



Acid washing and stabilization of an artificial arsenic-contaminated soil

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Abstract

An acid-washing process was studied on a laboratory scale to extract the bulk of arsenic(V) from a highly contaminated Kuroboku soil (Andosol) so as to minimize the risk of arsenic to human health and the environment. The sorption and desorption behavior of arsenic in the soil suggested the possibility of arsenic leaching under acidic conditions. Artificially contaminated Kuroboku soil (2830 mg As/kg soil) was washed with different concentrations of hydrogen fluoride, phosphoric acid, sulfuric acid, hydrogen chloride, nitric acid, perchloric acid, hydrogen bromide, acetic acid, hydrogen peroxide, 3:1 hydrogen chloride–nitric acid, or 2:1 nitric acid–perchloric acid. Phosphoric acid proved to be most promising as an extractant, attaining 99.9% arsenic extraction at 9.4% acid concentration in 6 h. Sulfuric acid also attained high percentage extraction. The arsenic extraction by these acids reached equilibrium within 2 h. Elovich-type equation best described most of the kinetic data for dissolution of soil components as well as for extraction of arsenic. Dissolution of the soil components could be minimized by ceasing acid washing in 2 h. The acid-washed soil was further stabilized by the addition of lanthanum, cerium, and iron(III) salts or their oxides or hydroxides which form insoluble complex with arsenic. Both salts and oxides of lanthanum and cerium were effective in immobilizing arsenic in the soil attaining less than 0.01 mg/l As in the leaching test. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Arsenic is one of the most toxic elements. Although industrial use of arsenicals has been rapidly decreased in recent years, arsenic is even now creating human health problems in various parts of the world (Wang et al., 1997; Rahman et al., 1999; Karim, 2000). Soils have been contaminated by arsenic through human activities, such as mining (Azcue et al., 1994), smelting (Manful, 1992), agriculture (Merwin et al., 1994), accident (Sierra

et al., 2000), burning coal (Rubin, 1999), disposal of chemical warfare agents (Schneider et al., 1999), preservation of wood (Pitten et al., 1999; Wong et al., 1999; Moore et al., 2000) and illegal waste dumping.

Occasionally, arsenic-contaminated soils have been excavated and disposed of at controlled-type landfill sites as hazardous materials, which is cost prohibitive. Alternately, contaminated soils have been treated by containment (Barker et al., 1997), capping (Berger et al., 1998), soil replacement, and solidification/stabilization (Zarlinski et al., 1997). By such conventional remediation technologies, arsenic still remains in the environment. There is always a risk of leaching which can be caused by changes in the environmental conditions. One permanent solution to such soil contamination

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problems is to remove the bulk of arsenic from soils so that environmental risk can be drastically reduced. To do so, chemical extraction is the most promising method. For soils contaminated by heavy metals, chelating agents such as EDTA and DTPA have been successfully applied as extractants (Davis and Hotha, 1998; Wasay et al., 1998; Papassiopi et al., 1999). But these chelating agents are not effective in extracting arsenic which is in an anionic form, because they do not form stable chelate complex with arsenic.

Alam et al. (2001) studied extraction of arsenic from a yellow–brown forest soil using potassium phosphate as an environment-friendly extractant. Approximately 40% of arsenic was extracted by washing the soil with 0.9 M phosphate solution. Arsenic was also effectively removed from a contaminated loam soil using phosphate (Wasay et al., 2000). Legiec et al. (1997) demonstrated that 50–70% of arsenic was extracted by washing a sandy loam with sodium hydroxide solution. Percentage removal of arsenic from soil should be further increased in order to minimize both short-term and long-term risk to human health and to the environment. In the present paper, the authors attempted to increase efficiency of arsenic extraction by an acid-washing process. An artificially contaminated soil was washed with various common acids and their performance was compared. Additionally, as the post-treatment of acid-washed soil, remaining arsenic was immobilized using materials which form practically insoluble complexes with arsenic.

2. Materials and methods

2.1. Soil sample

Kuroboku soil (Andosol) was collected from horizon A of a forest land in Ibaraki, Japan. The soil was air dried and sieved through a 2 mm opening sieve. Approximately 1.5 kg of the fine fraction was shaken for three months with 3 l of 20 mM sodium arsenate solution at pH 4. Thereafter, the supernatant liquid was removed by decantation and the residual soil was washed with deionized water, which was repeated three times. At the time of decantation, some colloidal particles were lost. The soil was filtered, dried at room temperature under vacuum, and stored in an air-tight container. The arsenic content of the soil was determined by atomic absorption spectrometry (AA-6200; Shimadzu Corp., Kyoto, Japan) with a continuous hydride generator after hot digestion with $\text{HNO}_3 + \text{HClO}_4 + \text{H}_2\text{SO}_4$. The elemental composition was determined by X-ray fluorescence spectroscopy (SXF-1200, Shimadzu Corp.) using geological reference materials (Imai et al., 1996) for constructing calibration. The content of organic carbon was determined by the dry

combustion method (Nelson and Sommers, 1996) using a TOC analyzer (TOC-5000; Shimadzu Corp.) furnished with a solid sample module (SSM-5000A; Shimadzu Corp.). The particle size distribution was measured using standard sieves. The pH of the soil was measured by equilibrating it in deionized water at a soil-to-water ratio of 1:5. The cation exchange capacity (CEC) was measured with ammonium acetate solution.

2.2. Sorption and desorption of arsenic in Kuroboku soil

Twenty-five milliliters of either 0.025 or 0.25 mM arsenic(V) solution was prepared in a polycarbonate centrifuge tube. The pH was adjusted in the range 0–12 with either hydrogen chloride or sodium hydroxide solution. Approximately 0.1 g of uncontaminated Kuroboku soil was added and the suspension was shaken for 16 h at 20°C. The suspension was centrifuged at 9000 rpm for 20 min, and the supernatant was further filtered through a 0.45 μm membrane filter. The filtrate was analyzed for pH and residual arsenic concentration.

Sorption selectivity was measured by adding 1 g of uncontaminated Kuroboku soil to 25 ml of mixture containing 5 mM phosphate and 5 mM arsenate (pH 4). The suspension was shaken for 24 h at 20°C and the same procedure was followed for centrifuge, filtration, and analysis.

For desorption study, 1 g of the arsenic-contaminated soil was added to 25 ml of water (pH 0–12). The suspension was shaken for 6 h at 20°C.

2.3. Washing of arsenic-contaminated Kuroboku soil with acids

Twenty-five milliliters of hydrogen fluoride, phosphoric acid, sulfuric acid, hydrogen chloride, nitric acid, perchloric acid, hydrogen bromide, acetic acid, hydrogen peroxide, 3:1 hydrogen chloride–nitric acid, and 2:1 nitric acid–perchloric acid of different concentrations were prepared in centrifuge tubes. These acids were prepared by diluting concentrated acids. One gram of the arsenic-contaminated soil was added to each solution and the suspension was shaken for 6 h at 20°C. The suspension was centrifuged and filtered. The filtrate was analyzed for arsenic, aluminum, iron, magnesium, calcium, and silica. Aluminum, iron, magnesium, calcium, and silica were determined by inductively coupled plasma spectrometry (ICPS-7500; Shimadzu Corp.).

2.4. Kinetic study

Five-hundred milliliters of 9.4% phosphoric acid and 11% sulfuric acid were prepared in a 500 ml beaker. Twenty grams of the contaminated soil was added in

each acid solution and the suspension was stirred at 500 rpm with a magnetic stirrer at 20°C. At adequate intervals of time, ≈ 10 ml of aliquot was sampled and filtered. The filtrate was subjected to analysis for arsenic, aluminum, iron, magnesium, calcium, and silica.

2.5. Stabilization of acid-washed soil

One gram of the contaminated soil was treated with 9.4% phosphoric acid or 11% sulfuric acid for 2 h according to the above washing procedure, which was replicated nine times. The suspension was centrifuged at 9000 rpm for 30 min. To stabilize the washed soil, one milliliter of 1 N aqueous solution of lanthanum chloride, cerium(III) chloride, iron(III) chloride, or calcium chloride was added to the resultant residue and mixed well, which was duplicated. The pH was adjusted to ≈ 7 with 1 M sodium hydroxide. The suspension was shaken vigorously, allowed to stand for 24 h at 20°C, and centrifuged. The residue was then subjected to the leaching test using deionized water (Environment Agency, Japan, 1973). Instead of the above metal salts, solid particles of 0.1 g of lanthanum oxide, cerium(IV) hydroxide, iron(III) oxyhydroxide, or calcium hydroxide was examined for stabilizing acid-washed soil.

3. Results and discussion

3.1. Characterization of soil sample

Our Kuroboku soil, a typical forest soil in Japan originating from volcanic ash, was artificially contaminated with arsenic(V) ions by sorption process and used as a model-contaminated soil. The soil was weakly acidic [pH(water) 5.94] and of sandy texture (69.5% sand; 29.4% silt; 1.1% clay). The chemical composition was 43.7% SiO₂, 1.4% TiO₂, 22.0% Al₂O₃, 12.2% Fe₂O₃, 0.3% MnO, 0.9% MgO, 1.5% CaO, 0.7% Na₂O, 0.9% K₂O, 0.3% P₂O₅, 5.6% H₂O, and 8.0% organic carbon. At the end of artificial contamination of the soil with 20 mM arsenic, the residual arsenic concentration in the supernatant was only 0.002 mM, indicating that arsenic spike was almost entirely sorbed by the soil. The total arsenic content of the soil was found to be 37.8 mmol/kg, or 2830 mg/kg.

3.2. Sorption of arsenic by Kuroboku soil

For the development of an effective remediation technology, it is important to understand how Kuroboku soil retains arsenic. Fig. 1 depicts the sorption of arsenic ions on to Kuroboku soil as a function of pH at initial arsenic concentrations of 0.25 and 0.025 mM. The

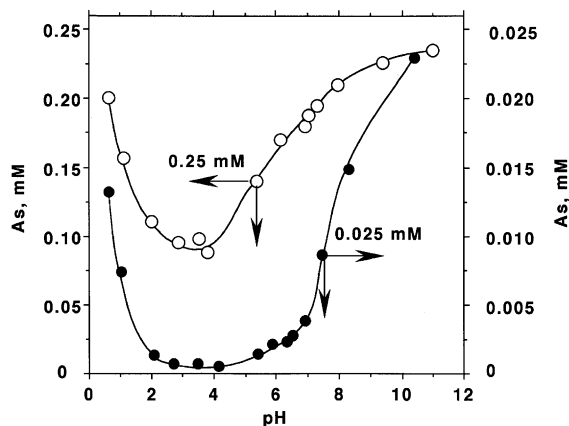


Fig. 1. Sorption of arsenic(V) ions by Kuroboku soil as a function of pH (initial arsenic concentration: 0.025 and 0.25 mM).

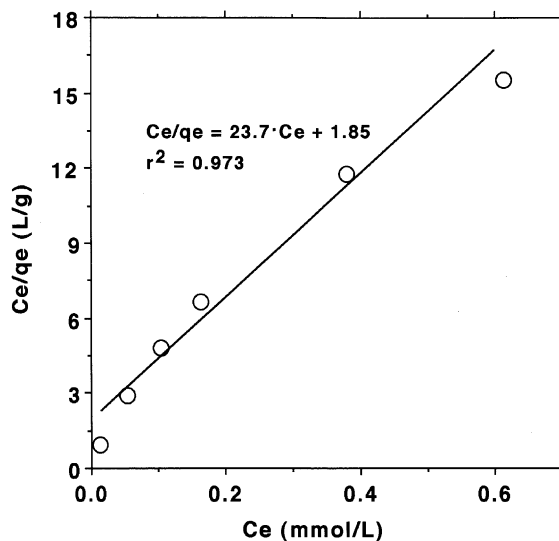


Fig. 2. Isotherm for sorption of arsenic(V) ions by Kuroboku soil (Langmuir model).

sorption of arsenic was highly pH-dependent. At an initial concentration of 0.25 mM, the lowest residual arsenic concentration was attained at around pH 3–4. At an initial concentration of 0.025 mM, the lowest arsenic concentration was attained in the wider pH range. In both cases, little arsenic was sorbed in the pH range of 10 or higher. In the pH range of 1 or lower, the arsenic sorption was also insignificant. Therefore, sorption of arsenic is favored only in the pH range 2–7. If sorption and desorption of arsenic are reversible, it is expected that arsenic sorbed in the soil can be leached out by simply controlling pH either in alkaline or acidic range.

The arsenic sorption isotherm was measured at pH 4 and the results are summarized using Langmuir

equation (Fig. 2). The maximum sorption capacity was calculated to be 3150 mg/kg, indicating that the artificially contaminated soil used was $\sim 90\%$ saturated with arsenic.

Arsenic is retained mainly by hydrous oxides of iron(III) and aluminum in the soil (Jacobs et al., 1970). Although hydrous oxides of calcium, magnesium, and manganese are also capable of retaining arsenic, their contribution is negligible because their concentration is generally much less than those of iron and aluminum. Soil organic matter plays an important role to retain heavy metals (Lee et al., 1998), but participation of soil organic matter in arsenic retention is insignificant (Weng and Liu, 1997). Silica, a major soil component, does not participate in the retention of arsenic (Wasay et al., 1996).

3.3. Desorption of arsenic from contaminated soil

The desorption behavior of arsenic from the contaminated soil was studied in the pH range 0–12 (Fig. 3). The desorption pattern was similar to that of the sorption, indicating that the sorption and the desorption were relatively reversible. In the wide pH range 2–8, arsenic was stable to leaching, only small amount of arsenic being desorbed. Despite this, the arsenic concentration in the leachate obtained in the neutral pH range was ≈ 0.4 mg/l, which exceeded the Japanese Treatment Standard (JTS) of 0.01 mg/l available leaching As (Environment Agency, Japan, 2000). Therefore, some effective remediation measures still need to be taken for arsenic-contaminated soils. By increasing pH

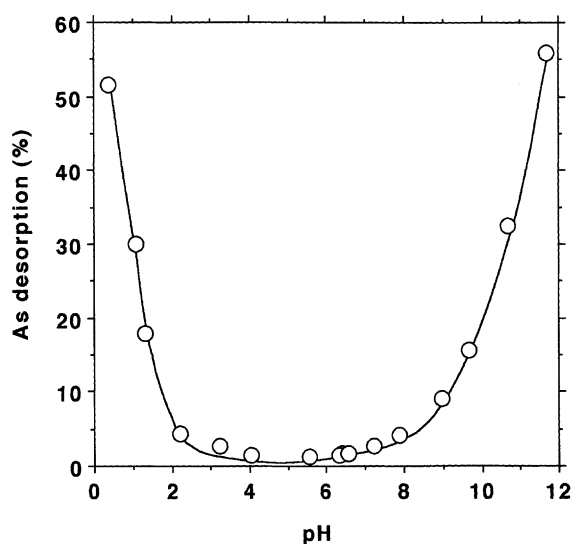


Fig. 3. Desorption of arsenic from artificially contaminated Kuroboku soil as a function of pH.

to >11 , significant amount of arsenic was extracted, 56% of arsenic being leached out at pH 11.8. Such an alkaline treatment is one of the effective remediation methods for arsenic-contaminated soils (Legiec et al., 1997). On the other hand, arsenic desorption was appreciable also in the pH range of <1 , suggesting acid treatment as a possible remediation method.

3.4. Acid washing of arsenic-contaminated Kuroboku soil

Percentages of arsenic extraction are plotted against acid concentrations in Fig. 4. The concentrations of the mixed acids are expressed in the sum of the respective acid concentrations. There was a marked difference in the extraction efficiencies among the acids. One of the effects of acids on a soil is to dissolve metallic components of the soil, such as hydrous oxides of iron(III) and aluminum, which are capable of sorbing arsenic. Arsenic sorbed by these soil components can also be concomitantly solubilized by acid washing. When compared with the acid dissociation constants, strong acids did not always attain high percentages of arsenic extraction. For instance, perchloric acid is the strongest acid in terms of the acid dissociation constant, its arsenic extraction was only less than 50%. On the other hand, mild acids such as phosphoric acid and hydrogen fluoride attained much higher arsenic extraction. Therefore, specific chemical action other than that as acid is involved in the arsenic extraction. The highest percentage arsenic extraction attained by each acid decreased in the order: hydrogen fluoride \approx phosphoric acid \approx hydrogen chloride \approx hydrogen bromide \approx sulfuric acid \approx 3:1 hydrogen chlo-

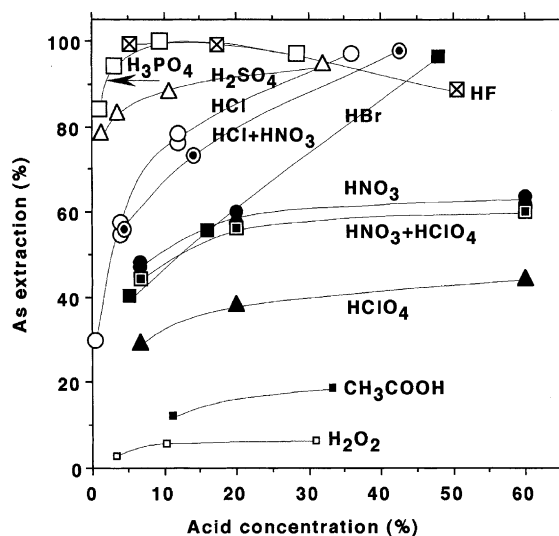


Fig. 4. Extraction of arsenic from artificially contaminated Kuroboku soil by various common acids as a function of acid concentration.

ride–nitric acid > nitrid acid \cong 2:1 nitric acid–perchloric acid > perchloric acid > acetic acid > hydrogen peroxide.

Hydrogen fluoride was highly effective in extracting arsenic in the wide acid concentration range. But fluorine is one of the toxic elements and designated as a ground water contaminant to be regulated. In addition, it was found that the soil was severely damaged by hydrogen fluoride, silica and aluminum components being dissolved almost entirely. The other two hydrogen halogenides, i.e., hydrogen chloride and hydrogen bromide, were effective only at their highest concentrations, which is disadvantageous for economy and safety. Arsenic extraction by these two acids decreased significantly by decreasing their concentrations. Therefore, hydrogen halogenides are not suitable for field remediation of contaminated soils.

Sulfuric acid extracted more than 80% of arsenic at acid concentrations lower than \approx 10%. Mixtures of different acids are commonly used to facilitate the function of acids to solubilize analytes in environmental samples. But there were no significant advantages in using mixed acids. The 3:1 hydrogen chloride–nitric acid and 2:1 nitric acid–perchloric acid exhibited almost the same percentage extraction as those of the single acids, i.e., hydrogen chloride and nitric acid, respectively. The oxidizing acids such as nitric acid, perchloric acid, and hydrogen peroxide exhibited lower arsenic extraction than hydrogen halogenides. These results, in part, support the fact that arsenic is not retained by the organic materials in soil which is decomposed by these oxidizing acids.

Among the acids studied, phosphoric acid is the most promising extractant. Phosphoric acid was effective in the wide acid concentration range, and as high as 99.9% extraction was attained in 6 h at 9.4% (\cong 1.6 M) concentration, which was higher than the efficiency of neutral phosphate solution. Alam et al. (2001) showed that 1.5 M potassium phosphate solution extracted 53% of arsenic in the pH range 6–8, while other potassium salts of chloride, nitrate, perchlorate, and sulfate were ineffective in arsenic extraction. They proposed a mechanism that sorbed arsenic is displaced by phosphate ions through ligand exchange. In the present study, the sorption selectivity of Kuroboku soil was measured using a mixture containing both phosphate and arsenate. The sorption selectivity coefficient of Kuroboku soil for phosphate against arsenate

$$K_{P/As} = \frac{[P \text{ in soil}][As \text{ in solution}]/[P \text{ in solution}]}{\times [As \text{ in soil}]} \quad (1)$$

was calculated to be \approx 5, indicating higher selectivity of the soil for phosphate than for arsenate. Thus, the effectiveness of phosphoric acid can be attributed to the

synergetic function as a donor of phosphate ions which displace arsenic through ligand exchange mechanism and to the function as an acid to dissolve metallic components of the soil with which arsenic is associated.

3.5. Kinetic study

To better understand the acid-washing process, a kinetic study was conducted on the washing of the contaminated soil with 9.4% phosphoric acid and 11% sulfuric acid (Figs. 5 and 6, respectively). The acid concentrations are equal to one ninth those of the concentrated acid. The rates of dissolution were measured on the soil components such as aluminum, iron, magnesium, calcium, and silica as well as those of arsenic

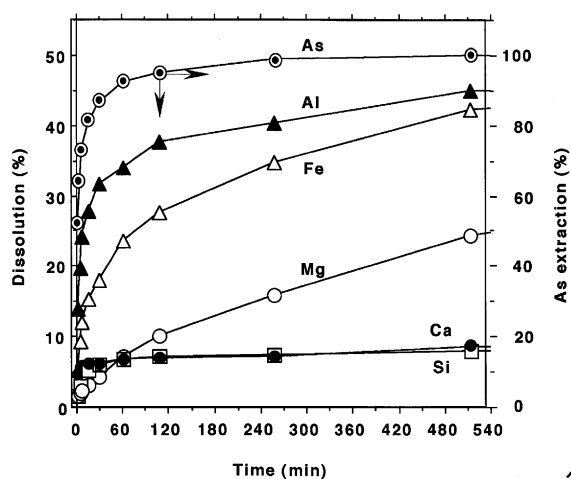


Fig. 5. Kinetics of arsenic extraction and dissolution of soil components for washing with 9.4% phosphoric acid.

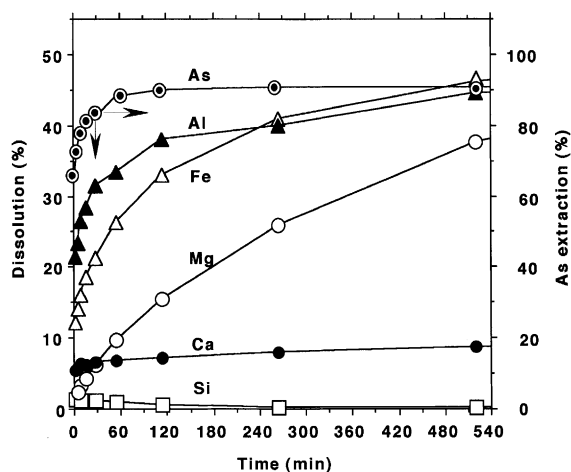


Fig. 6. Kinetics of arsenic extraction and dissolution of soil components for washing with 11% sulfuric acid.

extraction. In every case, arsenic extraction reached a maximum within 2 h, indicating that arsenic sorbed in the soil can be rapidly extracted.

Excessive dissolution of soil components concomitant with arsenic extraction results in difficulty of reuse and post-treatment of spent acid. Among soil components, silica and calcium dissolved only at the initial stage of washing, reaching equilibrium almost instantly. The amount of silica and calcium dissolved in 6 h was less than 8%, indicating that they were stable to acid washing. Particularly in sulfuric acid, dissolution of silica was inappreciable. On the other hand, dissolution of aluminum, iron, and magnesium was significant, but slower than the extraction of arsenic. Thus, the dissolution of soil components can be minimized by ceasing acid washing after 2 h when arsenic extraction reaches maximum. By washing with phosphoric acid, 38%, 28%, and 10% of aluminum, iron, and magnesium, respectively, dissolved in 2 h. By washing with sulfuric acid, 37%, 33%, and 15% of aluminum, iron, and magnesium, respectively, dissolved in 2 h.

The kinetic data were analyzed using eight different models, namely, zero-order, first-order, second-order, third-order, parabolic diffusion, two-constants rate, Elovich-type, and differential rate models (Onken and Matheson, 1982), which were evaluated by least-

squares regression. Among these models, Elovich-type model proved to best describe the kinetic data, in terms of coefficient of correlation, for the extraction of arsenic and dissolution of aluminum, iron, and calcium. Dissolution of magnesium was exceptional, which followed the first-order rate equation with correlation coefficient of 0.999. The Elovich equation can be written

$$C_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t, \quad (2)$$

where C_t (mg/l) is the concentration of an element in extract at any time t , t (min) is the reaction time, and α (mg/l/min), β (l/mg) are the constants. Elovich-type equation was successfully applied to describe sorption and desorption of phosphate in soils (Chien and Clayton, 1980). The advantages of phosphoric acid are high efficiency of arsenic extraction at low acid concentration, rapid extraction, low material cost, and environmental safety.

3.6. Stabilization of acid-washed soil

Post-treatment of acid-washed soils treated with 9.4% phosphoric acid or 11% sulfuric acid for 2 h was studied in accordance with the JTS as the criteria that arsenic concentration in the leachate be <0.01 mg/l after the leaching test (Environment Agency, Japan, 1973). The acid washing of the arsenic-contaminated soil was replicated nine times for each acid (Table 1). The average arsenic extraction was $97.9 \pm 3.1\%$ and $87.7 \pm 2.6\%$ for phosphoric and sulfuric acids, respectively. The residual arsenic content in the soil could not be reduced to 0 even by prolonging washing, indicating that environmental risk still remained. The acid-washed soils showed strong acidity due to residual acid adhering to the soil surface. By rinsing these soils with water three times, the

Table 1
Acid washing of contaminated Kuroboku soil ($n = 9$)

	As extraction (%)	Leachate ^a	
		pH	As ($\mu\text{g/l}$)
9.4% Phosphoric acid	97.9 ± 3.1	2.91 ± 0.2	177 ± 6
11% Sulfuric acid	87.7 ± 2.6	2.44 ± 0.1	375 ± 10

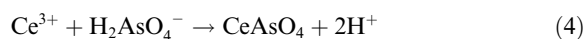
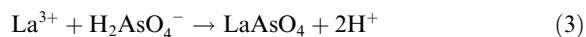
^a Obtained from the leaching test.

Table 2
Stabilization of acid-washed soils: results of leaching test (mean of duplicate)

Reagent	9.4% Phosphoric acid			11% Sulfuric acid		
	pH	As ($\mu\text{g/l}$)	Metal (mg/l)	pH	As ($\mu\text{g/l}$)	Metal (mg/l)
Neutralization	4.29	83	–	3.77	17	–
Salt						
LaCl ₃	7.12	0	2.4	6.35	0	5.7
CeCl ₃	7.70	5	5.2	5.45	7	6.3
FeCl ₃	5.30	4	0.1	8.01	7	0.0
CaCl ₂	7.17	201	11.3	7.05	35	65.4
Oxide and hydroxide						
La ₂ O ₃	6.33	0	3.6	6.25	0	4.5
Ce(OH) ₄	6.60	3	0.2	6.82	3	3.6
FeO(OH)	7.18	54	3.9	8.55	37	12.7
Ca(OH) ₂	9.75	71	82.7	9.49	72	95.0

pH increased to 2.4–2.9, but the leachate arsenic concentrations were much higher than the JTS.

Chemical stabilization of the soil was examined by simple neutralization with sodium hydroxide or by the addition of salt, hydroxide, or oxide of lanthanum, cerium, iron(III), or calcium (Table 2). These latter are effective in removing arsenic from water through precipitation and/or sorption processes. Although simple neutralization of the acid-washed soil decreased leachate arsenic concentration, the JTS was not satisfied. Among the salts examined, lanthanum, cerium(III), and iron(III) chlorides successfully immobilized arsenic in the soil. Calcium salt has been widely used as coagulant for arsenic removal from wastewater (Sorg, 1993), but it was ineffective in meeting the JTS, with high calcium concentrations in the leachate as well as arsenic concentration. Utilization of iron has been practiced for immobilization of arsenic and heavy metals (Boisson et al., 1999; Moore et al., 2000). Lanthanum and cerium are among the more abundant rare earth elements and effective in removing arsenic(V) by precipitation from aqueous solution in the wider pH range and to lower arsenic concentration than iron(III) (Tokunaga et al., 1999). Thus, trace arsenic dissolving from acid-washed soils can be immobilized by the following complex formation reactions:



To ensure the stabilization, the amount of rare earth added should exceed that of remaining arsenic in the soil.

As an alternative to applying aqueous solutions of salts of lanthanum, cerium, iron(III), and calcium, the suspensions of the oxides or hydroxides of these metals were added to the acid-washed soils. Treatment with hydroxides of iron(III) and calcium did not meet the JTS, giving higher arsenic leachate concentrations. On the other hand, lanthanum oxide and cerium hydroxide were effective in immobilizing arsenic in the soil, attaining lower leachate arsenic concentration than their salts. The mechanism of the immobilization by these rare earth oxide or hydroxide is sorption of arsenic ions on their surface (Tokunaga et al., 1997).

4. Conclusions

Acid-washing and stabilization processes have been developed for the remediation of arsenic(V)-contaminated soil. Kuroboku soil, a model soil, sorbed arsenic ions in the pH range 2–7 with the maximum sorption capacity of 3150 mg/kg. The arsenic desorption from the

model-contaminated soil (2830 mg As/kg soil) became appreciable in the pH range of <1.

Phosphoric acid is the most promising extractant, and its effectiveness can be attributed to the synergetic function as a donor of phosphate ions which displace arsenic through ligand exchange mechanism as well as its function as an acid dissolving metallic components of the soil. Arsenic extraction with phosphoric acid reached a maximum within 2 h, indicating that arsenic sorbed in the soil can be rapidly extracted. Acid-washed soil can be further stabilized by the addition of lanthanum, cerium, and iron(III) salts or their oxides or hydroxides. Both salts and oxides of lanthanum and cerium were effective in immobilizing arsenic in the soil attaining less than 0.01 mg/l As in the leaching test.

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