This paper was downloaded from the Online Library of the International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE). The library is available here:

https://www.issmge.org/publications/online-library

This is an open-access database that archives thousands of papers published under the Auspices of the ISSMGE and maintained by the Innovation and Development Committee of ISSMGE.

The paper was published in the proceedings of the 3rd International Symposium on Coupled Phenomena in Environmental Geotechnics and was edited by Takeshi Katsumi, Giancarlo Flores and Atsushi Takai. The conference was originally scheduled to be held in Kyoto University in October 2020, but due to the COVID-19 pandemic, it was held online from October 20th to October 21st 2021.
Formation of pyromorphite by hydroxyapatite in soil during lead migration through water-unsaturated soils

Masahiko Katoh i) and Kazuki Hamada ii)

i) Associate Professor, Department of Agricultural Chemistry, Meiji University, 1-1-1, Higashimita, Kawasaki 214-8571, Japan.
ii) Undergraduate Student, Department of Agricultural Chemistry, Meiji University, 1-1-1, Higashimita, Kawasaki 214-8571, Japan.

ABSTRACT

Chemical immobilization using a hydroxyapatite is one of the promising approach to soil with high level lead (Pb) contamination. To enhance the effectiveness of Pb immobilization by the hydroxyapatite, it is important to understand that how Pb reacts with the hydroxyapatite and forms insoluble Pb phases in the soil pore. This study conducted the up-flow-unsaturated column percolation test with the combined application of X-ray diffraction (XRD) analysis to understand the relation between the amount of Pb migrated and Pb transformed into pyromorphite in the water-unsaturated soil with regarding to the distance of Pb migration. The XRD analysis could quantify the amounts of Pb as pyromorphite formed during the water percolation test. Pb existed as water-soluble gradually migrated from the soil in the layer to the soil in the next layer with the water percolation despite the presence of hydroxyapatite. In opposite, the formation of pyromorphite was favor in the soil near the inflow side.

Keywords: immobilization, lead mobility, pot percolation test, X-ray diffraction analysis

1 INTRODUCTION

Shooting range and mine soils, which cover an extensive area, and have a very low asset value, are frequently contaminated with lead (Pb) at an extremely high level. Chemical immobilization technique, which can alter Pb to more insoluble state by applying the material to contaminated soil, can suppress its mobility and bioavailability in situ. In such soils, chemical immobilization is an effective option for soil remediation compared with the excavation and transport to landfill sites. Various immobilization materials have been designed and developed for Pb immobilization. Within these materials, an application of hydroxyapatite is an effective option although its inappropriate application has a potential to cause the eutrophication.

Not all soluble Pb is transformed into insoluble Pb phases when the hydroxyapatite is applied in the soil. The Pb not transformed into insoluble phases has a potential for leaching. Therefore, understanding how Pb reacts with the hydroxyapatite and forms insoluble Pb phases in the soil pore is an important for reducing the environmental risk in the soil. Several factors in the soil influence the magnitude of pyromorphite formation. Ogawa et al. (2018) provides the first experimental evidence that Pb migration can induce Pb to transform into pyromorphite by the hydroxyapatite in the water-unsaturated soil despite the soils having different Pb mobilities. In addition, They quantitatively demonstrates that the amount of Pb migrated without the hydroxyapatite is almost equal to that of Pb formed into pyromorphite. However, it has not been described that how Pb migrating through the soil profile is transformed into pyromorphite with regarding to the distance of Pb migration. Answering this question is informative for the enhancement in the effectiveness of Pb immobilization using the hydroxyapatite.

In this study, the up-flow-unsaturated column percolation test was conducted with the combined application of X-ray diffraction (XRD) analysis to non-destructively determine the amount of pyromorphite formed during the Pb migration. The aims of the present study was to understand the relation between the amount of Pb migrated and Pb transformed into pyromorphite in the water-unsaturated soil with regarding to the distance of Pb migration.

2 MATERIALS AND METHODS

2.1 Preparation of soil and hydroxyapatite

A commercial Andosols was air-dried, passed through a 2-mm sieve, and used for physicochemical analysis and preparation for an artificially Pb-contaminated soil. The uncontaminated soil had the following physicochemical properties (Table 1). The artificially Pb-contaminated soil was prepared by mixing with lead chloride at a ratio of 57 mg-Pb/g. The level of lead contamination was relatively high, but that was within the range reported in the shooting range soils (Katoh et al. 2012, 2015). Hydroxyapatite was synthesized from gypsum and diammonium hydrogen phosphate (Furuta et al. 1998). The material was passed
through a 0.425-mm sieve before use.

### 2.2 Up-flow-unsaturated column percolation test

Figure 1 shows a schematic of the up-flow-unsaturated column percolation test. Acrylic pots (65 × 65 × 95 mm high) were used as column, the bottom of which contained 25 holes with 5 mm diameter. A 172 g of contaminated soil with and without 5 wt% hydroxyapatite was placed in the bottom of each pot adjusting the soil height to 5 cm; i.e., the soil packing density was 0.81 g/cm³. Following this, a 16.0 g of recovery sorbent to trap Pb migrated from the contaminated soil was added on top of the contaminated soil. Hydroxyapatite was also used as recovery sorbent. A 50.0 g of uncontaminated soil was placed on top of recovery sorbent layer for cover soil not to influence the contaminated soil layer by heat of the lights. Each layer was separated using a 25-μm nylon mesh sheet. The side of each column was then covered with an aluminum foil to provide shade, and three columns were prepared for each treatment. Ultra-pure water was added to maintain 60% of the water-holding capacity of each soil or sorbent. The column was placed under six fluorescent lights at the distance of 200 mm between the lights and the surface of cover soil, and the light was lit for 24 hours. During test, the water content of each column was maintained at its initial level by adding ultra-pure water via the bottom of the column without leakage every at two or three times a week. This experimental design provided the unsaturated water flow from the lower parts toward the upper parts. The test continued till the 469 ml of water was supplied, which correspond to the level of precipitation for almost a month.

After the test, the contaminated soil was collected separating 5 layers of 1 cm thickness. The sorbent was carefully collected. The samples collected were well mixed, air-dried, and passed through a 2.0 mm and 0.425 mm sieve for the soil and sorbent analysis. Water-soluble Pb content in the contaminated soil was extracted using ultrapure water with a liquid to solid ratio of 10 and analyzed using an inductively coupled plasma–atomic emission spectrometer (ICP-AES; Optima 8300, PerkinElmer Co., Ltd., USA). The total Pb content in the sorbent was determined for the amount of Pb trapped (migrated) during the percolation test. The sorbent was digested with HNO₃ and HCl using a microwave. The digested solution was analyzed to determine the Pb concentration by ICP-AES. The contaminated soils with the hydroxyapatite after the percolation test was also provided to the XRD analysis following the procedure described below to determine the amount of Pb as pyromorphite formed during the percolation test.

### 2.3 XRD analysis and determination of pyromorphite-Pb

Standard soil samples were prepared by mixing the uncontaminated soil with pyromorphite, which was synthesized following the procedure described in Scheckel and Ryan (2002), at ratios of 0, 5, 10, 20, 30, and 50 mg-Pb/g. The samples were mixed with the 5% (w/w) α-aluminium oxide for an internal standard substance, and ground in an agate mortar finely for at least 10 minutes. The XRD profiles were obtained using an XRD meter (MultiFlex; Rigaku Co., Japan). The X-ray source was a Cu anode operating at 40 kV and 40 mA using CuKα radiation with a diffracted beam graphite-monochromator. Scans were conducted by convergence method from 5 to 60° at a rate of 2° per min and scanning step of 0.04° per sec. The XRD data were analyzed using PDXL software (Rigaku Co. Japan) equipped with the ICDD Powder Diffraction File. In the figure of XRD profile, Y axis presented as the intensity ratio to α-aluminium oxide peak intensity (1.73–1.82 Å).

In addition, the peak intensity at 2.99–3.00 Å was used to determine the Pb of pyromorphite. The reason that these peaks were used for the determination was that these were only peaks that was not disturbed by uncontaminated soil, lead chloride, and hydroxyapatite.
A calibration curve was calculated using the standard soil samples. A limit of detection and quantitation for the analysis was obtained by the 10 times measurement of 5 mg-Pb/g standard soil sample, and calculated from 3.29 and 10 times, respectively, of its standard deviation.

3 RESULTS AND DISCUSSION

3.1 Pb migration by up-flow-unsaturated column percolation test

An average of daily water supply was 3.3 ml/day, which could be converted to $5.35 \times 10^{-5}$ cm/min of Darcy flow rate. In the unsaturated column percolation test using lysimeter and suction-type column previously reported, the Darcy flow rate ranged $10^{-1}$–$10^{-2}$ cm min$^{-1}$ (Álvarez-Ayuso et al. 2013; Spuller et al. 2007). Thus, in this study, it could be represented lower Darcy flow rate.

In the contaminated soil with the hydroxyapatite, the amount of Pb migrated from the soil was 660 mg-Pb/kg, which was corresponded to 2.2% of Pb added, and it was low as compared with the soil without the hydroxyapatite (1260 mg-Pb/kg). Thus, the presence of hydroxyapatite in the contaminated soil could suppress 50% of Pb leaching.

3.2 Determination of Pb as pyromorphite

Figure 2 shows the XRD profiles of standard soil samples for the determination of pyromorphite. No Pb minerals were identified from the uncontaminated soil amended without pyromorphite (0 mg-Pb/g). The strongest XRD peak of pyromorphite (2.99–3.00 Å) was observed from all the soils that pyromorphite added, and it was stronger with increase in pyromorphite content. Using the data of the standard soil samples, the least-squares regression equation:

$$Y = 0.067X + 1.259, \quad R^2 = 0.994 \quad (P < 0.01)$$

where $x$ is the Pb of pyromorphite (mg-Pb/g) and $y$ is the peak ratio of pyromorphite to alumina. This high positive relationship with high correlation coefficient indicates that the amount of Pb as pyromorphite in the soil after the percolation test can be determined using the regression equation if pyromorphite is formed during the percolation test. The limit of detection and quantitation for the analysis was 2.5 mg-Pb/g and 8.4 mg-Pb/g, respectively.

Figure 3 shows the XRD profiles of contaminated soil with the hydroxyapatite after the percolation test. The apparent peaks of pyromorphite was identified from the soil in the 0–1 and 1–2 cm layer from the inflow side after the percolation test. On the basis of the peak intensity ratio and regression equation (Fig. 2 (B)), the amount of Pb as pyromorphite formed during the percolation test was determined, and pyromorphite was significantly detected despite the soil layer (Fig. 4 (a)). The amounts of Pb as pyromorphite were 990, 346, 142, 116, and 117 mg-Pb/layer for the soil in the 0–1 cm, 1–2 cm, 2–3 cm, 3–4 cm, and 4–5 cm layer from the inflow side, respectively, which was corresponded to 50%, 18%, 7.2%, 5.9%, and 6.0% of total Pb added (Table 1). These results demonstrate that the formation of pyromorphite
in the soil pore is favor in the soil near the inflow side, and the % of pyromorphite formed decreases with the increase in the distance from the inflow side. It should be noted that the XRD analysis can detect the crystalline minerals, but not non-crystalline minerals. Thus, if the non-crystalline pyromorphite was formed in this study, the % of Pb as pyromorphite formed would be underestimated in this study. Taking this implication into consideration, the % of Pb as pyromorphite would be high as compared with the estimation in this study.

3.3 Determination of water-soluble Pb and Pb as pyromorphite in soil with and without hydroxyapatite

Figure 4 shows the amount of Pb as pyromorphite and water-soluble Pb of soil with and without the hydroxyapatite in the layer. In the soil without the hydroxyapatite, the content of water-soluble Pb in the layer was 110 and 1770 mg-Pb/layer, and the levels of water-soluble Pb increased with the increase in the distance from the inflow side. In addition, the content of water-soluble Pb was lower in the 0–3 cm layers, but was higher in the 3–5 cm layers than that before the percolation test (590 mg-Pb/layer). These strongly suggest that the Pb existed as water-soluble gradually migrated from the soil in the layer near inflow side to the soil in the adjacent layer. In similar, the level of water-soluble Pb increased with the increase in the distance from the inflow side in the soil with the hydroxyapatite, but their content was lower than those without the hydroxyapatite in all the layer. The level of water-soluble Pb decreased at 32%–57% in the soil with the hydroxyapatite compared with the soil without the hydroxyapatite except the 2–3 cm soil layer where the % of water soluble Pb decreased was 5%. As mentioned in section 3.2, the amounts of Pb as pyromorphite decreased with the increase in the distance from the inflow side, and this trend was opposite to the water-soluble Pb. These demonstrated that the presence of hydroxyapatite could immobilize Pb by the formation of pyromorphite, and suppress the level of water-soluble Pb in all the layer. However, a part of Pb existed as water-soluble could not be immobilized by the hydroxyapatite, and was migrated with the water percolation. The summed total of Pb as pyromorphite in each layer was higher than the summed total of water-soluble Pb decreased by the addition of hydroxyapatite in each layer, suggesting that a part of Pb not migrated but sorbed on the soil particles could be immobilized without the Pb migration.

4 CONCLUSION

This study combined the original unsaturated-column-percolation test with XRD analysis to understand how Pb is migrated and transformed into pyromorphite by hydroxyapatite in the water-unsaturated soil. The XRD analysis could quantify the amounts of Pb as pyromorphite formed during the water percolation test. Pb existed as water-soluble gradually migrated from the soil in the layer to the soil in the next layer with the water percolation despite the presence of hydroxyapatite. In opposite, the formation of pyromorphite was favor in the soil near the inflow side.

ACKNOWLEDGEMENTS

This study was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI [grant number 25740036].

REFERENCES


