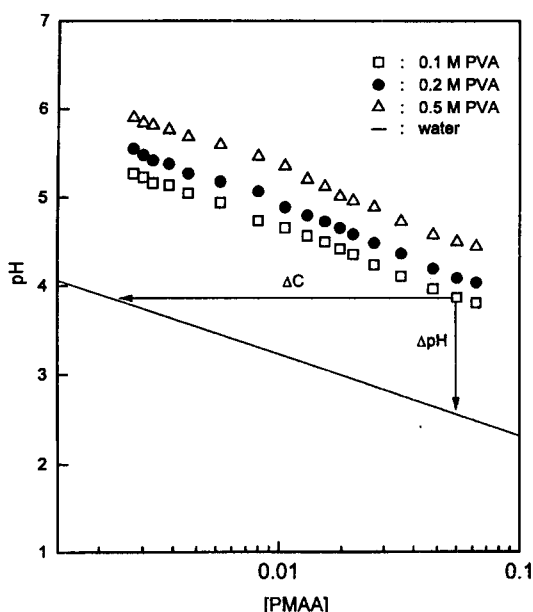


Fig. 2. Plot of pH Against Log [PMAA] Under Various Initial PVA Concentration

PVA solution and $[PMAA]_w$ represents a concentration of PMAA in water at a given pH, respectively. If we subtract the Eqn. 1 from the equation where the $[A]$ value in Eqn. 1 is replaced with $[PMAA]_P - C$, Eqn. 3 is obtained.

$$\Delta pH = - \frac{m}{m+1} \log (1 - \Delta C / [PMAA]_P) \quad (3)$$

The dependence of pH on the $\log (1 - \Delta C / [PMAA]_P)$ is plotted in Fig. 3. All the points are within the line irrespective of $[PMAA]_w$. The dependence of $\log [PMAA]$ on pH in Fig. 2, however, does not show linearity. Dissociation of carboxylic group of PMAA is influenced by the steric effect or electrostatic interaction in an intermacromolecular complex. A variation of pK value was considered as a slight volume change of PMAA at $[PMAA]_P$. The correction term (β) which is expressed as a polynomial was used in the calculation of the effective concentration of PMAA.

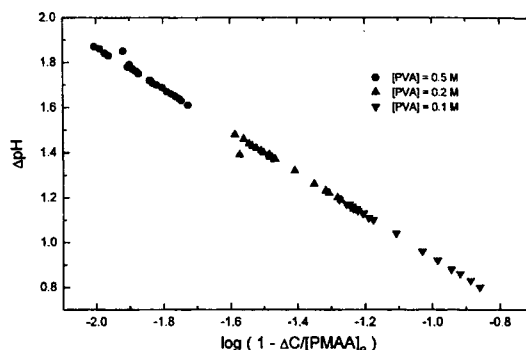


Fig. 3. Plot of pH Against Log(1 - $\Delta C / [PMAA]_P$)

$$\beta = 1 + k [PMAA]_P + k^2 [PMAA]_P^2 + k^3 [PMAA]_P^3 \dots \quad (4)$$

where, the coefficient k is related to the volume change of PMAA per unit mass of PVA. When the $[PMAA]_P$ is sufficiently low, the terms in the right side of Eqn. 4 except the first two terms can be neglected. In an intermacromolecular complex, $[PVA]$ and effective concentration of PMAA can be expressed as following relations.

$$\frac{V_0 [PVA]_0}{V + V_0} = [PVA], \quad [PMAA]_e = \frac{V [PMAA]_0}{V + V_0} \quad (5)$$

$$= [PMAA]_P (1 + k [PMAA]_P)$$

where, $[PVA]_0$ and V_0 represent an initial concentration and initial volume of PVA, respectively. $[PMAA]_0$ and V represent an concentration and volume of PMAA as a titrant, respectively.

When a part of PMAA interacts with PVA, the other part of PMAA also becomes to interact. Therefore, PMAA which behaves as an acid would be a dissociated carboxylic group in a complex[15]. Then, the stability constant can be expressed as a following relation.

$$K = \frac{[\text{complex}]}{[PMAA]_e [PVA]} \quad (6)$$

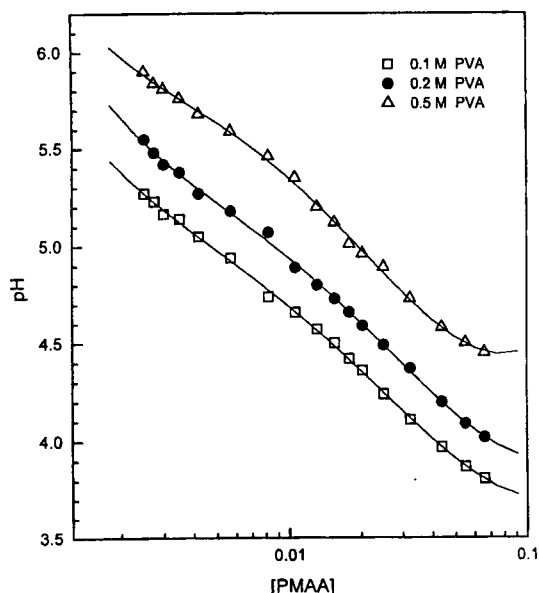


Fig.4(a). Cuving Fitting According to the Model Equation

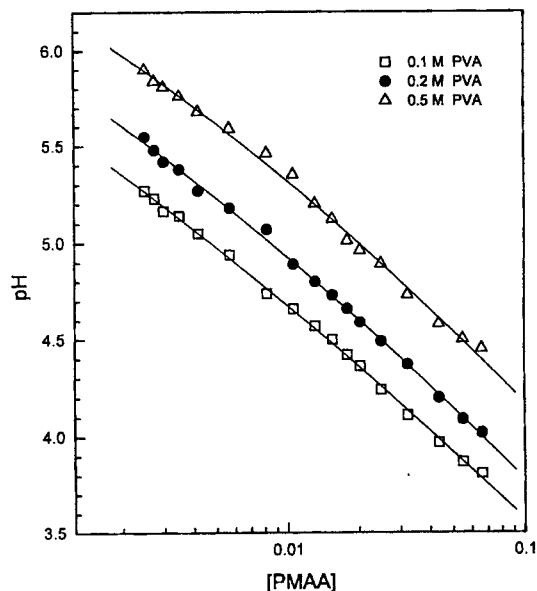


Fig.4(b). Cuving Fitting According to Horiuchi Equation

When we replace $[PVA]$ and $[PMAA]_e$ by the relation of Eqn. 5 and rearrange variables, the Eqn. 7 is obtained.

$$[\text{complex}] = K[PVA]_0[PMAA]_0^{-1} \{ k[PMAA]_0[PMAA]_p + (k^2 + k[PMAA]_0)[PMAA]_p^2 - 2k^2[PMAA]_p^3 + k^2[PMAA]_p^4 \} \quad (7)$$

where, $[PVA]_0$, K , $[PMAA]_0$ and k are constants.

$[PMAA]_p - [\text{complex}]$ is a concentration of PMAA which behaves as an acid. If we rearrange and simplify variables followed after the substitution of $[PMAA]_p - [\text{complex}]$ for $[A]$ of Eqn. 1, Eqn. 8 is obtained.

$$\text{pH} = \log \{ A + B[PMAA]_p + C[PMAA]_p^2 + D[PMAA]_p^3 + E[PMAA]_p^4 \} \quad (8)$$

where, the characteristic values of A , B , C , D and E are 6.08, -96.93, 2830.42, -42530.89 and 246088.19, respectively. The irreversible precipitation reaction becomes to occur when the mole ratio of PVA to PMAA is 1. Therefore, the

effective range of the above model is $0 \text{ M} \leq [PMAA] \leq 0.1 \text{ M}$. The R-square value and standard deviation of Eqn. 8 are 0.998 and 0.0246, respectively. Curve fittings of experimental data by Eqn. 8 and by Horiuchi Eqn.[15] are shown in Fig. 4(a) and in Fig 4(b), respectively. Comparing the two plots, the above model equation well describes the potentiometric behaviour of the PVA-PMAA system. Especially, the equation satisfactorily describes the potentiometric behaviour when the initial PVA concentration is 0.5 M.

3.2. Fixation Characteristic According to the Fixative Solution

The average γ -radioactivities of contaminated sands (size: 0.25 - 0.5 mm) are summarized in Table 3. The radioactivities are in the range from 9010.4 to 9242.3 Bq. The ratio of γ -radioactivity in the effluent against initial radioactivity of sands is defined as the transfer coefficient. And, the transfer coefficients are listed in Table 4. Because

Table 3. Radioactivity of Contaminated Sands

Nuclides	Radioactivity (Bq)			
	lignin	lignosulfonate	PVA	PVA-PMAA
²⁴¹ Am	125.4	126.8	130.2	124.7
¹⁵⁴ Eu	326.5	316.0	331.1	324.9
¹⁵⁵ Eu	204.7	199.0	201.7	199.4
¹⁴⁴ Ce	484.2	498.4	506.3	482.9
¹²⁵ Sb	26.6	40.1	24.8	38.0
¹³⁴ Cs	412.3	408.9	413.2	410.7
¹³⁷ Cs	7520.9	7473.6	7561.2	7382.7
¹⁰⁶ Rh	56.9	62.1	73.8	47.1
Total	9157.5	9124.9	9242.3	9010.4

Table 4. Transfer Coefficient on γ - radionuclide

Radionuclide	Transfer Coefficient(X 10 ⁻¹)			
	lignin	lignosulfonate	PVA	PVA-PMAA
Am	5.23	5.30	3.28	3.80
Eu	5.55	4.98	2.87	3.23
Ce	4.73	3.82	1.39	2.63
Cs	0.79	0.60	0.99	0.56
Total	1.34	1.09	1.15	0.87

the chemical properties of Cs-134 and Cs-137(Eu-154 and Eu-155) are same, we used the sum of the radioactivity of each radionuclide during the calculation of the transfer coefficients.

Fig. 5 shows a plot of transfer coefficient and zeta potential against pH. The zeta potential changes from -16.67 mV at pH 3 to -69.67 mV at pH 11. From Table 4 and Fig. 5, we can find several characteristics. 1) For all the tested fixative solutions, transfer coefficients on ^{134,137}Cs are lower than those on minor radionuclides(²⁴¹Am, ^{154,155}Eu and ¹⁴⁴Ce). 2) The total transfer coefficient of PVA-PMAA is lower than those of the other ones. This is due to the effective fixation of Cs of which the content is more than 85 % of total radioactivity. 3) As for ^{134,137}Cs, transfer

coefficient of lignosulfonate (pH=8.8) is comparable to that of the PVA-PMAA system. 4) The transfer coefficients of lignin(pH=10.3) on minor radionuclides are higher than those of PVA(pH=6.9). Lignin is also composed of various alcohols such as coniferyl, p-coumaryl and sinapyl alcohols. We can infer that the chemical property of lignin is similar to that of PVA[polyvinyl alcohol]. The mobilization of minor radionuclides, therefore, is considered to be affected by the acidity of the fixative solution.

As listed in Table 4, the transfer coefficients of lignin and lignosulfonate on Eu, Ce and Am are higher than those of PVA and PVA-PMAA system. From Table 2 and Fig. 5, the transfer coefficients of these minor radionuclides are

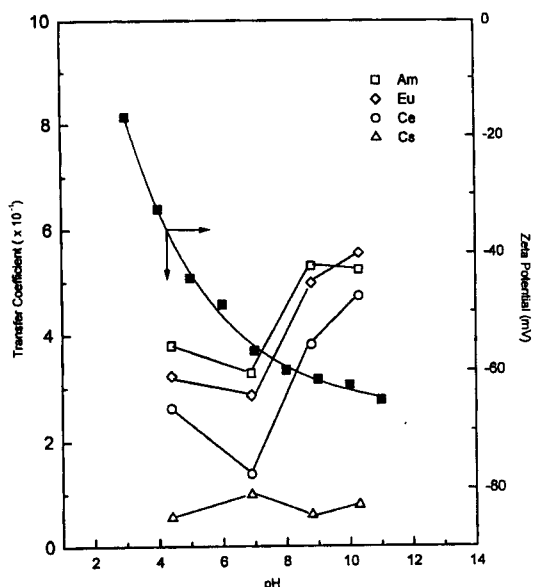
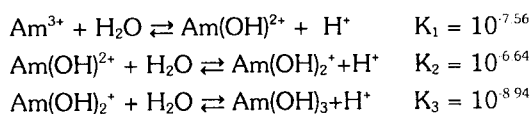


Fig. 5. Transfer Coefficient and Zeta Potential Against pH

increased with the solution pH in neutral and base solution. The transfer coefficients of lignin on Eu and Ce are higher than those of lignosulfonate. And, the difference of the transfer coefficient between lignin and lignosulfonate on Am is negligible. We can explain these tendencies by the stepwise hydrolysis reactions of minor radionuclides and the variation of the zeta potential of the sands. The stepwise hydrolysis reactions of Am^{3+} in an aqueous solution proceed as followings[16].



where, K_i represents a hydrolysis constant. Relative fraction of each hydrolysis species at a given pH value was calculated from the overall stability constant. Fig. 6 shows a plot of mole fraction of hydrolysis species of Am ion against pH. When the solution pH exceeds 9, the portion of $\text{Am}(\text{OH})_2^+$ and $\text{Am}(\text{OH})_3$ in which hydroxyl ion

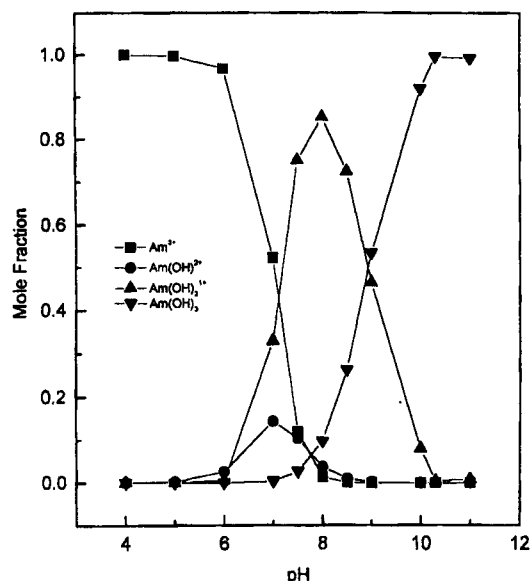


Fig. 6. Fraction of Hydrolyzed Species of Am vs. pH

repulses a negatively charged sand surface becomes predominant. This explanation, although not drawn as a plot, can be applied equally to Eu and Ce. The transfer coefficient on Eu is slightly higher than that on Am in the lignin system. This would be attributed to the $\text{Am}(\text{OH})_3$ as a precipitate.

Comparing PVA and the PVA-PMAA system, transfer coefficient on minor radionuclides decreases with the decrease of zeta potential. The electrostatic interaction affects the mobilization of these radionuclides. But, the behaviour of the PVA-PMAA system as a ligand can not be neglected.

Mobilized portion of Cs is less than that of minor radionuclides for all tested solutions. Several explanations are possible: (1) Contrary to polyvalent minor radionuclide cations, the positive charge of Cs^+ ion is distributed effectively in an adsorption site. (2) Cs^+ ion does not form hydrolysis species in the experimental pH range. (3) Cs^+ ion hardly forms a complex with ionizable

ligands. Irrespective of the solution pH, the transfer coefficient of anionic lignosulfonate and PVA-PMAA on Cs is low. The adsorption of polyanions on clay surface was enhanced by the presence of indifferent electrolytes, added in concentrations below what is required for particle coagulation[17,18]. This observation was explained in terms of charge screening effect through cation binding with the anionic groups of the polymer[19]. As the agreements of results obtained in this work with those in the literatures give some confidence, we can infer that the considerable adsorption of Cs^+ ions occurs between anionic fixative and sand surface.

4. Conclusions

The fixation capability of lignin, lignosulfonate, PVA and PVA-PMAA systems on soluble γ -radionuclides originated from a nuclear accident was investigated. The total radioactivities of contaminated sands were in the range from 9010.4 to 9242.3 Bq. The capability of PVA-PMAA system was better among the candidate solutions for the fixation of total γ -radioactivity. Intermacromolecular complex in which dissociation of the carboxyl group of PMAA is suppressed can be formed by mixing the two component solutions. $^{134,137}\text{Cs}$ which will be the main γ -radionuclides after the severe accident could be fixed effectively by applying the anionic macromolecular fixative. This can be explained by the adsorption of macromolecules on sand surface through Cs^+ ion. However, the minor γ -radionuclides such as Am, Eu and Ce were difficult to fix. This could be explained by the repulsion between adsorptive hydrolysis species and negatively charged sand surfaces. Although the fixation of minor radionuclides were difficult, a major portion of γ -radioactivity could be fixed by the PVA-PMAA system.

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