

Recovery of Pb from Soil Contaminated by Heavy Metals Using the Ion Adsorption Electrode

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Recently, the pollution of the soil by heavy metal ions from the industrial effluents is a major threat. Remedial measures were taken by adopting various extraction processes such as the diffusion prevention, the elution prevention, the extraction and the removal process, the decomposition and the decontamination process. It is realized that electro kinetic process is more effective. In this process, the ionized heavy metal ions in the contaminated soil move towards the cathode electrode by the electroendosmose process. The major problem is that heavy metal ion has to be recovered from the water and discharged. Otherwise, it causes secondary pollution. It is realized that the natural zeolite, which is available in abundance, could mitigate the problem of secondary pollution. In the present study, it is realized that by using the zeolite as a cathode material, the heavy metal ion content could be absorbed by the zeolite material. In the present work, a detailed experimental study was formulated to understand the metal ion adsorption characteristics of the natural zeolite material.

Key Words : Removing Pollutants, Natural Zeolite, Electrokinetic phenomenon

1. Introduction

With the rapid industry growth, in recent times, the industrial effluents have become a major threat to the eco system due to their discharge of heavy metal ions to the soil. In general, the soil pollution occurs due to heavy metal ions from industry effluents, organic compounds and radioactive material discharge. Many techniques are available to process the polluted soil such as the diffusion prevention, the elution prevention, the extraction and the removal, the decomposition and the decontamination. Recently, the technique using the electrokinetic phenomenon is noticed. In this method, ionized heavy metals, which are included in the contaminated soil move to cathode side with the water by the electroendosmose. The basic advantages of the process are;

1. In situ processing is possible.
2. It is cost effective process.

However, the recovery efficiency of heavy metal does not rise by the existence of the hydroxide ion in the vicinity of the cathode. In addition, there is danger of the secondary pollution by the drainage. Therefore, many researchers carried out further research including authors^{(1)~(3)}. We thought about the following two as this measures. One is to lower the pH by adding the acid. When the electrokinetic phenomenon is used, OH⁻ ion is generated by electrolysis of water at the cathode. Therefore, the pH is increased and the heavy metal ion precipitates as the hydroxide. To prevent an increase in pH, the acid is added. Another is to use the natural zeolite for the cathode^{(4)~(6)}. The danger of secondary pollution decreases if the concentration of the heavy metal ion with drain can be decreased. We paid attention to the natural zeolite. A large amount of the natural zeolite exists as resources in the inland and

it has the very high ion adsorption. We used the natural zeolite as a cathode, and the heavy metal ion under drainage is adsorbed to it.

In this paper, the improvement of the recovery efficiency by these measures was examined.

2. Experimental apparatus and artificially polluted soil

2.1 Experimental apparatus

In this research, the electrode insertion part on the cathode side was widened⁽⁷⁾ as shown in Figure 1. The soil was filled from the center part of the container to the anode side. The anode was inserted 10 mm apart from the edges, and the cathode was put 160 mm apart from anodes. As a result, pH jump caused by the reaction of an acid area and an alkaline area is made in the solution and it is thought that the heavy metal moves from the soil before it precipitates in the soil as a hydroxide. The titanium mesh [ϕ 0.3×68×68, 20 mesh] being of high acid proof was used for the anode. On the other hand, a stainless mesh [ϕ 0.3×68×68, 20 mesh] with high alkali proof or the natural zeolite electrode was used for the cathode. The natural zeolite electrode was made by thinly coating the cement and the natural zeolite on a stainless mesh. The mixture ratio of the cement and the natural zeolite was 4:6. Neither the cement nor the natural zeolite has conducting properties. However, an electric conductivity equals to a stainless mesh in the solution. There was no soil in the electrode insertion parts because the boundaries of the electrode insertion part and the soil filling part were partitioned by the furnace papers. In order to prevent evaporation, the upper part of the container was covered with an acrylic board. To observe the pH and the electric conductivity, the five holes were made for the cover. The positions

Table 1 Some properties of contaminated soil

void ratio	0.92
porosity [%]	48
water content [%]	38.4
dry density [g/cm^3]	1.25
unit weight of the soil particle [g/cm^3]	2.4

of the hole were 20, 50, 80, 110, 140 mm from the anode. A constant voltage or current was applied between the anode and the cathode by a DC power supply. To increase the processing speed, the ion exchanged water was supplied from the anode side with a pump in Case1 and Case2. In Case3, 0.1 mol/L HNO_3 was supplied from the anode side. Flow rate was 0.3 mL/min, and the liquid including the heavy metal was drained from the cathode side to the tank.

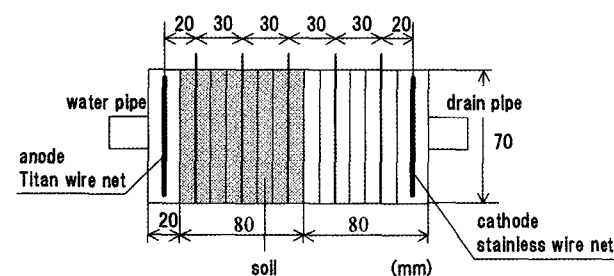
2.2 Artificially polluted soil

The soil polluted with Pb, Cu, and Zn was used in this study. Pb of 20, 400 mg, Cu of 50.4 mg and Zn of 74.0 mg were included in the 1 kg polluted soil. In this research, the recovery efficiency of Pb that the highest concentration in the soil was examined. Some properties of the contaminated soil used in the experiment are shown in Table 1.

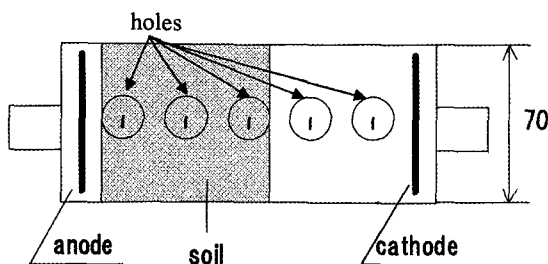
3. Experimental results

3.1 Effect of supply of acid

To neutralize the hydroxide ion generated near the cathode, HNO_3 was added near the cathode. Because lead hydroxide can be dissolved by HNO_3 more than by HCl which generates by the electrolysis. The addition of an excessive acid has the possibility of remaining of the impurity ion such as nitric acid ion in the soil. Therefore, it is necessary to decide a minimum amount of the acid addition required for neutralizing the hydroxide ion. From the previous paper⁽⁷⁾, the concentration of the acid of 0.05 mol/L is



(a) Side view



(b) Top view

Figure 1 Conceptual diagram of experimental unit

Table 2 Experimental conditions

Test Number	Supply liquid	
	anode	cathode
Case1	Ion exchange water	0.01 mol/l HNO_3
Case2	Ion exchange water	0.05 mol/l HNO_3
Case3	0.01 mol/l HNO_3	0.05 mol/l HNO_3

necessary to neutralize the hydroxide ion generated when the current of 25 mA flows. Table 2 shows experimental conditions. The processed soil is 250 g and the constant voltage of 35 V was applied for 120 hours. In the previous experiment, the same examination was done without adding the acid for the comparison and the collection efficiency of Pb was 7%. Figure 2 shows the change of the amount of Pb in the drain. From the Figure, it is found that Pb included in the drain is a little in Case1 and Pb included in the drain is abundant in Case2 and Case3. This is because neutralizing the OH^- is not enough in Case 1.

After the experiment, the soil was divided into three blocks as shown in Figure 3 and the concentration of Pb at each part was measured. Figure 4 shows the amount of Pb in soil 1 g. It was found that a lot of Pb was left for position 3 in Case 1. In Case 1, neutralizing the OH^- was not enough. Therefore, a lot of Pb precipitated there as the hydroxide. On the other hand, the amount of precipitation of the Pb ion has decreased in Case 2 and Case 3 that the acid solution of higher concentration was added to the cathode. From these results, it was found that the neutralizing of hydroxide ion by addition of HNO_3 is effective for the suppresses

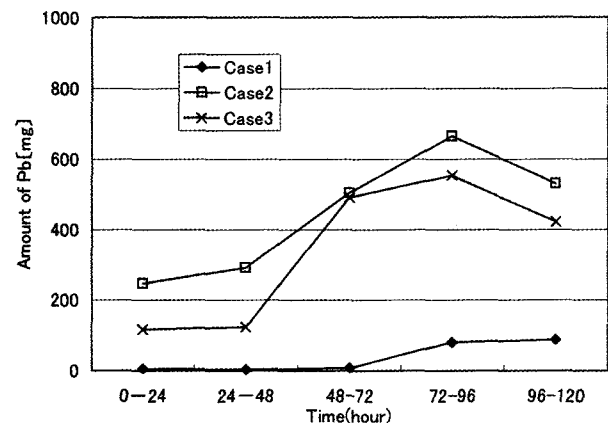


Figure 2 Recovery quantity in the every unit time

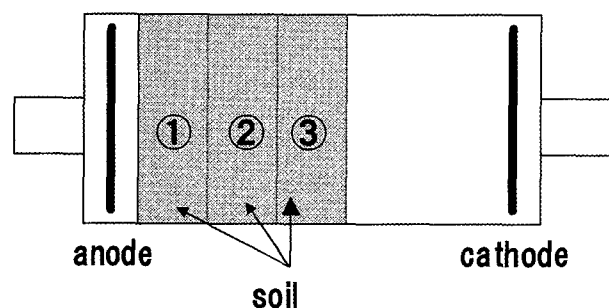


Figure 3 The number of soil position

of the precipitation of the $Pb(OH)_2$.

3.2 Effect of ion adsorption electrode

The ion adsorption electrode was used to decrease the concentration of Pb ion in the drain. The experimental conditions are similar to Case 3, however, a constant current of 25 mA was applied instead of a constant voltage.

In the beginning, the amount of Pb ion collection from the soil is shown in Figure 5. In Figure 5, the amount of Pb in precipitation was measured as follows. After the hydrochloric acid was added, precipitation was filtered by the furnace paper. The amount of Pb contained in the filtered solution was measured by ICP. The amount of Pb that adsorbed by the electrode was obtained by subtracting the amount of Pb in the precipitation and the drain from the amount of Pb contained in soil before the experiment. Because the cement was alkalinity, the extraction of Pb as the hydroxide was seen on the surface of the electrode. The total amount of Pb is slightly higher in the case using the ion adsorption electrode than using the stainless mesh electrode. In latter case, a lot of Pb was collected from the drain, when the collection places were compared. The amount of the collection from the drain was 70% of the amount of all collections. On the other hand, in the

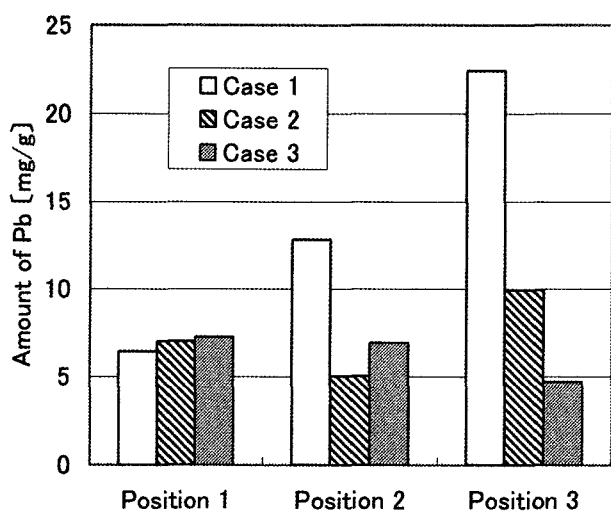


Figure 4 Pb quantity which is included under soil after experimental

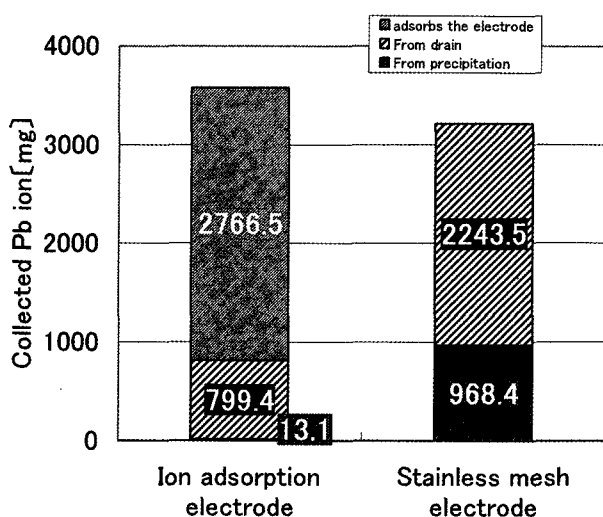


Figure 5 The amount of Pb ion collection

case of the ion adsorption electrode was used, a large amount of Pb ion was adsorbed by the electrode. The amount of Pb ion adsorbed by the electrode became 77% of the amount of all adsorption and Pb ion included in the drain was only 22%.

Figure 6 shows the change in the amount of Pb in the drain. A black dotted line shows the amount of the exhaust of Pb for every 24 hours, and a black solid line shows an exhausted amount of total Pb when the zeolite electrode was used. On the other hand, a gray dotted line shows the amount of the exhaust of Pb for every 24 hours, and a gray solid line shows a exhausted amount of total Pb when the stainless mesh electrode was used. From the Figure, it can be seen that the amount of Pb in the drain is suppressed when the zeolite electrode is used.

From these results, the danger of the secondary pollution was able to be decreased by greatly decreasing the amount of Pb in the drain by using the zeolite electrode with the ion adsorbent.

Figure 7 shows the change in the pH for the experiment period. Immediately after the start of the examination, the rise of pH can be seen on the cathode side by the generation of OH^- at the cathode. However, pH decreases gradually with time because the HNO_3 was added to the vicinity of the cathode. After 12 hours

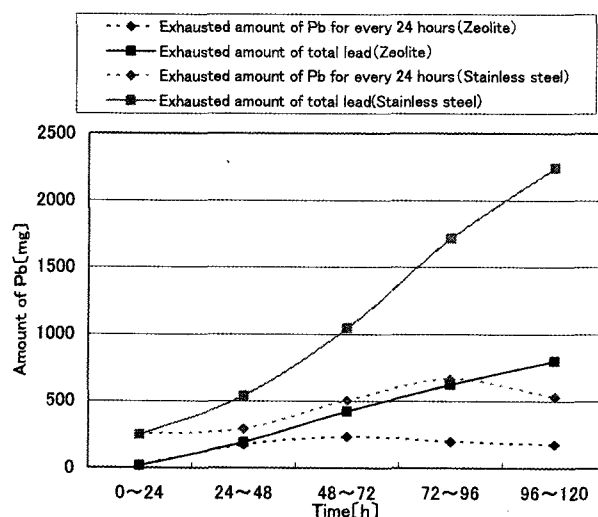


Figure 6 Change in amount of Pb in the drain

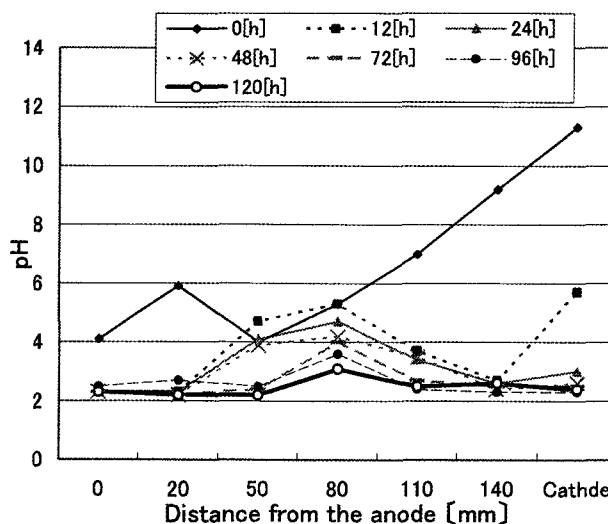


Figure 7 Distribution of pH

from the experiment beginning, the pH is 6 or less in all places and the area of the alkali doesn't exist. Therefore, it seems that Pb ion moves to the cathode side without precipitating as the hydroxide.

The applied voltage changes by the change in the electric conductivity of the soil because the constant current was applied between the electrodes while experimenting. Figure 8 shows the voltage change for the experiment period. The voltage rises immediately after beginning of the experiment. This is because Pb ion is adsorbed from the soil, and it did not ionize in the soil. Therefore, the electric conductivity of the soil is still low. However, the voltage decreases rapidly when about ten hours pass. This is because Pb ion ionized due to the decrease in the pH of the soil. The voltage rose again when 96 hours were passed from the experiment beginning. This is because a lot of Pb ions were removed from the soil and the electric conductivity of the soil has decreased.

Finally, the amount of Pb left in the soil was measured. The soil was divided into three blocks as shown in Figure 3 and the amount of Pb contained in the soil of 1 g was measured. The experimental results are shown in Figure 9. The amount of the residual Pb when

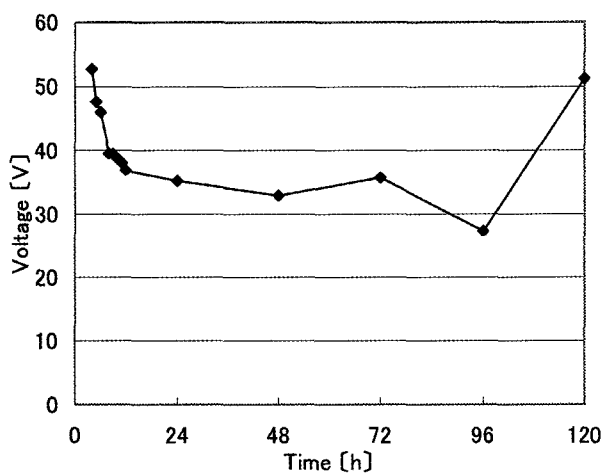


Figure 8 Change of voltage

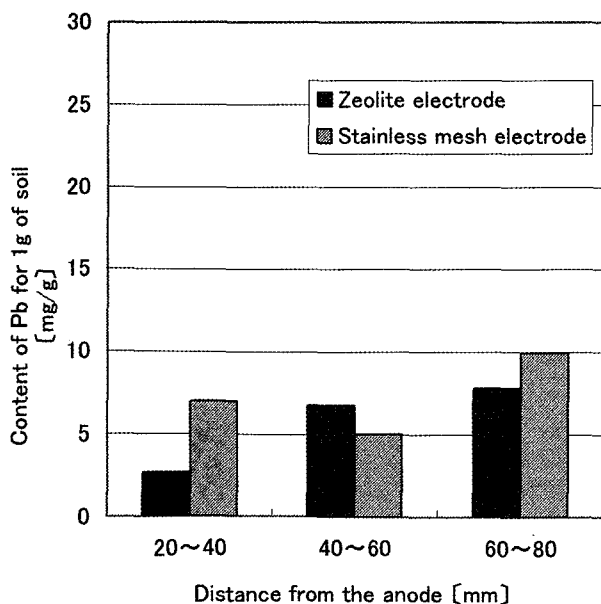


Figure 9 Amount of lead left in soil

the zeolite electrode is used has decreased compared with the case of the stainless mesh electrode is used. Especially, a decrease in the amount of the residual Pb is remarkable in the vicinity of the anode.

Pb of 20.4mg was contained in the soil of 1g before the experiment. Therefore, in the case of zeolite electrode was used, more than 85% Pb has been decreased in the soil near the anode.

The concentration of Pb in the vicinity of the anode was lower than the vicinity of the cathode. From the results, it can be seen that Pb in the soil moved to the cathode side well by the electro kinetic process.

4. Conclusions

In order to raise the collection efficiency of Pb, the HNO₃ was added to the vicinity of the cathode in the present study. In addition, the ion adsorption electrode made by the zeolite was used to decrease the danger of the secondary pollution. The result of the present research is summarized as follows.

1. The collection efficiency of Pb from the soil was greatly improved by adding HNO₃ to the vicinity of the cathode. This is because Pb was prevented from precipitating as a hydroxide by making the vicinity of the cathode acidity.
2. It succeeded in making the electrode with the ion adsorbent by mixing cement with the natural zeolite. This electrode had high electro conductivity in the solution and high ion adsorption characteristics.
3. The concentration in the drain of Pb ion was greatly decreased by using the natural zeolite electrode. This is because Pb was adsorbed by the electrode, and the danger of the secondary pollution with the Pb ion under drain was reduced.

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