

Remediation of Pb-contaminated soils by washing with hydrochloric acid and subsequent immobilization with calcite and allophanic soil

Masahiro Isoyama, Shin-Ichiro Wada*

Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

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Abstract

Removal of heavy metals from contaminated soil is not popular because of its high cost. Reducing the bioaccessible heavy metals content to an allowable level by washing with inorganic acids and subsequent immobilization of remained metals may be a low cost option for soil remediation. The applicability of this combined treatment was investigated using three different types of soil, a kaolinitic, a smectitic and an allophanic soil, which were artificially contaminated with Pb. The effectiveness of the treatment was evaluated using two main criteria: (i) reduction of the HCl extractable Pb (bioaccessible Pb) below 150 mg kg^{-1} , reduction of water extractable Pb below the concentration of 0.01 mg L^{-1} . These values correspond to allowable levels suggested by the Japanese Ministry of Environment. The soils were washed batch-wise at a solution to soil ratio of 5 L kg^{-1} successively with 1 mol L^{-1} HCl and 0.1 mol L^{-1} CaCl_2 solutions. The two solutions were separated by filtration from one batch and reused for washing the next batch of soil without processing. The Pb concentration in the solutions increased after repeated use and removal efficiency gradually declined. The efficiency of the treatment was highly dependent on the type of soil. In the kaolinitic soil, HCl extractable Pb content of the soil from the first batch was about 50 mg kg^{-1} and it exceeded 150 mg kg^{-1} in that from sixth batch. But the combined soils from 1st to 10th batches gave bioaccessible Pb content barely below 150 mg kg^{-1} . For the smectitic soil having higher cation exchange capacity, the acceptable number of times of reuse was estimated to be 4. For the allophanic soil, treatment with the HCl solution was efficient only for the first batch of the soil, and the reuse of the acid solution was found to be ineffective.

The application of 50 g kg^{-1} of calcite or slacked lime was effective for reducing the water extractable Pb content. To keep soil pH near neutral and secure long term stability, the application of 50 g kg^{-1} of calcite and 100 g kg^{-1} of allophanic soil was chosen as the best method. This combination of amendments could reduce the water extractable Pb to almost undetectable levels after 3 days of aging.

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1. Introduction

The disposal of waste in landfills should be the last option in the waste management. Actually, however, the excavation and disposal in landfills is the most frequently employed countermeasure for soils contaminated with toxic heavy metals. According to a statistics by the Japanese Ministry of Environment [1], the disposal of excavated soil was practiced in 356 out of 527 soil pollution cases in 2002. It is technically difficult and costly to reduce the heavy metal content of soils to an extremely low level. But decontamination may be much easier and economical if a more realistic clean up goal is set. Such a goal may be to remove only the soluble fraction of heavy metals or, more particularly, to remove the bioaccessible fraction,

i.e., the fraction of metals that is soluble in the gastrointestinal tract. It is noted that the Japanese Ministry of Environment has adopted a 1 mol L^{-1} HCl extraction procedure for simulating the dissolution in the acidic environment of the gastrointestinal tract, and has established maximum allowable levels for some contaminants in terms of this procedure [2]. Whatever decontamination goal is set, the immobilization of heavy metals that remain after the decontamination treatment is indispensable in order to prevent the leaching of the metals from backfilled soils and pollution of surface and ground waters.

Several technologies including soil washing [3] and electrokinetic methods [4,5] have been developed and tested, but no all-round technology that can treat all types of contaminated soils at a reasonable cost has been established. The soil washing can be practiced in two ways, i.e., mixing a soil and washing solution followed by soil-solution separation (batch-washing) and passing the solution through a packed soil column (column-washing). The latter technology is often termed soil flushing.

* Corresponding author. Tel.: +81 92 642 2844; fax: +81 92 642 2845.
E-mail address: wadasi@agr.kyushu-u.ac.jp (S.-I. Wada).

According to a compilation by Abumaizer and Smith [3], various extraction agents including acids, neutral salts and chelating agents have been employed. In recent years, many researches have been focusing on the use of chelating agents such as EDTA, SCMC (s-carboxymethyl-cysteine), etc. [6–8] and organic acid [9]. Some chelating agents have been proven to be effective in removing cationic heavy metals because they form stable anionic chelate compounds which exhibit lower tendency to be retained on the surface of soil particles via ion exchange and surface complexation mechanisms. However, they are disadvantageous in terms of cost of chemicals, toxicity of some chelating agents and increased mobility of the chelated heavy metals that may remain after the treatment. On the other hand the immobilization of heavy metals after washing with inorganic acids is easier because most cationic heavy metals forms sparingly soluble hydroxides or are adsorbed onto soil minerals when soil is neutralized. For these reasons, washing of contaminated soils with inorganic acid or alkali and subsequent immobilization are still worth further study. Unexpectedly, however, there is little published report on the combination of acid-washing and stabilization.

In the present study, laboratory scale batch-washing with dilute hydrochloric acid (HCl) is applied to three artificially lead (Pb)-contaminated soils to reduce the Pb content. The decontamination goal is set at reducing the amount of bioaccessible Pb below 150 mg kg^{-1} , which is the maximum allowable level according to the Japanese Law [2]. Then, the unextracted Pb is immobilized by application of some amendments. Since the present decontamination goal is moderate and the soils are still acidic after washing, they may contain significant amounts of water soluble Pb. The objective of the present study is two-fold. One is to find out suitable amendments that can effectively reduce the lability of the remaining Pb. Another objective is to test the possibility of reducing the volume of waste solution by recycled use of the acid. In soil washing, it is difficult to drastically reduce the cost for agitation, solid–liquid separation and mixing amendments. But it is possible to reduce the cost for waste water processing by reducing the volume of washing solution.

The experimental results showed that the washing solution can be recycled several times and that the combined application of calcite and allophanic soil can effectively reduce the solubility of the remained Pb.

2. Materials and methods

2.1. Soil sample preparation and characterization

Three soil samples that differ in chemical and mineralogical properties were collected in Japan. The soil samples were air-dried and passed through a 2 mm sieve. The soil samples were analyzed for pH, organic carbon content, and exchangeable cation content following the standard methods [10]. The content of allophane plus imogolite was determined by the oxalate-oxalic acid dissolution method [11,12]. Clay content and clay mineralogy was determined by the method described by Wada and Umegaki [13]. The values of the measured properties are

listed in Table 1. The Yoshiki soil was taken from the subsurface layer of a soil derived from saprolite of granite. It has relatively low organic matter content and effective cation exchange capacity (ECEC), i.e., the summed amount of exchangeable cations. The Chikugo soil was taken from the surface layer of a soil developed on an alluvial sediment rich in smectite and it is characterized by high ECEC. The Goshi soil was taken from the surface layer of a humus-rich soil derived from volcanic ash. It contains large amount of humus as well as allophane. The content of allophane determined by the selective dissolution was 162 g kg^{-1} .

The soil samples were spiked with 1000 mg kg^{-1} of Pb(II) with $\text{Pb}(\text{NO}_3)_2$. Four hundred and eighty milliliter of 0.01 mol L^{-1} $\text{Pb}(\text{NO}_3)_2$ solution was sprayed onto 1 kg of an air-dried soil sample spread on a shallow plastic vat with frequent mixing with plastic spoon. The spiked soil sample was aged for 3 months at a room temperature without cover and stored in a plastic bag after grinding to pass through a 2 mm screen. The total Pb contents of the prepared samples are listed in the last column of Table 1. The extractability of Pb in the contaminated soil samples was characterized by a simplified sequential extraction with water, 1 mol L^{-1} MgCl_2 and hot 6 mol L^{-1} HCl [5].

2.2. Batch-washing

Thirty grams portions of a contaminated air-dried and sieved soil sample were placed in 10 250 mL plastic bottles with fitted stoppers and numbered from 1 to 10. A 150 mL portion of a 1 mol L^{-1} HCl was added to the first bottle and it was shaken for 1 h. The reacted soil suspension was transferred onto a $0.45 \text{ }\mu\text{m}$ -membrane filter and the extract was collected by suction. A small amount of the extract was drawn for measurements of its pH and Pb concentration and the remaining extract was applied to the second bottle and fresh HCl solution was added to compensate the volume of the extracting solution. All 10 batches of the soil were washed with this manner. At each extraction, the amounts of recovered solution and added HCl solution were estimated by weighing.

To remove a part of remaining Pb and reduce the acidity of the soil, the soil left on the filter was washed by suction with 150 mL of a 0.1 mol L^{-1} CaCl_2 solution. The CaCl_2 solution was used because it is effective in extracting exchangeable Pb retained on layer silicate minerals. Mori and Wada [14] reported that a part of Pb released from surface complexes is re-adsorbed on cation exchange sites of layer silicate minerals having permanent negative surface charge. Also in CaCl_2 washing, the filtrate from the first batch was reused for washing the second batch and so on in a similar way as in HCl washing.

The Pb concentration of the filtrates was determined by atomic absorption spectroscopy, the pH was determined with glass electrode.

The soil samples after CaCl_2 washing were air-dried and the content of 1 mol L^{-1} HCl extractable Pb was determined by the method specified by the Ministry of Environment of Japan [2]. In the procedure, a soil sample was shaken with 1 mol L^{-1} HCl for 2 h at a soil to solution ratio of 0.030 kg L^{-1} and the extracted Pb was determined after filtration through a $0.45 \text{ }\mu\text{m}$

Table 1
Selected chemical and mineralogical properties of soil samples used

Sample name	pH	Organic carbon (g kg ⁻¹)	Clay content (g kg ⁻¹)	ECEC ^a (cmol _c kg ⁻¹)	Major ion adsorbent	Total Pb (mg kg ⁻¹)
Yoshiki	5.3	9	82	1.9	Kaolin, iron oxides	1078
Chikugo	5.7	18	351	21.9	Smectite	1069
Goshi	5.9	71	214	13.0	Allophane, humus	995

^a Effective cation exchange capacity.

membrane filter. The Pb in the extract was determined by atomic absorption spectroscopy. The amount of Pb extracted by this procedure is adopted as a measure of the amount of Pb that may be released from ingested soil in gastro-intestinal tract in Japan [2]. As previously mentioned the maximum allowable Pb content is set to 150 mg kg⁻¹ [2]. Hereafter this Pb is referred to as bioaccessible Pb.

Equal amounts of the treated soil from each batch were mixed, homogenized and air-dried. Approximately 10 g was used for determination of the bioaccessible Pb and the remainder was used for the following immobilization treatments.

2.3. Immobilization treatment

Ten grams portions of the homogeneously mixed soil samples after the CaCl₂ washing were mixed in glass Petri dishes with amendments including calcium carbonate, calcium hydroxide, allophanic soil, silica and mordenite zeolite and aged in shallow plates covered with air-permeable thin polyethylene film. During aging the water content of the samples was kept at 300 g kg⁻¹ by spraying deionized water. The rates of the amendments addition are summarized in Table 2.

After 1 day of aging, small amounts of the soil samples were taken and air-dried. The air-dried samples were shaken with deionized water for 6 h at a soil to water ratio of 100 g L⁻¹ and the pH and concentration of dissolved Pb was determined by electrothermal atomic absorption spectroscopy with NH₄NO₃

as a matrix modifier after filtration through a 0.45 μm membrane filter. This method is the standard test method stipulated in the Soil Pollution Countermeasure Law of Japan and the maximum allowable concentration of Pb is 0.01 mg L⁻¹ [2]. For some of the treatment, the aging was continued and the water extractable Pb was determined again after 3, 10, and 30 days of aging.

3. Results and discussion

3.1. Efficiency of batch washing

The results of the sequential extraction of the prepared contaminated soils with water, 1 mol L⁻¹ MgCl₂ and hot 6 mol L⁻¹ HCl are presented in Fig. 1. The results are in accordance with the major cation adsorbent composition. In the Yoshiki soil that has low ECEC, approximately 20% of Pb was in water soluble form and 50% was extractable in MgCl₂. In the Chikugo and Goshi soils, most part of Pb was found in the hot HCl extractable fraction. This results suggest that the Pb in the Yoshiki soil is easier to remove but more difficult to immobilize.

The results of the batch washing with the HCl and CaCl₂ solutions are presented in Figs. 2 and 3. Fig. 2 shows the Pb concentrations in the HCl and CaCl₂ solutions separated from each batch of soil. Fig. 3 shows the net Pb extractions by the HCl and CaCl₂ solutions as well as the sum of them. The net Pb extraction was calculated by subtracting the amount of Pb carried over from the preceding extraction from the amount of Pb found

Table 2
Rate of amendments incorporation and aging period

Treatment code	Addition (g kg ⁻¹)					Aging (day)
	Calcite	Ca(OH) ₂	Allophane	Silica	Zeolite	
None	–	–	–	–	–	–
C50	50	–	–	–	–	1
C100	100	–	–	–	–	1
C200	200	–	–	–	–	1
C50-A50	50	–	50	–	–	1
C50-A100	50	–	100	–	–	1
C50-A100(3)	50	–	100	–	–	3
C50-A100(10)	50	–	100	–	–	10
C50-A100(30)	50	–	100	–	–	30
C100-A100	100	–	100	–	–	1
C50-A150	50	–	150	–	–	1
C50-S50	50	–	–	50	–	1
C50-Z50	50	–	–	–	50	1
C100-Z100	100	–	–	–	100	1
C100-A50-Z50	100	–	50	–	50	1
L50	–	50	–	–	–	1
L50-A100	–	50	100	–	–	1
L50-Z100	–	50	–	–	100	1

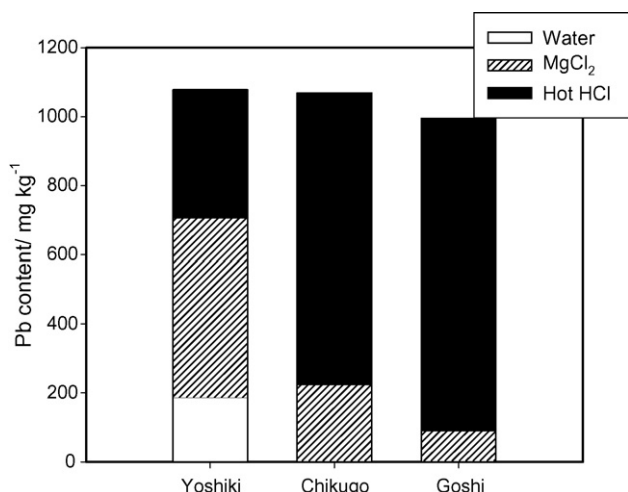


Fig. 1. The amounts of Pb sequentially extracted from the prepared contaminated soil samples.

in the extract. The amount of Pb that was carried over from the preceding extraction was calculated from the Pb concentration in the preceding extract and the volume of the entrained solution that was estimated by weighing.

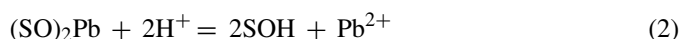
Since both the HCl and CaCl₂ solutions separated from a batch of soil were reused for washing the next batch of soil without being processed, the Pb concentration increased gradually as the number of times of reuse increased (Fig. 2). In the 2nd to 10th washings, 15–35 mL of fresh washing solutions were added to compensate the entrained solution in the previous washing. This addition of the fresh solution might have contributed to buffer the increase of the Pb concentration to a certain extent. In the Yoshiki and Chikugo soils, the pH of the HCl solution was kept below 0.5 even after 10 times of reuse. On the other hand, in the Goshi soil, the pH of the HCl solution was 0.5 in the first batch and it increased to 1.4 after five times of reuse. The marked rise in pH in the Goshi soil is obviously due to the high acid buffering capacity of allophanes in the soil.

The net Pb extraction from each batch of soil decreased as the number of the times of reuse of the extracting solution increased (Fig. 3). Approximately 890 mg kg⁻¹ of Pb was extracted by the HCl extraction and about 88 mg kg⁻¹ of Pb was extracted by the subsequent CaCl₂ washing from the first batch of the Yoshiki soil. But the net Pb extractions from the 10th batch were 457 and 250 mg kg⁻¹. The Chikugo soil exhibited the similar trend. In the Goshi soil, the reuse of the washing solutions seriously lowered the extraction efficiency.

Major Pb adsorbing sites on soil materials are the negatively charged sites in layer silicate minerals and surface functional groups including Si–OH, Al–OH, Fe–OH and COOH groups. The desorption of Pb by acid can be expressed as:



and



where X stands for the negatively charged site in layer silicate minerals and SOH represents the surface functional groups. The

stoichiometry of both reactions indicates that the higher acidity and lower Pb concentration in the washing solution favor the desorption of Pb. The decrease in the net Pb extraction after repeated reuse of the washing solutions (Fig. 3) can be explained with this stoichiometry. The major cause of the drop in extraction efficiency after repeated reuse of the washing solutions would be the increased Pb concentration in the washing solutions, particu-

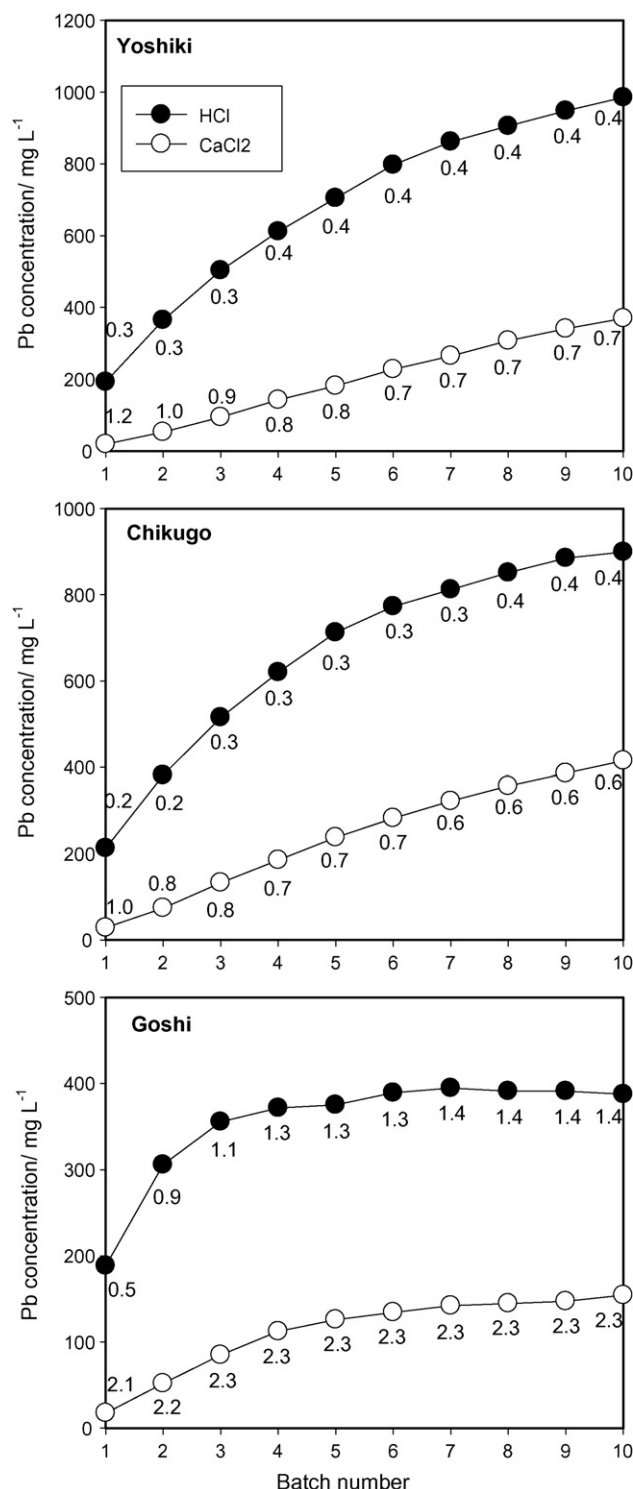


Fig. 2. Pb concentration and solution pH of HCl and CaCl₂ solutions separated from batches.

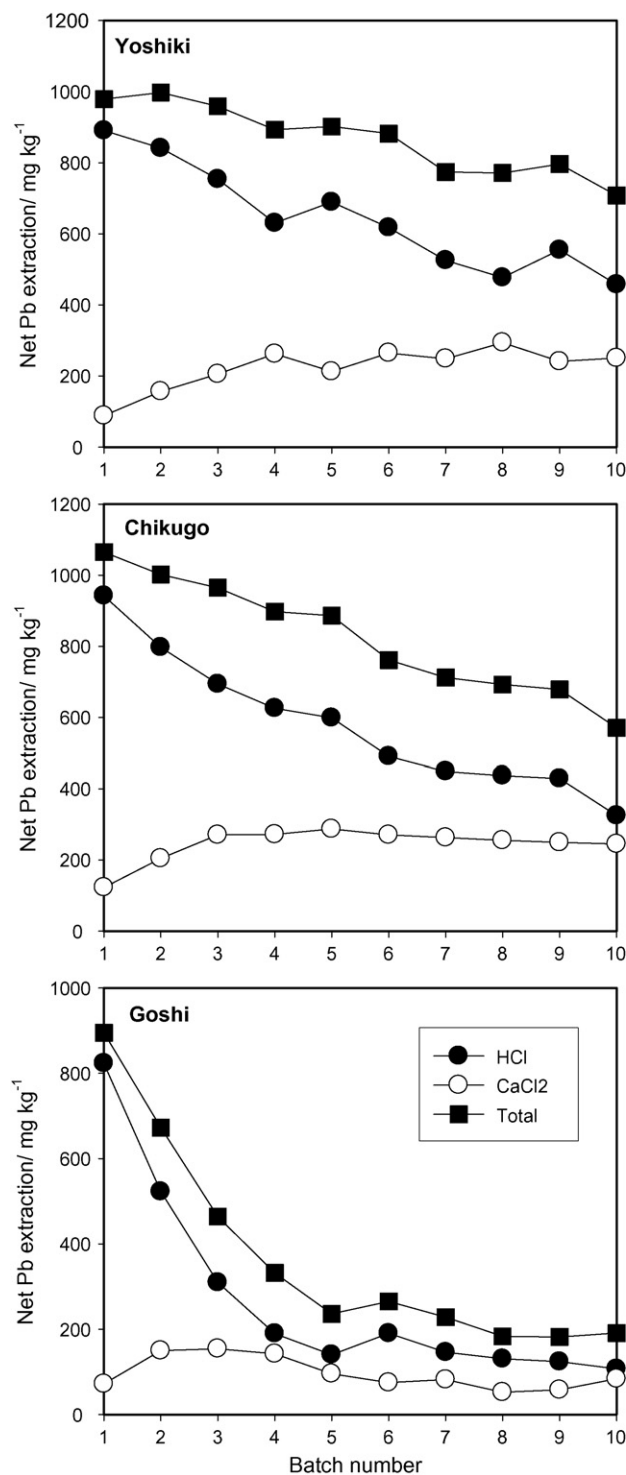


Fig. 3. Net amount of Pb extracted by the HCl and CaCl₂ solutions from each batch.

larly for the Yoshiki and Chikugo soils. The significant reduction of acidity would be another factor in the Goshi soil.

Among the surface functional groups, COOH groups on humic substances have higher affinity for Pb than other groups on mineral surfaces [15–17]. The markedly lower extraction efficiency in the Goshi soil is at least partly due to its high humic substance content (Table 1). The difference in extraction effi-

ciency between the Yoshiki and Chikugo soils can be explained in terms of the higher humic substance content and higher ECEC in the Chikugo soil (Table 1). Mori and Wada [14] reported that heavy metal cations released from functional groups in acid solutions are re-adsorbed as exchangeable cations by layer silicate minerals.

Fig. 4 shows the bioaccessible Pb of soil samples after the HCl and CaCl₂ washings. The rightmost data point in each series of plot shows the result for the mixture of equal amounts of soils from the 10 batches. The horizontal dashed line at 150 mg kg⁻¹ shows the maximum allowable bioaccessible Pb content of soils stipulated in the Japanese soil quality standards [2]. As expected from the results shown in Figs. 2 and 3, the larger amount of bioaccessible Pb remained after repeated use of the washing solutions. The treated soils from the 1st to 5th batches of the Yoshiki soil met the standard and the remaining batches failed. By mixing the soils from the 10 batches the excess over the standard was canceled and the mixture barely met the soil quality standard. For the Chikugo soil, only the soils from the 1st to 3rd batches met the standard and the excess was not canceled by mixing the soils from 10 batches. For the Goshi soil, the amount of bioaccessible Pb was below the limit of 150 mg kg⁻¹ only for the first batch of soil that was treated with fresh HCl solution. Reuse of the washing solution was completely ineffective.

The results shown in Fig. 4 show that the repeated use of the washing solutions is effective at least for some types of soils. The maximum number of times of reuse would depend on soil properties as well as on the content and chemical forms of Pb in the soil. The estimated maximum numbers of times of reuse to securely meet the Japanese standard, for example, are nine for the Yoshiki soil, four for the Chikugo soil and one for the Goshi soil. Under the present experimental conditions, 150 mL of HCl and CaCl₂ solutions were applied to each batch, 120–130 mL of them were recovered by filtration, and they were applied to the next batch with additional fresh solutions to make the volume 150 mL. In the case of Yoshiki soil, 339 mL of the HCl solution and 228 mL of the CaCl₂ solution were used for washing nine batches of the soil (total amount = 270 g) and 126 mL of the HCl

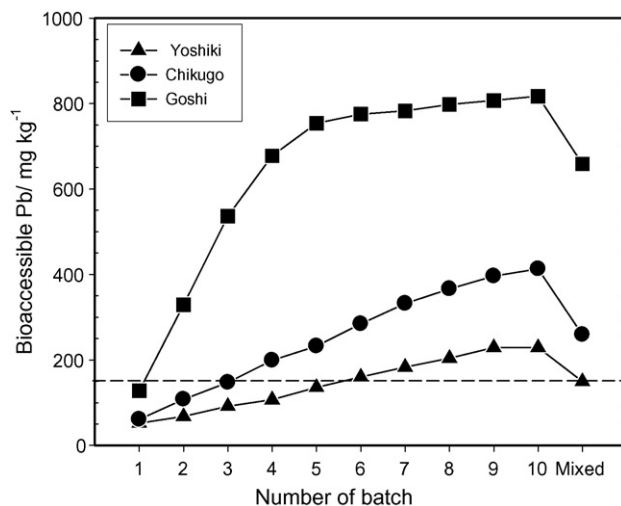


Fig. 4. The bioaccessible Pb content of soils from each batch and that of mixture of soils from 10 batches.

Table 3

Required volume of washing solutions and produced volume of waste solutions required to reduce the bioaccessible Pb content below 150 mg kg⁻¹

Soil	Times of reuse	Volume of washing solutions (m ³ /1000 kg)		Volume of waste solutions (m ³ /1000 kg)	
		HCl	CaCl ₂	HCl	CaCl ₂
Yoshiki	9	1.25	0.84	0.47	0.51
Chikugo	4	1.99	1.41	1	1.13
Goshi	1	5.00	5.00	4.33	

solution and 138 mL of the CaCl₂ solution were separated from the 9th batch. The solutions separated from the last batch have to be processed to remove Pb and neutralize before discharge. Under the assumption that the present washing procedure could be scaled up, the volumes of the washing solutions and waste water to be processed for treating 1000 kg of the three soils were estimated and summarized in Table 3.

Since the prices of industrial grade HCl and CaCl₂ are low, the cost of waste water processing is the primary factor that determines the total cost of soil washing. Table 3 shows that the repeated use of the washing solutions greatly contributes to reduce the cost of soil washing. The conventional method for processing acidic solutions containing heavy metals is the precipitation of heavy metals by neutralization. The major component that constitutes the precipitate would be aluminum (Al) hydroxide but not hydroxides of Pb. Thus the approximate weight of the sludge produced after processing the HCl and CaCl₂ solutions can be estimated from their Al concentrations. The Al concentration of the HCl and CaCl₂ solutions from the 9th batch of the Yoshiki soil were 2.1 and 1.0 g L⁻¹, respectively. Thus, the weight of sludge produced after washing 1000 kg of the Yoshiki soil in nine batches is estimated to be 4.3 kg on a dry matter basis.

Tampouris et al. [18] developed a pile leaching method to decontaminate heavy metals contaminated soils, in which a soil

was leached with a mixed HCl–CaCl₂ solution and tap water. They reused the solution after heavy metal removal by precipitation and addition of HCl. The same method can be used to regenerate the CaCl₂ solution in the present method and the volume of the waste solution to be processed and discharged can be further reduced.

The study by Tampouris et al. [18] and studies cited therein showed that keeping the soil agglomerated to attain high hydraulic permeability is crucial for successful column-washing. In the batch-washing, hydraulic conductivity of soils is not relevant to the efficiency and the method is applicable to heavily textured soils as well as to sandy soils. However, keeping soil particles flocculated is equally important for quick soil-solution separation. The layer silicate minerals of soils flocculate in acidic solution and in solutions of high ionic strength. The use of 0.1 mol L⁻¹ CaCl₂ solution instead of water would be a good option to keep soil particles flocculated.

3.2. Selection of materials suitable for immobilization

The basic immobilization strategy in the present study is to promote surface complexation reaction of Pb by increasing soil pH [19]. To that end, calcite and slacked lime were used for neutralization and one of allophanic soil, silica and zeolite were incorporated as auxiliary amendment to enrich

Table 4

Results of water extraction test after immobilization treatments

Treatment code	Pb concentration in water extract (mg L ⁻¹) (solution pH)		
	Yoshiki	Chikugo	Goshi
None	6.74	13.2	10.0
C50	0.0218 (6.89)	0.0180 (6.57)	0.0354 (6.48)
C100	–	–	0.0318 (6.25)
C200	–	–	0.0209 (6.30)
C50-A50	0.0170 (6.81)	0.0167 (6.44)	0.0359 (6.45)
C50-A100	0.0160 (7.57)	0.0160 (7.21)	0.0200 (6.86)
C50-A100 (3-day)	nd (7.55)	0.0011 (7.45)	0.0009 (7.46)
C50-A100 (10-day)	0.0021 (7.49)	0.0031 (7.44)	0.0018 (7.44)
C50-A100 (30-day)	nd (7.4)	nd (7.29)	0.0004 (7.13)
C100-A100	–	–	0.0169 (6.11)
C50-A150	–	–	0.0316 (6.12)
C50-S50	0.0268 (6.93)	0.0202 (6.55)	0.0414 (6.50)
C50-Z50	0.0170 (6.99)	0.0162 (6.58)	0.0359 (6.54)
C100-Z100	–	–	0.0305 (6.24)
C100-A50-Z50	–	–	0.0218 (6.18)
L50	0.0069 (12.46)	nd (12.02)	0.0057 (7.82)
L50-A100	0.0219 (12.29)	0.0032 (11.43)	nd (7.77)
L50-Z100	0.2000 (12.39)	0.0287 (11.93)	0.0016 (9.08)

nd, not detectable.

active surface functional groups. The results of the immobilization tests are summarized in Table 4. The soil sample used for the immobilization experiment was a uniform mixture of equal amounts of HCl–CaCl₂ washed soils from 10 batches. The sample for the Yoshiki soil met the soil quality standard for the bioaccessible Pb content but other samples did not (Fig. 4).

The concentration of Pb in the water extract of soils without immobilization treatment greatly exceeded the maximum allowable concentration of 0.01 mg L⁻¹ that is stipulated in the soil pollution countermeasure law [2]. The addition of 50 g kg⁻¹ of slacked lime alone was effective for reducing water extractable Pb below 0.01 mg L⁻¹ but the soil pH was too high. The application of the same amount of calcite was also effective but it failed to reduce the water extractable Pb concentration below 0.01 mg L⁻¹. The increased application of calcite seemed not much effective. The additional application of silica did not contribute to reduce the solubility of Pb but the combined application of calcite and zeolite or allophanic soil was effective. Since allophanic soil is cheaper than zeolite and the former is available in abundance at least in Japan, the effect of prolonged aging was studied on this combination.

The Pb concentrations in the water extract of the soils mixed with 50 g kg⁻¹ of calcite and 100 g kg⁻¹ of allophanic soil slightly exceeded 0.01 mg L⁻¹ after 1 day of aging. The Pb concentration markedly decreased after 3 days and gradually decreased thereafter and became almost undetectable after 1 month for all three soils (Table 4). Darmawan and Wada [20] spiked Cu, Pb and Zn to several soils at field moisture content and determined the chemical forms of the metals as a function of time. Their results showed that the added metals are first retained on cation exchange sites on layer silicate minerals and gradually transformed to surface complexes on oxide minerals and humic substances in 30–40 days. The gradual reduction of the solubility of Pb in the present experiment is probably due to the same mechanism.

4. Conclusions

The successive batch washing with 1 mol L⁻¹ HCl and 0.1 mol L⁻¹ CaCl₂ solutions is effective for reducing 1 mol L⁻¹ HCl extractable Pb content at least for soils whose clay fraction is dominated by crystalline layer silicate minerals. Both the HCl and CaCl₂ solutions from a batch can be reused to wash next batch without any processing several times, depending on soil properties and decontamination goal. The solutions could be reused nine and four times to reduce the content of 1 mol L⁻¹ HCl extractable Pb to below 150 mg kg⁻¹ for kaolinitic and smectitic soils, respectively. For allophanic soil, treatment with HCl solution is efficient only for the first batch of the soil, but reuse of the acid solution is ineffective.

The application of 50 g kg⁻¹ of calcite or slacked lime is effective for reducing the water extractable Pb content. To keep soil pH near neutral and secure long term stability, the combined application of 50 g kg⁻¹ of calcite and 100 g kg⁻¹ of allophanic soil is recommended. In the present experiments, this combi-

nation of amendments could reduce the water extractable Pb to almost undetectable levels after 3 days of aging.

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