

## Relationship between suppression of leachability and formation of insoluble phase in Pb contaminated soil with hydroxyapatite on basis of column and batch leaching test

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### Abstract

The batch leaching test may cause the overestimation of immobilization effectiveness in the lead (Pb) contaminated soil amended with hydroxyapatite (HAP) as compared with the column leaching test, but the mechanisms of overestimation are unclear. In this study, the suppression of Pb leachability and the formation of insoluble Pb phase were evaluated by both tests using the soil amended with or without HAP. The level of Pb leaching from the soil evaluated by the batch leaching test was higher than that evaluated by the column leaching test despite HAP amendment. Furthermore, the addition of HAP greatly reduced the level of Pb leaching when applying the batch leaching test. However, the X-ray diffraction analysis showed that the insoluble Pb phase (pyromorphite) was formed at the same level despite the leaching test types. This study suggests that other mechanisms than the formation of insoluble phase induces the overestimation of immobilization effectiveness.

### INTRODUCTION

Reducing the leachability of heavy metal in the soil added with an amendment is a target of heavy metals immobilization. One of the immobilization mechanisms is the formation of insoluble heavy metal phases by an amendment, resulting in the reduction in the leachability of heavy metals. Therefore, immobilization effectiveness was evaluated comparing the level of heavy metal leached from the soils with and without the amendment. Two kinds of technique are generally applied to evaluate the immobilization effectiveness.

A column leaching test, which is one of the techniques to evaluate the immobilization effectiveness, can design continuous water migration by water percolation through the saturated or unsaturated soil column. In the natural soil condition, the heavy metal on soil particles would be transported through water migration, repeating various processes, such as ion exchange, precipitation and dissolution, sorption and desorption to soil minerals and organic matters, and colloidal transportation [1, 2]. The heavy metal leaching designed by the column leaching test can simulate well the heavy metal transport including these reaction processes in the natural soil. In addition, these reaction processes on the column leaching test would be conducted in un-equilibrium condition because of the continuous water migration [3].

A batch leaching test is another technique to evaluate the immobilization effectiveness because it can extract easily the heavy metal leachable from the soil. However, heavy metal reactions on the batch leaching test are facilitated by shaking in controlled condition to make their reactions equilibrium [4]. Hence, the batch leaching test would evaluate much leaching of heavy metal as compared with the column leaching test. These differences of heavy metal leaching may mislead the evaluation of the immobilization effectiveness. The suppression mechanisms of heavy metal leaching by amendment are proved by evaluating the formation of insoluble heavy metal phases. Contact and reaction of heavy metal with the amendment in the soil pore water is required to transform to insoluble phases. Hence, the batch leaching test may cause the overestimation of the immobilization effectiveness because it probably facilitates the formation of in The sequential extraction is a major quantitative technique for determination of insoluble heavy metal phases in the soil after the leaching test.

The sequential extraction is a major quantitative technique for determination of insoluble heavy metal phases in the soil after the leaching test. However, the sequential extraction cannot evaluate the direct identification of the insoluble heavy metal phases because its procedure involves shaking to achieve the reactions equilibrium as similar to the batch leaching test [5, 6]. Therefore, the sequential extraction cannot clarify the reason of overestimation of immobilization effectiveness attributed to the facilitation of formation of insoluble heavy metal phases by the batch leaching test.

This study evaluated the immobilization effectiveness in the soil with the amendment by the column and batch leaching tests. In addition, non-destructive determination, X-ray diffraction (XRD), was applied to determine quantitatively the insoluble heavy metal phases in the soil. XRD can compare the level of insoluble heavy metal phases between column and batch leaching test because it does not involve the shaking. This study investigated the immobilization effectiveness using the column and batch leaching tests and determined the level of insoluble heavy metal phases using the soil after these tests. The purpose of this study was to elucidate the mechanism of overestimation resulted from the evaluation by the batch leaching test.

### MATERIALS AND METHODS

This study used a simulated Pb contaminated soil. A commercial Andosol was used as base soil of contaminated soil. The Andosol was air-dried and passed through a 2 mm sieve. Pb concentration was adjusted to the 50000 mg/kg adding the lead chloride. The contaminated soil and water were mixed to keep the 60% of water holding capacity, incubated for two weeks at room temperature (25 °C), and air-dried prior to the leaching test.

The Pb immobilization amendment was constituted mainly by hydroxyapatite (HAP). HAP was synthesized from gypsum and diammonium hydrogen phosphate [7], was sieved under 0.425 mm. HAP can effectively immobilize Pb by forming insoluble Pb phosphate minerals, such as pyromorphite, especially under acidic to weak acidic pH conditions [8, 9]. In addition, ferrihydrite was synthesized from iron nitrate hydrate [10], sieved under 0.425 mm. Ferrihydrite was mixed with HAP (1:9 Ferrihydrite:HAP ratio) because it can suppress the Pb leaching at weak alkaline pH condition [11]. The contaminated soil was mixed with the amendment in 10% (w/w) as amended soil. The contaminated soil without amendment was used as control soil. The levels of Pb leached from the control soil and amended soil were evaluated by the column leaching test or the batch leaching test, respectively. These leaching tests were conducted in triplicate.

Fig. 1 is a schematic of the column leaching test using an unsaturated soil. The column was comprised of three layers: contaminated soil, sorption, non-contaminated soil layers (CL, SL, and NC, respectively). Then, 65.0, 4.7, and 100.0 g of contaminated soil, amendment, non-contaminated soil, respectively, were added to each layer. The layers were separated using a 25-Bm nylon mesh. Ultra-pure water was added to maintain 60% of the water-holding capacity of each soil or amendment. The column was stood at room temperature (25 °C). Six fluorescent lights were placed 100 mm away from the surface of NL in the column, were lit for 24 hours. This column leaching test design represented water flow in unsaturated soil. The bottom of the pot had 25 holes with a diameter of 5 mm. The soil were supplied the water

corresponding to the lost weight of column by evaporation from the last water supply from the bottom at 2 or 3 times a week (Fig. 1). The total water supply was 650 mL, which was designed to match the soil:solution ratio of batch leaching test. After the test, the soils and amendment were collected, air-dried, and passed through a 0.425 mm sieve before the analysis of Pb content. The amendment was digested by acid with 14.5 M HNO<sub>3</sub> and 12 M HCl using a microwave. The digested solutions were passed through a 0.45 Bm filter, and analyzed to determine the Pb content of amendment by inductively coupled plasma optical emission spectrometry (ICP-OES; ULTIMA2 HORIBA Ltd., Japan). The Pb content of amendment in the SL multiplied by the amendment weight and divided by contaminated soil weight of CL to calculate the level of Pb leached from CL to the SL.

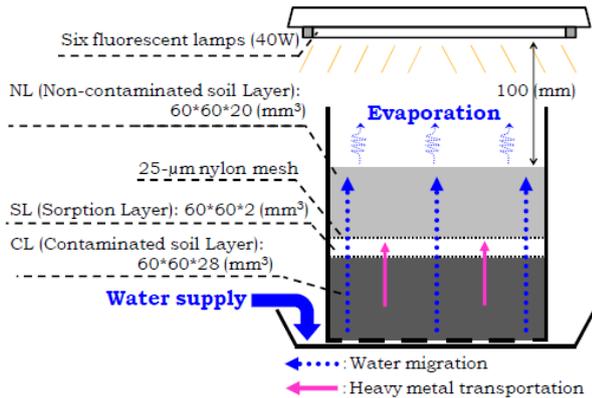


Fig.1 Schematic of the column leaching test using an unsaturated soil.

The batch leaching test was conducted to shaking with contaminated soil and ultra-pure water (1:10 soil:solution ratio) in the 50-mL polypropylene tube. After shaking for 24 h, centrifugation at 5000 rpm for 5 min, the suspension was passed through a 0.45µm filter, and the supernatant was analyzed to determine Pb concentration by ICP-OES. The Pb concentration in the supernatant was converted to the level of Pb leached from contaminated soil by using soil:solution ratio of the batch leaching test.

The amended soils after each leaching test were mixed with the 20% (w/w) aluminium oxide, and crushed to determine quantitatively the insoluble Pb phase. The pyromorphite was known as crystalline insoluble Pb phase formed by reaction of Pb and HAP [8, 9], was identified by using XRD (XRD; ULTIMA IV Rigaku Co., Japan). The pyromorphite peak area was calculated by the XRD profiles of pyromorphite peak range (29.46°–30.34°). The aluminium oxide peak area was calculated by the XRD profiles of range of aluminium oxide peak range (52.00°–52.90°). The Pb concentration as pyromorphite was determined quantitatively on the basis of calibration curve by using the peak area ratio of pyromorphite to aluminium oxide.

## RESULTS

### A. The column leaching test

Fig. 2 shows the level of Pb leached from CL to the SL through water migration by the column leaching test (a) and the level of Pb leached from contaminated soil to the water under the equilibrium condition by the batch leaching test (b). The 22500 mg/kg of Pb was found in the SL of control soil, indicating that approximately half of total Pb level in the contaminated soil was leached to SL of control soil through water migration. In contrast, the level of Pb leached from the SL of amended soil was greatly lower than the control soil, and it was less than 1% of total Pb level. Thus, the 22000 mg/kg of Pb which is corresponded to the 44% of total Pb level was suppressed leaching from CL to the SL by amendment (Fig. 2 (a)).

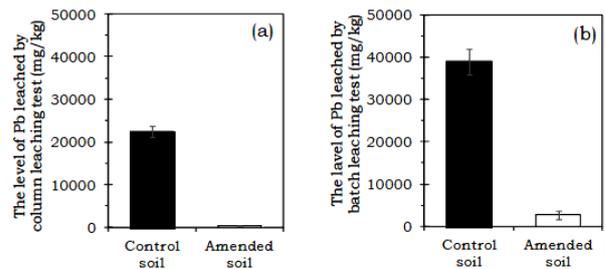


Fig.2. The level of Pb leached from CL to the SL through water migration by the column leaching test (a), from contaminated soil to the water under the equilibrium condition by the batch leaching test (b). The bars indicate the standard error.

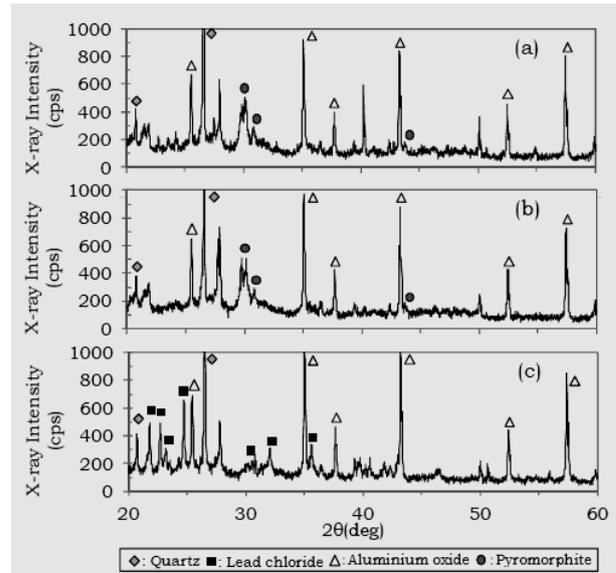


Fig. 3. Crystalline structure of amended soil after the column leaching test (a), after the batch leaching test (b) and before the leaching test (c).

Fig. 3 shows the crystalline structure of amended soil before and after the leaching tests. The XRD profile of soil before leaching test (Fig. 3 (c)) shows the identification of lead chloride. However, the lead chloride was not identified from the XRD profile of soil after the column leaching test (Fig. 3 (a)). Instead, insoluble Pb phase was identified such as pyromorphite. Table 1 shows the Pb concentrations as pyromorphite calculated by XRD profiles of contaminated soil added with HAP after the leaching tests, and their percentages to the total Pb level. Pb concentration as pyromorphite after the column leaching test was determined quantitatively to 29000 mg/kg by using the peak area ratio of pyromorphite to aluminium oxide. It was corresponded to the 58% of total Pb levels.

### B. The batch leaching test

The level of Pb leached from control soil was 39000 mg/kg, i.e., the 78% of total Pb level was leached by the batch leaching test. The level of Pb leached from amended soil was significantly lower than the control soil, which was corresponded to the 5% of total Pb level. Thus, the 36300 mg/kg of Pb which is corresponded to the 73% of total Pb level was suppressed leaching to the water by amendment (Fig.2 (b)).

The lead chloride was not identified from the XRD profiles of amended soil after the batch leaching test, the pyromorphite was identified (Fig. 3 (b)). The peak area ratio of pyromorphite to aluminium oxide after the batch leaching test was similar to that after the column leaching test. Pb concentration as pyromorphite after the batch leaching test was determined quantitatively to 30000 mg/kg by using the peak area ratio of pyromorphite to aluminium oxide. It was corresponded to the 60% of total Pb levels (Table 1).

Table 1. Pb concentrations as pyromorphite calculated by XRD profiles of amended soil after each leaching tests, and their percentages to the total Pb level.

Contaminated soils after the leaching test	Peak area rates of pyromorphite to aluminium oxide	Pb conc. as pyromorphite	percentages of Pb Conc. as pyromorphite to total Pb
After the column leaching test	2.28	2900	58
After the batch leaching test	2.35	3000	60

## DISCUSSION

### A. The suppression of Pb leaching by the amendment

The level of Pb leached from the soil evaluated by the column and batch leaching test was suppressed significantly by amendment. These results demonstrated that HAP amendment can reduce Pb leachability, i.e., HAP amendment was effective for the Pb immobilization. HAP can form the insoluble Pb phase, such as pyromorphite [8, 9], which has which has a very low solubility ( $\log K_{sp} = -76.8$ ) [12].

However, the levels of Pb leached from the soil evaluated by the batch leaching test were exceeded to those evaluated by the column leaching test, regardless of amendment. Therefore, the batch leaching test evaluates much Pb leaching as compared with the column leaching test. Furthermore, the suppression level of Pb leaching evaluated by the batch leaching test was higher than that evaluated by the column leaching test. These results indicate that immobilization effectiveness was overestimated by the batch leaching test comparing to the column leaching test. The difference of Pb leaching between the column and batch leaching tests would be explained for the facilitated formation of insoluble Pb phases because the contact and reaction of Pb with the amendment in the soil pore water is required to transform to insoluble Pb phases.

### B. The formation of insoluble Pb phase by the amendment

The pyromorphite was not identified by XRD profiles of amended soil before the leaching tests, and was identified by XRD profiles of amended soil after the both of leaching tests, indicating lead chloride was transformed to the pyromorphite by the HAP amendment and the Pb leaching. Pb leaching to the water would be essential for the formation of pyromorphite. However, contrary to Pb leaching difference, the Pb concentrations as pyromorphite were determined similar concentration between column and batch leaching test. Therefore, the formation of pyromorphite was not overestimated by the batch leaching test comparing to the column leaching test. The Pb sorption onto the HAP by forming the pyromorphite has higher sorption intensity calculated by Freundlich isotherm model than the other materials [13], and the solubility product ( $\log K_{sp}$ ) of pyromorphite is  $-76.8$  [12]. These report indicate that the affinity of HAP and Pb to form the pyromorphite was particularly high. The formation of pyromorphite were no difference between the column and batch leaching test because it has been achieved to maximum in the soil at after the column and batch leaching test.

### C. Mechanism elucidation of the overestimation resulted from the batch leaching test

From the column leaching test results, the percentage of suppression of Pb leaching (44%) was lower than the percentage of transformed Pb as pyromorphite (58%), it's indicating that the all suppressed amount of Pb leaching would be explained by the formation of pyromorphite. Thus, the pyromorphite are formed by Pb leaching through water migration in the soil designed by column leaching test, Pb leachability would be reduced accordingly.

In contrast, from the batch leaching test results, the percentage of the suppression of Pb leaching (73%) was exceeded than the percentage of transformed Pb as pyromorphite (60%), it's indicating that the formation of pyromorphite cannot be related with all suppressed amount of Pb leaching. This result means that the reduction of Pb leachability evaluated by the batch leaching test might be affected by other mechanisms, except for the formation of pyromorphite.

This amendment was constituted by 90% of HAP and 10% of ferrihydrite. Ferrihydrite has the hydroxyl groups on its surface, can sorb chemically Pb onto surface hydroxyl groups [11, 13]. And HAP has functional groups on its surface, can sorb chemically Pb onto surface functional groups [8, 9]. Through the batch leaching test, those sorption are facilitated by shaking in controlled condition to make their sorption equilibrium. In addition, Pb sorbed onto hydroxyl or functional groups would be more unstable than Pb formed as pyromorphite, because Pb desorption from hydroxyl or functional groups depend on variable charge and pH condition [13]. This study suggested that to evaluate the heavy metal leaching by only batch leaching test might lead overestimation of heavy metal immobilization effectiveness.

## CONCLUSION

The level of Pb leached by the batch leaching test was evaluated excessively, and the suppression level of Pb leaching of batch leaching test was overestimated comparing to the column leaching test. However, the formation level of insoluble Pb phase (pyromorphite) was not overestimated, was similar between the batch leaching test and the column leaching test.

In addition, the all suppressed amount of Pb leaching evaluated by column leaching test was related with the formation of pyromorphite. Therefore, the column leaching test can evaluate consistently the reduction of Pb leachability and the formation of pyromorphite.

In contrast, the all suppressed amount of Pb leaching evaluated by the batch leaching test might be affected by the formation of pyromorphite and other mechanisms, e.g., Pb sorption onto the hydroxyl and functional groups of ferrihydrite and HAP.

Hence, to evaluate the heavy metal leachability using only a batch leaching test might mislead overestimation of immobilization effectiveness. As a result, to evaluate the reduction of heavy metal leachability by the column leaching test was required for the reliable immobilization effectiveness evaluations.

## ACKNOWLEDGEMENT

The ICP-OES instrument used for the chemical analyses was made available by the Division of Instrumental Analysis at Gifu University. The authors are grateful to Prof. Y. Ohya (Gifu University) for permitting the use of the XRD.

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