INSOLUBLE EFFECT OF CONTAMINATED SOIL WITH HEAVY METAL BY FERRITIZATION

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ABSTRACT: There are several remediation techniques of contaminated soil with heavy metals. In this study, ferritization method is applied to contaminated soil with lead. In order to confirm the effect of insoluble by the ferritization, artificial contaminated soil with lead was prepared and batch tests were performed. From the test results, it was confirmed that the insoluble effect of the ferritization-treated soil or the compound hydroxide for Pb-contaminated soil is much higher over a wide range of pH levels. It was also observed that the insoluble property of lead increases gradually with the iron content. Furthermore, the magnetic property of the ferritization-treated soil was investigated. It is suggested that the ferrite method may be one of the techniques for the remediation of contaminated soil with heavy metals.

1. INTRODUCTION

Ferrite method has been widely used for the disposal of effluents including heavy metals in Japan (Okamoto 1976 and Takada 1977). Ferrite is a compound oxide with iron and heavy metals and it exhibits ferromagnetism. It is known that the solubility of ferrite is very low and this method is applicable for effluents with many kinds of heavy metals.

In this study, firstly, the ferrite method is applied to Pb-contaminated soil (Omine et al. 2006). The insoluble property of ferritization-treated soil and compound hydroxide for the contaminated soil are investigated by an elution test under different pH conditions. Furthermore, the magnetic property of the ferritization-treated soil is also investigated. Magnetic separation using a superconducting magnet is attempted. The applicability of the ferrite method for the remediation of the contaminated soil is discussed based on the test results.

2. REMEDIATION OF CONTAMINATED SOIL WITH HEAVY METALS BY THE FERRITE METHOD

2.1 Fundamental Consideration of Ferrite Method

Ferrite is a compound oxide with iron and metal. It is known that the solubility of ferrite is very low and it has ferromagnetism. The process of ferrite formation is shown in Fig. 1. Generally, white deposits of hexagonal tabular crystallite Fe(OH)₂ are formed by adding an alkali to an aqueous solution of Fe²⁺. If there exists a heavy metal ion, M, during the process of deposition, a compound hydroxide with Fe and M is deposited. In other words, the compound hydroxide is deposited by the following process:

\[ xM^{2+} + (3-x)Fe^{3+} + 6OH^- \rightarrow M_x Fe_{3-x} (OH)_6 \]  (1)

The compound hydroxide with Fe and M exhibits weak magnetism. The compound hydroxide transforms the ferrite during the oxidation process by introducing an air bubble at a high temperature of more than 60°C. This chemical reaction is indicated as follows:

\[ M_x Fe_{3-x} (OH)_6 + \frac{1}{2} O_2 \rightarrow M_x Fe_{3-x} O_4 \]  (2)

It is well known that the ferrite formation shows ferromagnetism.

Fig. 1 Process of ferrite formation

For a fundamental study on the remediation of contaminated soil with heavy metal, insoluble effect in the ferrite method is investigated in the following section.
2.2 Experimental Results and Discussions

2.2.1 Preparation and experimental method

Pb-contaminated soil was prepared by adding a standard solution of Pb for atomic absorption analysis (1000 mg/l) into Kaolinite clay with a Pb content of 1 g/kg. The equipment used for ferrite formation is shown in Fig.2. First, a prescribed volume of 0.2 mol/l ferric sulfate, FeSO₄, was added to the container, following which sodium hydroxide, NaOH, was mixed with a pH level greater than 10. The compound hydroxide with Fe and Pb can be generated by agitating the mixtures. Furthermore, ferrite is generated by heating the compound hydroxide at a temperature of 60-70°C and oxidation by introducing air bubbles slowly for maintaining high alkalinity. The sample obtained from these processes is referred to as "ferritization-treated soil" in this study. In addition, for comparison, an ideal ferrite sample was also prepared in an aqueous solution without clay. As indicated in reactions of Eqs. (1) and (2), when the heavy metal M is lead, 2Fe⁷⁺ and Pb²⁺ combine. Therefore, we used the ratio 2Fe⁷⁺/Pb²⁺ in mol in this study. In this test, four types of samples were prepared under the additive conditions with 2Fe⁷⁺/Pb²⁺ = 2, 6, 10, and 20.

X-ray diffraction and a scanning electron microscope (SEM) were used for the analysis of the Kaolinite clay, ferritization-treated soil, and the ferrite formation. A grain size analysis and elution test were performed for analyzing the Kaolinite clay, the compound hydroxide with iron and lead, and the ferritization-treated soil.

![Fig. 2 Equipment for ferrite formation](image)

In order to investigate the insoluble property of these samples, a batch test was performed under different pH levels of approximately 2, 4, 10, and 13 and a liquid-solid ratio of 10:1. The specimens were shaken in a reciprocating shaker for 6 h. and the supernatant was separated by centrifugation. The concentrations of Pb in the filtrates after passing through 0.45 mm membrane pore size filters were analyzed by atomic absorption photometry.

2.2.2 Physical and chemical properties

Figure 3 shows the results of the X-ray diffraction of each sample. The ideal ferrite formation prepared in the aqueous solution without clay has several peaks corresponding to the compound oxide with iron and lead as well as sodium sulfate Na₂SO₄. In fact, it is found that not only the ferrite, PbFe₂O₄, but also several compound oxides with iron and lead are generated. On the other hand, it is indicated that the main components of Kaolinite clay are silica, SiO₂, and pyrophyllite —Al₂Si₂O₅(OH)₃. The peak value of ferritization-treated soil are similar to those of the Kaolinite clay. This is because the ferritization-treated soil contains many components of the Kaolinite clay. However, there are a few small peak values corresponding the compound oxide with iron and lead.

![Fig. 3 Results of X-ray diffraction of each sample](image)

The SEM micrographs obtained from the scanning electron microscope are shown in Fig.4. A flat clay mineral observed in the particles of the Kaolinite clay. Many particles with an aggregate structure are observed in the ferrite formation. On the other hand, it is difficult to distinguish between the Kaolinite clay and ferrite particles in the ferritization-treated soil. This is attributed to the fact that the Pb content of the contaminated soil is 1 g/kg and the ratio is very small.

The grain size distributions of the samples are shown in Fig.5. The Kaolinite clay and compound hydroxide exhibit almost the same grain size distribution curve. The grain size of the ferritization-treated soil increases slightly as compared to that of the Kaolinite clay or
compound hydroxide. Thus, it may be said that the ferrite formation is deposited by the combination of several ions.

![Kaolin clay](image1)

![Ferritization-treated soil](image2)

![Ideal ferrite formation](image3)

Fig. 4 SEM micrographs by the scanning electron microscope of samples

2.2.3 Insoluble property of lead

The elution test under the condition of $2\text{Fe}^{2+}/\text{Pb}^{2+} = 20$ was performed on the contaminated soil without treatment, the compound hydroxide with iron and lead, and the ferritization-treated soil. The test results are shown in Fig.6. The Pb concentration of the contaminated soil increases under alkaline and acidic conditions, because lead is an amphoteric element. In other words, lead exists as Pb$^{2+}$ ion under acidic conditions, and it is deposited as lead hydroxide Pb(OH)$_2$ under weak alkaline conditions, following which it dissolves as Pb$^{2+}$ ions under strong alkaline conditions. On the other hand, the Pb concentration of the compound hydroxide and the ferritization-treated soil decreases significantly in the entire range compared to that of the contaminated soil. Particularly, the value of Pb concentration at the alkali condition was not detected for the measurement limit of 0.01 mg/l. It is considered that the ferrite method is very effective for the remediation of insoluble heavy metals in comparison with previous methods such as cement stabilization or the use of chemical agents.

![Fig. 5 Grain size distribution of the samples](image4)

![Fig. 6 Insoluble property of the contaminated soil by the ferritization](image5)
In order to investigate the influence of the iron content on the insoluble property, the elution test was performed under different conditions of $2\text{Fe}^{2+}/\text{Pb}^{2+}$ in the pH range of 5.8–6.3. Figure 7 shows the relationship between the concentration of Pb and $2\text{Fe}^{2+}/\text{Pb}^{2+}$ in mol ratio. As shown in this figure, the insoluble property of lead appears gradually with an increase in $2\text{Fe}^{2+}/\text{Pb}^{2+}$. The ferrite method was originally used for the disposal of effluents containing various types of heavy metals. Although this method is not considered to be suitable for lead ions, the insoluble property of lead-contaminated soil is confirmed to be significant by the increase in the Fe content.

![Fig. 7 Relationship between concentration of Pb and $2\text{Fe}^{2+}/\text{Pb}^{2+}$](image)

2.2.4 Magnetic property of ferritization-treated soil

Since ferrite is a ferromagnetic material, it is considered that magnetic separation is possible. For investigating the magnetic property, the state of the ferritization-treated soil when placed close to a permanent magnet was observed, as shown in Fig. 8. It is observed that the ferritization-treated soil is ferromagnetic. This indicates that ferrite formation exists in the soil. In order to clarify the magnetic separation property of ferrite and clay particles under a high-magnetic field, an experiment involving magnetic separation using a superconducting magnet was performed. An extreme magnetic field gradient is generated around the stainless filter under a high-magnetic field. The magnetic particles are attached to the filter. The ferritization-treated soil in slurry was poured into a hole with the filter under a high-magnetic field of 13 T (Tesla). The magnetic materials with a total dry weight of 20% were successfully removed from the treated soil. However, ferrite and clay particles could not be separated adequately.

![Fig. 8 State of the ferritization-treated soil when kept close to a permanent magnet](image)

In future studies, the effective separation of ferrite formation from soil will be required.

3. CONCLUSIONS

The ferrite method was applied to the contaminated soil. The insolubility of the ferritization-treated soil and the compound hydroxide were clarified by an elution test. Furthermore, the magnetic property of the ferritization-treated soil was investigated by a magnetic separation test.

The main conclusions drawn from this study are as follows:

1) The ferritization-treated soil and compound hydroxide exhibit significant insolubility over a wide range of pH. The insoluble effect increases gradually with the iron content.

2) It was confirmed that the ferritization-treated soil is ferromagnetic. Although ferrite and clay particles could not be separated adequately under a high magnetic field, it is suggested that the ferrite method may be one of the techniques for the remediation of contaminated soils with heavy metals.

REFERENCES

