Fixing of electrophoretically deposited natural zeolite particles by geopolymer reaction for heavy metal ion adsorbents

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The fixing of electrophoretically deposited natural zeolite particles on a metal substrate by “geopolymer reaction,” i.e. the polymerization of silicate monomers in a solution to form a polymer phase that can bind particles onto solid materials, was investigated. Finely ground natural zeolite (clinoptilolite) particles were dispersed in ethanol, and deposited on a stainless-steel electrode by electrophoretic deposition (EPD) with silica sol particles and polyvinylpyrrolidone (PVP) as binder materials. The deposit was then fixed to the electrode by curing in an alkali silicate aqueous solution containing Na\(_2\)SiO\(_3\) and NaOH at 40°C for 24 h. The addition of the mixed binder of silica sol and PVP to the suspension used for the EPD was effective for the fixing treatment. After the fixing treatment, the durability of the zeolite deposit in stirred water was largely enhanced. It was also found that fixed deposits treated in solutions containing a smaller amount of Na\(_2\)SiO\(_3\) showed better durability. Fixed deposits, containing the starting zeolite phase, moreover, showed the adsorption property of Pb\(^{2+}\) ions in the aqueous solution.

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1. Introduction

Heavy metal elements such as lead, cadmium, and chromium cause water and soil pollution problems when discharged into the environment. One solution for minimizing these pollution problems is the removal of heavy metal ions from industrial waste or from the environment using adsorbents. Natural mineral adsorbents with cation-adsorbing properties are especially useful because they are abundantly available in nature and inexpensive.

Zeolites, both natural and artificial, are particularly useful in controlling the level of pollution in the environment because of their high capacity for adsorbing cations. Zeolites have a crystal structure characterized by a framework of linked SiO\(_4\) and AlO\(_4\) tetrahedra, which contain open cavities occupied by exchangeable cations. There have, in fact, been many studies on adsorption of harmful cations such as various heavy metal ions\(^{(1–3)}\) and ammonium ions\(^{(4–6)}\) on natural zeolite.

The macroscale structure of natural zeolite is important for treating large volumes of polluted water rapidly. In this study, we have been discussing the preparation of “adsorbent modules,” i.e., adsorbent materials coated on the surface of porous substrates with large penetrating pores or interstices. When polluted water passes through the pores, for example, harmful dissolved materials can be removed rapidly with no large loss of pressure and with less clogging by solid impurities in the water. In addition, adsorbent modules are easier to handle, e.g., in the exchange or regeneration process, than a number of conventional adsorbent pellets.

As a basic technique to produce such adsorbent modules, we have been studying the electrophoretic deposition (EPD) of natural zeolite particles on metal substrates. EPD is one of the ceramic-powder-forming techniques in which charged and dispersed particles in a liquid medium are moved through a direct current (DC) electrical field to a targeted electrode and deposited on it as a thick film.\(^{(7–9)}\) We have discussed the basic EPD properties of clinoptilolite—a natural zeolite produced in Futatsui, Akita prefecture, Japan, the enhancement of the deposition amount, and the fixing of the deposit by the addition of a small amount of spherical silica sol particles prepared by the Stöber’s method\(^{(10)}\) during the EPD process.\(^{(11)}\) According to some studies, however, the fixing property of the zeolite/silica sol deposit on the substrate is found to be insufficient, especially when the amount of the deposit is relatively large. Some additional fixing processing of the deposit is therefore required to enable the application of “zeolite modules” in environmental cleaning.

We focused on the so-called “geopolymer reaction” for such purposes. The geopolymer reaction is the polymerization of inorganic species, mainly SiO\(_4^{4-}\) and AlO\(_4^{3-}\) with other cations, to make a polymer phase that can bind particles to solid materials.\(^{(12)}\) The geopolymer technique has been attracting special attention, mainly in the field of construction materials as an alternative to traditional Portland cement, especially because it can reduce a large amount of CO\(_2\) emissions into the environment during the preparation process.\(^{(13–15)}\) One of the characteristics of the geopolymer reaction is that the reaction needs to be performed at a relatively low temperature (<100°C), which is suitable for binding zeolite particles that decompose at the high temperatures used for sintering inorganic materials (>1000°C). By heating the EPD deposit in an alkaline silicate solution, the particle/particle or particle/substrate binding would be enhanced. This is because of the polymerization of silicate monomers with other cations in the solution permeated into the interspace of the deposit particles.

In this paper, the fixing of electrophoretically deposited clinoptilolite particles on a metal (stainless-steel) substrate by geopolymer reaction is studied. We focused especially on the effect of some experimental conditions on the fixing behavior, including the effects of adding an organic binder to the EPD sus-

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2. Experimental

2.1 Preparation of natural zeolite/silica sol suspension for EPD

The natural zeolite, clinoptilolite, used in the previous paper was also used in this study. The principal crystalline mineral phase is clinoptilolite.

The zeolite was ball-milled and sieved (<150 μm), and then ground into finer particles by wet planetary pot milling at 400 rpm for 4 h with 2 mm SiC balls in ethyl alcohol (EtOH, 99.5%, Nakalai Tesque, Japan). After milling, the concentration of the suspension was adjusted with EtOH to 10 g/100 cm³ for storage, and diluted to 2 g/270 cm³ for the EPD process.

For the binder, spherical silica sol was prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of aqueous NH₃ solution using the Stöber’s method. The process was almost the same as that discussed in the previous study, but the concentrations of TEOS and NH₃ in the reaction were adjusted to 0.28 and 5.0 M, respectively, and the concentration of the silica sol was fixed at 0.1 g in a 270 cm³ suspension containing 2 g of the zeolite.

The particle sizes of the finely-milled zeolite and the synthesized silica sol were measured by the laser scattering method (SALD-2100, Shimadzu, Japan).

In some samples, polyvinylpyrrolidone (PVP K90, WAKO Pure Chemical Industry, Ltd.; molecular weight approximately 630,000) was used with the EPD suspension as an additional binder to improve the durability of the deposit during the fixing treatment. The concentration of the PVP was fixed at 2.5 mass % of the zeolite in the suspension.

2.2 EPD procedure

A set of SUS304 stainless-steel electrodes was inserted into a prepared zeolite/silica sol/PVP suspension contained in a 300 cm³ glass beaker. A screw-bar anode 4 mm in diameter and 100 mm in length was placed vertically at the center of the suspension, and surrounded by a tubular net cathode with a diameter of 60 mm and length of 90 mm. The tip of the anode was kept at a depth of 45 mm in the suspension. A DC electric field of 50 V/cm was applied between the electrodes using a DC stabilized power source (GP-060-050R, Takasago, Japan) for 1–6 min. This EPD process deposited the zeolite particles on the screw-bar anode. After the EPD process, the zeolite-coated electrode was air-dried at room temperature for 24 h.

2.3 Fixing treatment of deposits by the geopolymer reaction

The fixing of the deposited zeolite/silica sol particles/PVP was carried out by a wet chemical treatment referred to as a geopolymer reaction. First, about 2.0 cm³ of diluted water glass (aqueous solution of sodium silicate) (0.163 M) and 4.0 cm³ of aqueous solution of sodium hydroxide (0.375 M) were mixed in a polyethylene test tube (10 mmφ × 120 mmL); this solution is referred to hereafter as an x1 solution. The electrode with a deposit was dipped into the reaction solution and cured at 40°C for 24 h in an oil bath. After the treatment, the sample was rinsed gently with distilled water and dried at room temperature for 24 h. The change in the weight of the sample during the fixing treatment was measured with an electric balance.

The same process was performed with different solutions, including different concentrations of sodium silicate, i.e., 0.0815 M (x1/2 solution) and 0.326 M (x2 solution), respectively.

2.4 Characterization

The effectiveness of the fixing treatment was evaluated by a peeling-off test conducted in water. The sample was soaked in water and then stirred with a magnetic stirrer at 400 rpm for 24 h. The amount of the sample remaining after stirring determined the durability.

The microstructure of the deposit before and after the fixing treatment was observed with a scanning electron microscope (SEM; JSM-6701F, JEOL, Japan).

The cation adsorption property of the fixed deposit was verified using Pb(NO₃)₂ aqueous solution to confirm whether or not the geopolymer reaction inhibits the ion adsorption property of the deposit. Approximately 40 mg of the deposit with the electrode was soaked in the Pb²⁺ solution (10 mg/L for Pb, 300 cm³) and stirred with a magnetic stirrer at 400 rpm. After a fixed interval from 5 min to 24 h, 1.5 cm³ of the solution was taken out, filtered through a 0.2-μm filter, and diluted to 10 times its volume, after which the concentration of Pb was measured by inductively coupled plasma atomic emission spectroscopy (SPS7700, Seiko Instruments, Japan).

3. Results and discussion

3.1 EPD and fixing treatment of natural zeolite particles with binder materials

The median diameters of the zeolite and the silica sol particles in the suspension for the EPD process were 0.53 and 1.01 μm, respectively.

The amounts of the zeolite deposit with and without binder materials obtained by the EPD are shown in Fig. 1. It is observed that the deposition rate was increased by adding the silica sol. This result agrees with the findings of the previous report; hence, it can be inferred that the silica sol particles work as a binder during the EPD process. The deposition was suppressed, however, by adding PVP to the suspension. The addition of PVP is assumed to either lower the zeta potential of the zeolite and/or the silica sol particles or promote the agglomeration of particles before deposition during EPD. This issue will be discussed in

Fig. 1. Amount of zeolite deposited by EPD with and without binder materials.
detail in future studies.

Figures 2(a) and 2(b) illustrate the changes in the weights of the deposits during the fixing treatment by geopolymer reaction without and with PVP, respectively. The effectiveness of the fixing treatment was analyzed using the data.

There are several factors that affect the weight of a deposit during the fixing treatment. Peeling-off is the major factor that decreases the weight of the deposit. Dissolution of the solid components in the alkaline solution also causes a decrease in weight. The formation of a geopolymer material, i.e., silicate polymer, on the other hand, increases the weight or on the surface of the deposit, increases its weight.

Without PVP, as in the case shown in Fig. 2(a), a large part of the data for residual ratios are <80%, and the ratio decreases with increases in the weight of the deposit. There seems to be no correlation between the amount of sodium silicate in the solution and the weight change. Furthermore, the dispersion of data is relatively large. These results suggest that the fixing is insufficient without PVP, and peeling-off is an important cause of the weight loss during the fixing treatment. Peeling-off often occurs accidentally due to voids or cracks in the deposit, which may cause dispersion of the residual ratio.

In the case shown in Fig. 2(b), however, data for all the residual ratios are >80% when PVP binder is used in the EPD suspension. The dispersion of the data in this condition is relatively small compared with the results in Fig. 2(a). These results suggest that PVP is useful for enhancing the fixing of the deposit during fixing treatment. It was also shown that the residual ratios increase with increases in the amount of the deposit in x1 and x1/2 samples, using relatively small amounts of sodium silicate in the solution. This also illustrates that the fixing treatment certainly enhances the binding of the particles under these conditions, because the number of contact points (i.e., connection points) of the particles was also increased with increases in the amount of the deposit.

In the case of the x2 samples, however, the residual ratio decreases with increases in the amount of the deposit, which shows that the fixing is relatively insufficient under these conditions. This result is unexpected because the binding phase should increase with increases in the concentration of the silicate component in the solution; one possible reason is that the alkalinity of the solution was too strong to form a sufficient amount of the binding phase in this series of the samples.

Based on the above results, it can be concluded that the addition of PVP to the EPD suspension was effective for the following fixing treatment. The role of PVP is considered to support deposits firmly on the substrate during the fixing reaction in the solution. Hereafter, the characterizations of fixed deposits were performed for samples using PVP in the EPD process.

Figure 3 shows the appearance of samples electrophoretically deposited and fixed by geopolymer reaction under different reaction conditions. There is no large crack or peeling-off in the deposits. In addition, changes in the color and surface texture of the samples are almost negligible.

### 3.2 Properties of the fixed deposits

The durability of the fixed deposit was estimated by the residual ratio during soaking in water followed by stirring for 24 h. The results are shown in Fig. 4.

For a small amount of deposit (about 1 mg cm⁻²), the residual ratio of the sample without any fixing treatment was similar to those of the other fixed samples, but it rapidly decreased to about 20% when the weight increased to around 3 mg cm⁻². For all samples after fixing treatment, on the other hand, durability was largely increased up to 70–80%. This shows the effectiveness of the fixing treatment performed in this study. The silicate monomers penetrating the zeolite deposits were successfully polymerized with cations dissolved from the deposited zeolite particles, mainly Al³⁺, to form aluminosilicate polymers to bind the particles. At this stage, moreover, it should be mentioned that part of the weight loss from the fixed samples may be due to the dissolution of the permeated components, alkaline hydroxide and...
alkaline silicate, remaining in the deposit after fixing treatment. This means that the durability of the deposit itself may be somewhat greater than indicated by the data obtained in this study. Further investigation is required to clarify this point.

Microstructures of the as-deposited and the fixed samples observed by SEM are shown in Fig. 5. Before fixing treatment, fine zeolite and silica sol particles are closely packed in the deposit [Fig. 5(a)]. After fixing treatment, in the x1 condition, the deposit seems to be more porous, and the shapes of individual particles are more clearly observed than in the as-deposited sample [Fig. 5(b)]. In the x1/2 sample, on the other hand, the particles are more closely packed and particle clusters are also observed [Fig. 5(c)]. These clusters should be mixtures of zeolite particles and precipitated materials formed by the fixing treatment. In the case of the x2 sample, moreover, the particles are slightly larger and more square-shaped compared with the other fixed samples [Fig. 5(d)]. This means that particle growth occurred preferentially in the solution containing the most sodium silicate in the x2 condition. In addition, the x2 sample is found to be more porous than the other two samples. This result is in good agreement with the fact that durability is larger in the order x1 > x1/2 > x2, as shown in Fig. 4; and more porous deposits were more susceptible to peeling-off.

Powder XRD patterns of the starting zeolite (taken with a standard sample holder) and the fixed deposits (taken with a reflection-free sample holder) are shown in Fig. 6. There was a risk that the zeolite phase was decomposed under the strong alkaline conditions during the fixing treatment. In all of the samples, however, the clinoptilolite phase is found to have remained in the fixed deposit. This result is important because a remaining zeolite phase is necessary for the fixed deposit to be used as a cation adsorbent. On the other hand, no halo pattern, which is usually considered as evidence of a geopolymer reaction, was found in the XRD patterns, even though cluster-like textures, which would contain the amorphous phase, are observed in the surface SEM observation in Fig. 5. These results suggest that the total amount of the precipitate in the deposit, including not only that on the surface but also that inside, seemed to be too small to be detected by XRD. This matter will be cleared up by characterization of the depth-profile of the fixed deposit.

The adsorption tendency of Pb²⁺ ions by fixed samples in an aqueous solution is shown in Fig. 7. The X-axis of the graph shows meq/g as the unit weight of the deposit. The initial amount of Pb²⁺ in the 300 cm³ solution of 10 mg/L corresponds to 0.73 meq/g for a deposit of 40 mg in the experiment. The cation exchange capacity of the used zeolite is 1.5 meq/g (measured by the vendor), and the largest possible adsorbed amount is thus 48% of the full capacity. As the adsorption experiments in this study are conducted only for checking the validity of the deposit for use as a cation adsorbent, we performed the experiment under these conditions.
For all samples, Pb\textsuperscript{2+} ions were rapidly adsorbed with increasing soaking time, and there was not much difference among the fixed samples under the different conditions. After soaking for 24 h, the adsorbed amount ranged from 90\% (0.66 meq/g for the \textit{x2} sample) to 97\% (0.71 meq/g for the \textit{x1} sample) of the possible amount. This result indicates that the samples after fixing treatment could be used as Pb\textsuperscript{2+} adsorbents due to the presence of the zeolite phase, as is verified by the above-mentioned XRD analysis. There is another possibility, however, that the alumino-siloxane polymer itself may contribute to the removal of Pb\textsuperscript{2+} ions through surface adsorption. The permeation of Pb\textsuperscript{2+} ions through the inorganic polymer phase between the particles, especially, should have some retarding effect on the adsorption behavior. More research is necessary to establish the relationship between the adsorption behavior and microstructure of the samples.

4. Conclusion

Fixing of electrophoretically deposited natural zeolite particles by application of a geopolymer reaction, i.e., the polymerization of silicate monomers in solution into the binding phase, was investigated to increase the durability of the deposit against peeling-off. A mixture of silica sol and PVP was found to be effective in supporting the deposit on the substrate during fixing treatment in an alkaline silicate solution. After the fixing treatment, the durability of the zeolite deposits was significantly enhanced. Fixed deposits treated in solutions containing smaller amounts of Na\textsubscript{2}SiO\textsubscript{3} showed better durability in the series of experiments. Fixed deposits containing the zeolite phase, moreover, showed the adsorption property of Pb\textsuperscript{2+} ions in the aqueous solution. The experimental results of this study suggest the possibility that electrophoretically deposited and fixed natural zeolite particles can act as high-performance heavy metal ion adsorbents, even in fast-flowing water.

References