

Characteristic of PVA-PMAA on the Fixation of Radioactively Contaminated Sand as a Result of a Nuclear Accident

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PVA-PMAA에 의한 방사성 오염 모래의 고정화 특성

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Abstract

Characteristics of poly(vinyl alcohol)-poly(methacrylic acid) system (PVA-PMAA system) for fixation of radioactive contaminants on sand were studied. Dissociation of carboxyl group in PMAA was found to be suppressed by PVA. Permeability of sand layer treated with PVA-PMAA solution is directly proportional to the PMAA concentration when the [PMAA] is below 0.082 M and the empirical proportional constant (k) is $-8.95 \times 10^{-4} \text{cm}^5/\text{mole}$. The change of permeability can be explained by the formation of an intermacromolecular complex between PVA and PMAA. The polymer bridge formed on a sand surface combines sand grains more firmly. The PVA-PMAA system is more effective than the PVA system for the fixation of deposited condensational radionuclides.

요 약

모래 입자를 대상으로 PVA-PMAA 계의 방사능 고정화 특성을 연구하였다. PMAA의 카르복시기 는 PVA에 의해 해리가 억제되는 경향을 나타내었다. PMAA의 농도가 0.082M 이하일 때, PVA-PMAA로 처리한 모래층의 투과율은 혼합 용액내에 존재하는 PMAA의 농도에 정비례 하고, 실험으로 부터 얻은 비례 상수(k)는 $-8.95 \times 10^{-4} \text{cm}^5/\text{mole}$ 이다. 투과도의 변화를 두 고분자 사이의 상호 작용에 의해 거대 분자간 착물이 형성됨에 의한 것으로 설명할 수 있었다. 모래 표면에 형성 된 고분자 가교는 모래 입자들을 더욱 견고하게 부착시키는 것으로 나타났다. 본 계의 이온성 방사 성 핵종에 대한 고정화 능력은 PVA를 단독 적용한 경우에 비하여 우수하다.

1. Introduction

Following a serious nuclear accident which results in widespread contamination, resuspension was observed to have significant influence on both

airborne activities and ground depositions. The detriment to man from the radioactive contaminants can be reduced by the application of decontamination techniques or by polymer coatings to fix the contaminants. The fixation prevents the resuspension

of radioactive particles in the air by wind or by other disturbance, reducing the health hazards of radionuclides such as cesium and plutonium via ingestion or inhalation and curtailing the spread of contaminants to clean areas. In addition, fixation can also increase the decontamination efficiency which involves removal of contaminated soil. For the cleanup of large areas contaminated as a result of the Chernobyl accident, the former USSR sprayed fixatives onto the soil from helicopters and trucks. The fixatives used were lignin, lignosulfonate, asphalt, oil slime, PVA, polyelectrolyte complex, silicate and latex[1, 2]. Since PVA is non-flammable, abrasion resistant, and easy to handle, it was used to stabilize highly contaminated areas. However, the effectiveness was maintained only for a few months because of rain and change of weather.

The fixation technique is used in other fields to control and reduce soil erosion by water and wind. Because of the desirable properties of PVA and poly(acrylamide), they are applied for increasing soil stability and permeability[3, 4]. Stefanson[5] reported that the application of dilute PVA solution enhanced the rainfall stability of soil. By spraying PVA solution, Oades[6] stabilized seedbeds so that seedling emergence, rainfall filtration, and water storage were also significantly improved.

There are a few cases of the ternary system in which the interaction between the different polymers is so strong that a polymer adduct can be isolated, and the system has properties different from parent polymers. Examples are the pH muscle system described by Kuhn[7] and the bending of ionic polymer gel under sinusoidally varying electric field investigated by Shiga[8]. The characteristics of interaction products formed between PVA and polycarboxylic acid also have been studied by investigators[9, 10, 11, 12].

The main purpose of this study is to determine the effect of PMAA on the fixation capability of PVA. Examination of fixation capability is attempted in the present paper, based on investigations of

potentiometric behaviour of the PVA-PMAA system, water stability and leaching of condensational radionuclides using sand treated with PVA-PMAA.

2. Experimental

2.1. Preparation of Polymers

PVA (Shinyo Pure Chemical Co. Ltd., average degree of polymerization : 1500) was saponified with NaOH. The saponified PVA was dissolved in distilled water and precipitated with acetone. The purified PVA was rinsed with ethyl alcohol. After drying, the PVA was dissolved in distilled water and this solution was used in the experiment. The pH of 0.5M saponified PVA was 6.9. PMAA was prepared by polymerization of methacrylic acid (Junsei Chemical Co.) with H_2O_2 (Aldrich Chemical Co. Ltd.) as an initiator. The polymerization was carried out in 30% aqueous solution of monomer at 80°C , and then the gelled polymer was dissolved in distilled water and precipitated with diethylether. The purified PMAA was dissolved in distilled water and this solution was used in the experiment. The molecular weight of PMAA was found to be about 6.6×10^5 through Mark-Houwink-Sakurada equation and viscosity measurement.

2.2. Conditioning of Sand

Sand used in this study was collected near the Pripjat River in the Ukraine. This sand was sieved for 30 minutes. Its size distribution is presented at Table 1. Radioactive solution used to simulate condensational radionuclides was prepared using the soil from southwest of the Chernobyl unit 4. The soil layer in the upper 2cm depth from the surface was collected. Acid type radioactive solution was prepared from soil by HNO_3 and H_2O_2 . The solution was applied to sand for the contamination experiment. After applying 0.3 wt% of polymer solution to the contaminated sand, it was used to investigate the

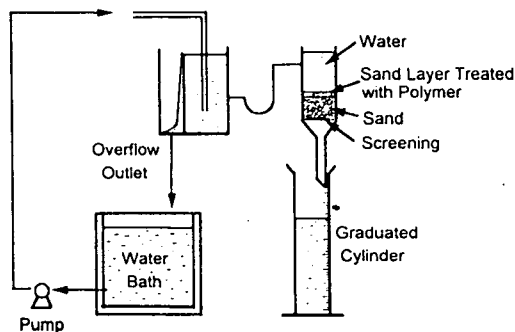
Table 1. Size Distribution of Sand.

| Grain Size (mm) | Content (wt%) |
|--------------------|------------------|
| > 1 | 1.2 |
| 0.5-1 | 12.2 |
| 0.25-0.5 | 53.4 |
| 0.1-0.25 | 32.9 |
| < 0.1 | 0.3 |
| Total | 100.0 |

leaching of condensational radionuclide.

2.3. Experimental Apparatus

PVA solutions were titrated with PMAA by 682 Titroprocessor (Metrohm Co.) at 20°C. Because the ionic strength affects pH of the system[13], only polymer-water systems were tested. Experimental apparatus for testing water stability of sand layer treated with PVA-PMAA is shown in Fig.1. To prevent a water leakage, polymer solution was used again around the contacting area between the sand and glass wall. A LABTECH counter(Bicron Corp.) was used to measure the number of β particles in sand. After applying water, 10ml of effluent flowing down from the system was collected. β -radioactivity of effluent was also measured. The transfer coefficient(Tc) was calculated from the following relation :

**Fig. 1. Schematic Diagram of Experimental Apparatus.**

$$T_c = \frac{\beta\text{-radioactivity of effluent (particles/cm}^2\text{.min)}}{\beta\text{-radioactivity of sand (particles/cm}^2\text{.min)}}$$

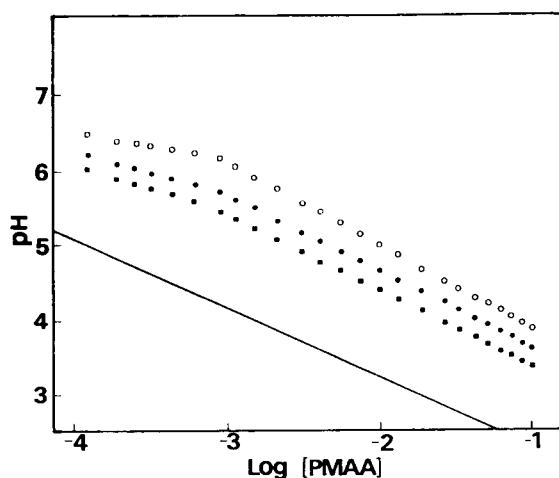
3. Result and Discussion

3.1. Potentiometric Titration of PVA with PMAA

To examine the interaction between PVA and PMAA in an aqueous solution, potentiometric titration of PVA with PMAA was performed. Fig. 2 shows a plot of pH against the log[PMAA] under various initial [PVA]. The dependence of polycarboxylic acid concentration on pH is explained by the following Katchalsky relation[14].

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

where [A] is a concentration of PMAA and m is a constant which represents a characteristic of PMAA. The increase of pH as the increase of [PVA] at a given [PMAA] is related to the property of PVA. PVA behaves as a base when it reacts with an acid. When 0.0016 M of HCl ($\log[H^+] = -2.8$) was added in 0.5 M PVA, the pH of this solution was 3.9. PVA as a

**Fig. 2. Plot of pH Against Log[PMAA] Under Various Initial PVA Concentrations, (—): Water, (■): 0.1 M PVA, (●): 0.2 M PVA, (○): 0.5 M PVA.**

base alone can not explain the pH difference between PVA-PMAA and water-PMAA.

Some undissociated carboxyl groups of PMAA were required to form intermacromolecular complex by hydrogen bonding between PVA and PMAA. Therefore, complexation between PVA and PMAA is believed to increase the pH additionally. This explanation is well coincided with the interpretation of viscometric behaviour of PVA-PMAA solution by Williamson et al.[9]. By comparing the observed intrinsic viscosity with the calculated one, they concluded that PVA and PMAA interact strongly in a mixed solution. Horiuchi[15] also suggested the existence of complex between PVA and PMAA by interpreting potentiometric titration curves, and change of density of more dilute PVA-PMAA mixed solutions.

The pH change of the PVA-PMAA system in high [PMAA] region is similar, within an acceptable error range, to that of the water-PMAA system. This means that PVA does not behave as a base in this region. When the pH of solution was less than 3.9, insoluble precipitate was formed. From pH and specific viscosity measurements of the mixed solution of PMAA and polyethylene oxide, Stockmayer[16] found a critical state of dissociation of hydrogen bonding intermacromolecular complex called critical pH. Tsuchida[17] explained that carboxylic groups in complex dissociate and reversible complexation occurs above the critical pH, but all the carboxylic groups in a complex do not dissociate and irreversible complexation occurs below the critical pH. Therefore, the precipitate is assumed to be caused by the irreversibly formed complex between PVA and PMAA.

3.2. Water Stability of Sand Layer Treated with PVA-PMAA

Fig. 3 shows a plot of effluent volume through the sand layer treated with polymer (grain size : 0.25 ~ 0.5mm) against time under various PVA-PMAA ratio.

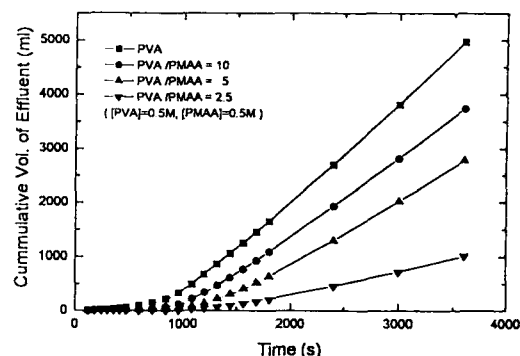


Fig. 3. Plot of Effluent Volume Against Time Under Various PVA-PMAA Ratio.

When sand is treated with PVA, effluent started to flow 1 minute after applying water. This period becomes longer and accumulated effluent volume at a given time becomes smaller by the increase of PMAA content. Differentiating the accumulated effluent volume with respect to time, flow rate of effluent is obtained. Fig. 4 shows a plot of effluent flow rate through the sand layer treated with polymer against time under various PVA-PMAA ratio. The increasing tendency of effluent flow rate with the lapse of time can be divided into three parts. This tendency is assumed to be related to the fine structure of sand treated with polymer and polymer property.

Mikeikin et al.[18] reported that four types of connection appeared between sand grains treated with polymer. Fig. 5 shows a SEM photograph of sand treated with polymer when [PMAA] of PVA-PMAA solution is 0.06M. As shown in Fig. 5, major connection type is the gluing of sand grains by polymer only at the contacting points. This indicates that flow rate just after the application of water was predominantly affected by the dissolution of polymer at the weak contacting points.

Thicker polymer layer becomes soft in this stage. And then, dissolution of polymer is considered to occur at all the contacting points. Because the free space blocked by the polymer begins to open, the flow rate increases steeply. After this stage, desorp-

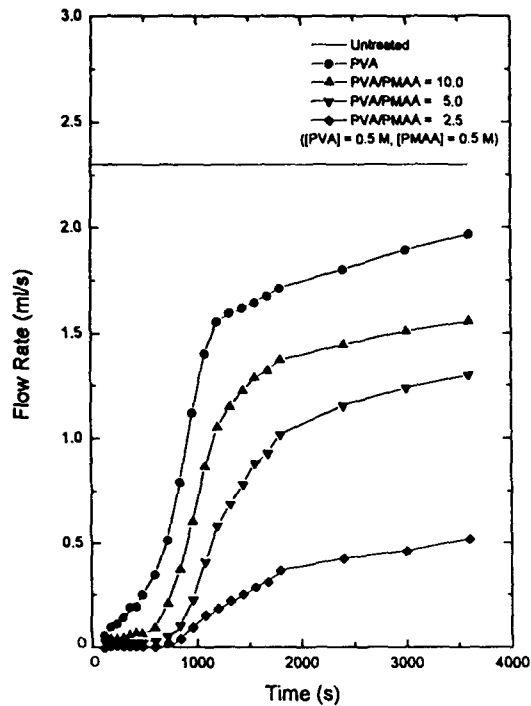


Fig. 4. Plot of Flow Rate Against Time Under Various PVA-PMAA Ratio.



Fig. 5. SEM Photograph of Sand Treated With PVA-PMAA.

tion of polymer from sand surface is considered to become predominant. And, the swelling effect of polymer on the flow rate can not be neglected.

The flow rate value of Fig. 4 per unit area was substituted for V of the Darcy equation (Eqn. 2).

$$K = \frac{\mu_t V L}{\Delta P} \quad (2)$$

where ΔP is a pressure drop across the sand layer (dyne/cm²), L is a depth of sand layer (cm), μ_t is a viscosity of effluent (dyne. s/cm²), V is a flow rate of effluent per unit area (cm/s), and K is a permeability (cm²). Permeability of sand layer against [PMAA] in PVA-PMAA solution is plotted in Fig. 6. As shown in Fig. 6, K does not directly depend on [PMAA] within ten minutes after applying water. This is caused by the assumption that the viscosity of effluent is the same as that of water. Therefore, the viscosity of effluent affects the permeability of sand layer at the beginning of permeation. As time passed, permeability shows linearity on [PMAA].

When [PMAA] is below 0.082 M, K can be expressed empirically as follows :

$$K = k [\text{PMAA}]^a,$$

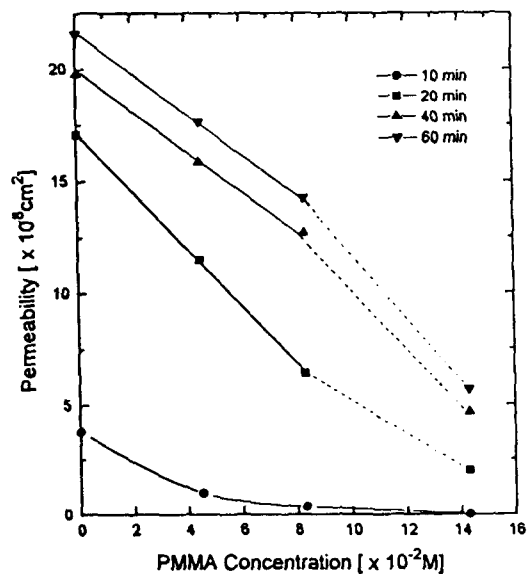


Fig. 6. Plot of Permeability Against PMAA Concentration at Initial [PVA]=0.5 M.

where $\alpha = 1$ and $k = -8.95 \times 10^{-4} \text{ cm}^5/\text{mole}$. k is related to the characteristics of sand such as size distribution, shape and arrangement. $\alpha = 1$ means that water stability of sand layer treated with polymer is directly proportionate to the concentration of PMAA. When $[\text{PMAA}]$ is 0.14 M, however, a deviation from linearity occurs. The deviation is presumed to be closely related to the insoluble precipitate appearing in this concentration range during the potentiometric titration. Fig. 7 shows a SEM photograph of sand treated with polymer when $[\text{PMAA}]$ of PVA-PMAA solution is 0.14 M. A long and thin polymer bridge around a sand grain is shown. This bridge also connects the other sand grains. From the investigation of the SEM photograph, it is reasonable to infer that the insoluble precipitate was changed to the polymer bridge during the drying of sand. Therefore, we came to a conclusion that the deviation was caused by the strong connection between sand grains by the polymer bridge, and K was additionally decreased.

3.3. Fixation of Ionic Condensational Radionuclide Contamination by Polymer Solution

Initial radioactivity of sand treated with polymer, radioactivity of 10 ml of collected effluent and Tc are listed in Table 2. Tc of lignosulfonic acid (LSA) is less than that of lignin. Tc of the PVA-PMAA system



Fig. 7. SEM Photograph Showing the Polymer Bridge Formed on Sand surface.

is less than that of the PVA system. The transfer of radionuclides from the sand layer treated with PVA-PMAA is shown to decrease with the decrease of grain size. The structure of sand is composed of an array of tetrahedral SiO_4 [19]. The external surfaces of sand have some exposed oxygen and hydroxyl groups which act as negatively charged sites [20, 21].

It was also reported that the polymer anion and the negatively charged surface of clay are connected through cations adsorbed on clay surface [22]. The considerable adsorption of PVA on sand surface takes place through hydrogen bonding between PVA and sand surface [23]. The results show that interac-

Table 2. β -radioactivity and Transfer Coefficient.

| Polymer Solution | Grain Size of Sand (mm) | β -radioactivity (particles/cm ² .min) | | Tc |
|--------------------|-------------------------|---|-------|----------------------|
| | | Sand | Water | |
| Lignin | 0.25–0.5 | 1842.6 | 174.4 | 9.5×10^{-2} |
| Lignosulfonic acid | | 1906.5 | 61.9 | 3.3×10^{-2} |
| PVA | | 2024.5 | 83.0 | 4.0×10^{-2} |
| PVA + PMAA | 0.1–0.25 | 1550.1 | 4.2 | 3.0×10^{-3} |
| | 0.25–0.5 | 1858.8 | 29.9 | 1.6×10^{-2} |
| | 0.5–1.0 | 1483.5 | 77.7 | 5.2×10^{-2} |

tion between polyanion and cationic radionuclides significantly occurred. Most of cationic radionuclides connect negatively charged sites of sand surface and negatively charged anions of LSA. This phenomena also occurred between the polyanion in the PVA-PMAA system and negatively charged sites of the sand surface. Polyanion also confers stability on fixation of radionuclides. As listed in Table 2, Tc decreases by the decrease of particle size of sand. If PVA-PMAA solution is applied to the surface of ordinary soil which is composed of smaller particles, this solution will effectively fix the deposited condensational radionuclide contamination.

4. Conclusion

The intermacromolecular complex can be formed between PVA and PMAA in a mixed solution. Water stability of sand layer treated with PVA was improved by the addition of PMAA. Insoluble precipitate formed above 0.14M of PMAA in PVA-PMAA mixed solution changed to a polymer bridge which combines sand grains more firmly. The fixation ability of PVA on condensational radionuclides was also improved by the addition of PMAA. Polyanion was considered to be adsorbed on sand surface through bonding with cations.

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