


## Article

# Effects of Soils on Environmental Stability of Spent Mg-Based and Ca-Based Adsorbents Containing Arsenite

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**Abstract:** Spent adsorbents used in As removal treatment may re-leach As. In this study, the effects of soil on spent Mg-based and Ca-based adsorbents were investigated. The spent adsorbents containing arsenite (As(III)) were prepared by adsorbing As(III) on MgO, Mg(OH)<sub>2</sub>, CaO, and Ca(OH)<sub>2</sub> powder reagents. Kuroboku soil (Ku), yellow-brown forest soil (YF), Kanuma soil (Ka), river sand (RS), and mountain sand (MS) were used as soil samples. The As leaching ratio was examined in coexistence with soil via shaking tests, and the results were compared with those of a previous study on adsorbents containing arsenate (As(V)). The environmental stability of the spent adsorbents was found to vary greatly depending on the combination of the As valence, adsorbent type, and soil type. However, regardless of the adsorbent or soil type, the spent adsorbents containing As(III) were more likely to leach As than those containing As(V). Additionally, the As leaching ratio was generally lower in Ku and YF and higher in Ka, RS, and MS. For environmentally friendly and sustainable As removal treatment, disposal, and management, the selection of MgO as the adsorbent and treatment involving the oxidation treatment of As(III) to As(V) before adsorbing As onto adsorbents are recommended.

**Keywords:** arsenic pollution; leaching ratio; adsorbent; disposal; environmental stability; environmentally sustainable treatment; magnesium oxide; magnesium hydroxide; calcium oxide; calcium hydroxide



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## 1. Introduction

Arsenic (As) is generally widely known as an element with extremely high toxicity to the human body. The World Health Organization (WHO) has set a provisional value for As at 0.01 mg/L in its guidelines for drinking water quality [1]. The As contamination of groundwater occurs in many parts of the world, mainly in Asia [2–19], Latin America [20–24], and Africa [25,26]. In some areas of these developing areas, many people directly use As-contaminated groundwater (well water) for drinking, resulting in significant health damage. Therefore, the purification of As-contaminated water is essential.

Typical purification methods for As-contaminated water have been introduced by Jadhav et al. [27], Sarkar and Paul [28], Ghosh et al. [29], and Kumar et al. [30], including co-precipitation methods, ion-exchange methods, adsorption methods, microfiltration methods, oxidation methods, and electrocoagulation methods. In developing countries, As treatment methods using inexpensive adsorbents may be recommended owing to economic and operational conditions. Among the adsorbents, Mg-based and Ca-based adsorbents are particularly suitable for arsenic removal [31–38]. Mg and Ca are unlikely to have any negative effects on the human body or the ecosystem. Therefore, both Mg-based and Ca-based adsorbents can be recommended as environmentally friendly and sustainable adsorbents.

However, the spent adsorbents recovered after being used in As-purification processes end up as As-rich waste. Therefore, the spent adsorbents need to be recovered, treated, and

managed appropriately. If the spent adsorbents are not appropriately treated or dumped untreated, they could re-leach As, causing secondary environmental contamination. Sugita et al. [39] examined the environmental stability of spent Mg-based and Ca-based adsorbents in coexistence with soil; the spent adsorbents were prepared by adsorbing arsenate, As(V); the effects of soil on As leaching from the spent adsorbents were evaluated via leaching tests. They found that the spent adsorbents based on MgO and Mg(OH)<sub>2</sub> exhibited high environmental stability because the As leaching ratios for all soil samples were low. Furthermore, a high risk of secondary environmental pollution was suggested owing to As re-leaching under sandy soil conditions. The aforementioned study focused only on As(V), and no similar study on arsenite, As(III), has been conducted thus far. As(III) is known to be more toxic than As(V); therefore, the leaching of As(III) from the spent adsorbents containing As(III) would cause serious environmental issues.

To bridge this knowledge gap, in this study, spent Mg- and Ca-based adsorbents containing As(III) were studied, and leaching tests with soils were performed. In these tests, the leaching behaviors of As, Mg, and Ca from the spent adsorbents was investigated. Subsequently, the effects of soil on the environmental stability of spent Mg-based and Ca-based adsorbents with As(III) were evaluated. Additionally, by comparing the data for the As(III) obtained in this study and for As(V) presented in a previous study [39], more environmentally friendly adsorbent selection and sustainable processing methods were suggested.

## 2. Materials and Methods

The reagents used in this study were purchased from FUJIFILM Wako Pure Chemical Corporation (formerly Wako Pure Chemical Industries, Ltd., 3-1-2 Doshomachi, Chuo-ku, Osaka, Japan), unless specified otherwise.

### 2.1. Adsorbents

In this study, two types of commercially available Mg reagents, MgO and Mg(OH)<sub>2</sub>, and Ca reagents, CaO and Ca(OH)<sub>2</sub>, were used as Mg- and Ca-based adsorbents, respectively. The purity (nominal)  $P$  (%), median particle size  $D_{p50}$  ( $\mu\text{m}$ ), Brunauer–Emmett–Teller (BET) surface area  $S_{\text{BET}}$  ( $\text{m}^2/\text{g}$ ), and Mg content  $\alpha_{\text{Mg}}$  (%) or Ca content  $\alpha_{\text{Ca}}$  (%) of these adsorbents are shown in Table 1. The data in Table 1 were taken from Sugita et al. [39].

**Table 1.** Purity (nominal), median particle size, BET surface area, and Mg and Ca contents of the four adsorbents used in this study.

Adsorbent	$P$ (%)	$D_{p50}$ ( $\mu\text{m}$ )	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$\alpha_{\text{Mg}}$ (%)	$\alpha_{\text{Ca}}$ (%)
MgO	98.0	1.54	4.3	59.1	-
Mg(OH) <sub>2</sub>	99.9	4.13	22.0	40.6	-
CaO	99.6	19.6	2.7	-	71.2
Ca(OH) <sub>2</sub>	98.9	41.7	14.3	-	53.5

$P$ : nominal purity,  $D_{p50}$ : median particle diameter,  $S_{\text{BET}}$ : BET surface area,  $\alpha_{\text{Mg}}$ : Mg content, and  $\alpha_{\text{Ca}}$ : Ca content; data were taken from Sugita et al. (2016) [39].

### 2.2. Synthetic As-Contaminated Water

A powdered reagent of sodium arsenite (NaAsO<sub>2</sub>, 90%) was dissolved in ion-exchange water, and a stock solution of As(III) (2000 mg-As/L) was prepared. A portion of each stock solution was diluted with ion-exchange water to prepare a 20 mg As/L solution. These solutions used synthetic As-contaminated water whose pH had been adjusted to near neutral by adding hydrochloric acid (HCl).

### 2.3. Preparation of Spent Adsorbents

Each unspent adsorbent (1 g) was weighed into a TPX beaker, and synthetic As-contaminated water (0.2 L) was added to the beaker and stirred with a magnetic stirrer at

approximately 500 rpm for approximately 24 h. Then, suction filtration was performed using a Teflon filter (pore size of 0.45  $\mu\text{m}$ ). The concentrations of As, Mg, and Ca in each filtrate were measured using inductively coupled plasma–mass spectrometry (ICP–MS) (7700X, Agilent Technologies, Inc., Santa Clara, CA, USA, or ICPM-8500, Shimadzu Co., Kyoto, Japan) and ICP–atomic emission spectrometry (ICP–AES) (SII SPS3500DD, Seiko Instruments Inc., Chiba, Japan). The calculation methods applied to determine data pertaining to each filtrate were similar to those employed in previous studies [39–41].

Table 2 lists the data in relation to the production of four types of spent adsorbents containing As(III);  $W_{\text{AD}}$  (g) is the amount of unspent adsorbent added to the synthetic As-contaminated water.  $V$  is the liquid volume (L) of the synthetic As-contaminated water.  $W_{\text{AD}}/V$  is the amount of the unspent adsorbent added per unit volume of As-contaminated water (g/L).  $pH_0$  is the pH of the solution immediately before adding the adsorbent, which is referred to as the initial pH.  $C_{\text{AS}0}$  is the initial As concentration (mg/L) of the As-contaminated water,  $C_{\text{AS}}$  is the As concentration of the filtrate, and  $R_{\text{AS}}$  is the As removal ratio, which was calculated as follows:

$$R_{\text{AS}} = (C_{\text{AS}0} - C_{\text{AS}})/C_{\text{AS}0} \times 100. \quad (1)$$

$C_{\text{Mg}}$  and  $C_{\text{Ca}}$  in Table 2 refer to the Mg and Ca concentrations in the filtrate (mg/L), respectively, and  $\beta_{\text{Mg}}$  and  $\beta_{\text{Ca}}$  are the Mg and Ca leaching ratios (%), respectively, which are defined by the following equation:

$$\beta_X = C_X / ((W_{\text{AD}}/V) \times 1000 \times \alpha_X / 100) \times 100 \quad (2)$$

where  $C_X$  is  $C_{\text{Mg}}$  or  $C_{\text{Ca}}$ ,  $\alpha_X$  is  $\alpha_{\text{Mg}}$  or  $\alpha_{\text{Ca}}$ , and  $\beta_X$  is  $\beta_{\text{Mg}}$  or  $\beta_{\text{Ca}}$ . Note that in Equation (2),  $W_{\text{AD}}/V$  is multiplied times 1000 to make the units match.

The adsorbents containing As collected by the solid–liquid separation operation were dried at  $\sim 40^\circ\text{C}$  for approximately half a day in a constant-temperature dryer and then stored in a closed polypropylene bottle. The adsorbents containing As were used as “spent adsorbents” in the leaching tests, as described later. The calculation method of the As content of the spent adsorbents is outlined below.

The residual ratio of adsorbent  $\gamma$  (%) is defined by the following equation:

$$\gamma = 100 - \beta_X. \quad (3)$$

The amount of As adsorbed per unit mass of the adsorbent remaining as solid  $\delta_{\text{AS}}$  (mg As/g) was calculated using the following equation:

$$\delta_{\text{AS}} = (C_{\text{AS}0} - C_{\text{AS}}) / (W_{\text{AD}}/V \times \gamma / 100). \quad (4)$$

The weighed value of a spent adsorbent was taken as the total value of the adsorbent and As adsorbed onto its surface. Then, the As content was determined per unit mass of the recovered spent adsorbent  $Q_{\text{AS}}$  (mg As/g) was determined using the following equation:

$$Q_{\text{AS}} = \delta_{\text{AS}} / (1 + \delta_{\text{AS}} / 1000). \quad (5)$$

In this study,  $\delta_{\text{AS}} \approx Q_{\text{AS}}$  was assumed, because  $\delta_{\text{AS}} \ll 1000$ . The main reason that the  $Q_{\text{AS}}$  values of the spent Ca-based adsorbents were higher than those of the spent Mg-based adsorbents is the difference in  $\beta_X$ . The values of  $Q_{\text{AS}}$  in Table 2 were used to calculate the leaching ratio of As from each spent adsorbent, as described later.

**Table 2.** Data relating to the production of spent Mg-based and Ca-based adsorbents.

No.	As(Valence)	Adsorbent	$W_{AD}/V$ (g/L)	$pH_0$	$C_{AS0}$ (mg/L)	$C_{AS}$ (mg/L)	$C_{Mg}$ (mg/L)	$C_{Ca}$ (mg/L)	$R_{AS}$ (%)	$\beta_{Mg}$ (%)	$\beta_{Ca}$ (%)	$Q_{AS}$ (mg/g)
(1) <sup>1</sup>	As(III)	MgO	5.004	6.99	21.79	0.149	6.23	-	99.3	0.21	-	4.32
(2) <sup>1</sup>	As(III)	Mg(OH) <sub>2</sub>	5.007	7.10	21.85	1.013	7.80	-	95.4	0.38	-	4.16
(3) <sup>2</sup>	As(III)	CaO	5.009	7.09	22.35	1.437	-	837	93.6	-	23.5	5.42
(4) <sup>2</sup>	As(III)	Ca(OH) <sub>2</sub>	5.009	7.09	22.73	1.378	-	858	93.9	-	32.0	6.23

<sup>1</sup> The data for Nos. (1) and (2) were taken from Sugita et al. [41]. <sup>2</sup> The data for Nos. (3) and (4) were taken from Sugita et al. [40].

#### 2.4. Soils

The following soils were selected for the leaching tests as representative of the soil characteristics of main Japanese soil types.

1. Kuroboku soil (Ku) is Andosols-type distinguished by the chemical properties of aluminum such as aluminum–humus complexes; volcanic ash soils rich in organic components and particularly common in Japan.
2. Yellow-brown forest soil (YF) is a slightly acidic and inorganic volcanic ash soil.
3. Kanuma soil (Ka) is an acidic soil formed from weathered pumice. It is high in allophane, which is a type of clay mineral made of hydrated aluminosilicate.
4. River sand (RS) is a sandy soil with a high silica content and an alkaline pH.
5. Mountain sand (MS) is a sandy soil with a high iron content and an alkaline pH.

The chemical compositions of the soils and water content (adsorbed and structured waters) were described in Sugita et al. [39]. Additionally, the experimental condition with no soil is denoted as NS.

The soil samples were sieved to a particle size of 0.5–2 mm for the leaching tests.

#### 2.5. Leaching Tests (Shaking Tests)

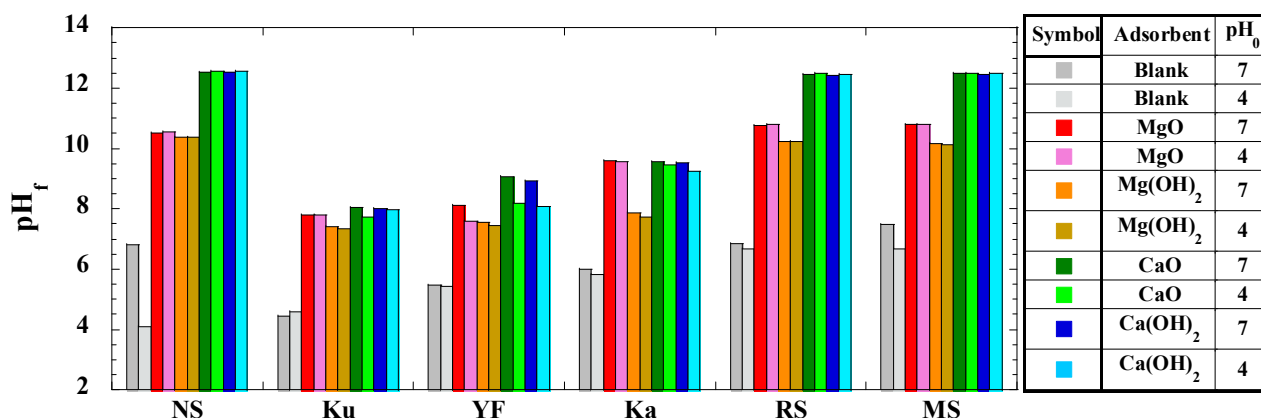
Two types of water solvents were prepared with hydrochloric acid to simulate acid rain: ion-exchange water adjusted to approximately pH 7 and pH 4. Next, 0.08 g of spent adsorbent and 4 g of soil were weighed into a 50 mL centrifuge tube, 40 mL of the abovementioned water solvent was added, and the tube was sealed. The tube was shaken in a thermostatic shaker for 24 h (approximately 150–180 rpm, room temperature), followed by centrifugation for solid–liquid separation (4500 rpm, 20 min). The supernatant was filtered using a syringe filter (0.45 µm), and the filtrate (leachate) was collected in a polypropylene bottle. The As, Mg, and Ca concentrations in the leachate were determined using ICP–MS and ICP–AES. Si and Fe were also measured in most of the leachates. Additionally, shaking tests with only-water solvent (without the spent adsorbent and soil) were conducted to check the change in solvent pH due to shaking. Leaching tests with only water solvent and soil (without the spent adsorbent) were also performed to check the pH of the leachate in the presence of only soil.

### 3. Results

#### 3.1. pH of Leachate

The pH values of the leachate ( $pH_f$ ) obtained from the leaching tests in this study are shown in Figure 1, where “Blank” refers to the leaching tests (or the shaking tests) without the spent adsorbent. As shown in Figure 1, almost no difference in  $pH_f$  was observed with variation in  $pH_0$ , except for the Blank in the NS case (the shaking test with only water as a solvent). Therefore, under these test conditions,  $pH_f$  was influenced by the type of soil and adsorbent more than by  $pH_0$ . In the leaching tests with only spent adsorbent without soil (NS), the  $pH_f$  values for the Ca-based adsorbents were higher than those for the Mg-based adsorbents, with  $pH_f$  following the order of  $Mg(OH)_2 \leq MgO < CaO \approx Ca(OH)_2$ . In the leaching tests with only soil without spent adsorbent (Blank), the magnitude order of  $pH_f$  was  $Ku < YF < Ka < RS < MS$ . Moreover, in the leaching tests with both spent adsorbent

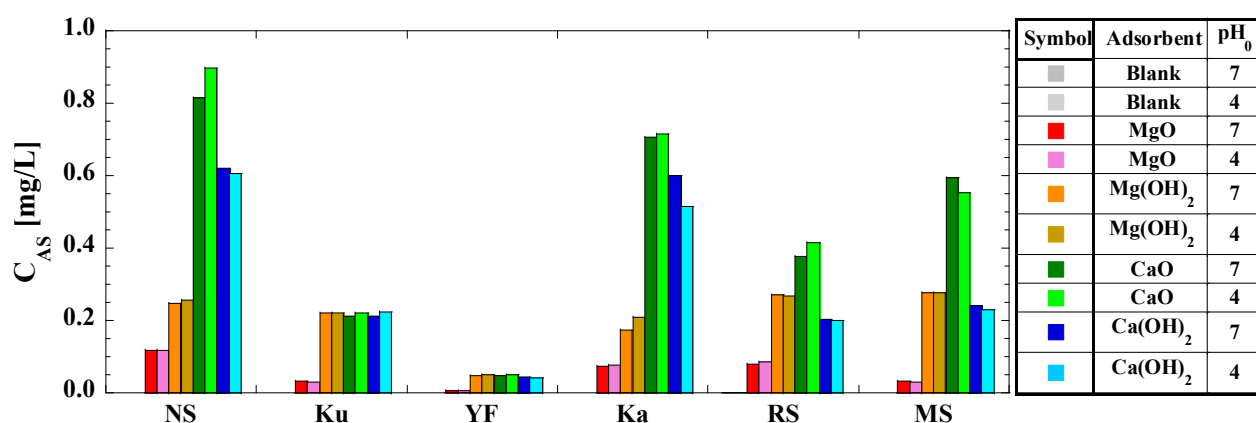
and soil,  $pH_f$  followed the order of Ku, YF, Ka < RS, MS, regardless of the type of the spent adsorbent.



**Figure 1.** pH values of leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

### 3.2. As Concentration in Leachate

The As concentrations in the leachate,  $C_{AS}$  (mg/L), obtained from the leaching tests in this study are shown in Figure 2.

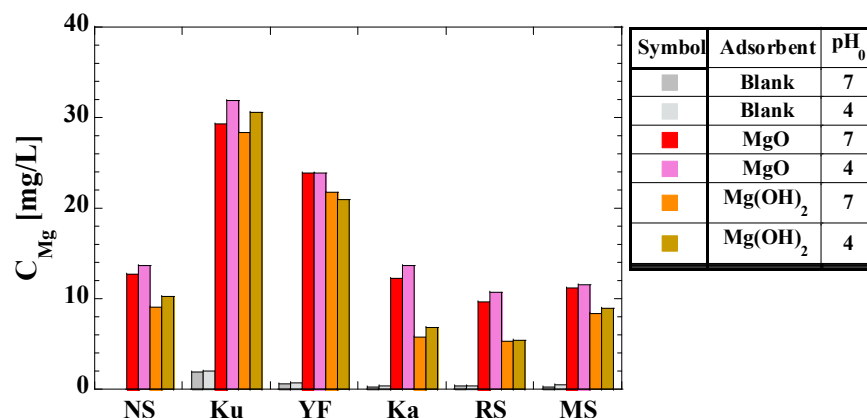


**Figure 2.** As concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In the leachate from only soil without the spent adsorbent, a small amount of As was evident only in the leachate in RS (approximately 0.001 mg/L); no As was detected in the leachates of the other soils. For the spent adsorbents containing As(III), no significant difference in  $C_{AS}$  due to  $pH_0$  was observed (Figure 2). Focusing on each soil in Figure 2,  $C_{AS}$  follows the order  $MgO \ll Mg(OH)_2 \approx Ca(OH)_2 \approx CaO$  in Ku;  $MgO < Ca(OH)_2 \leq Mg(OH)_2$ ,  $CaO$  in YF;  $MgO < Mg(OH)_2 \ll Ca(OH)_2 < CaO$  in NS and Ka; and  $MgO \ll Ca(OH)_2 < Mg(OH)_2 < CaO$  in RS and MS. Focusing on each spent adsorbent in Figure 2,  $C_{AS}$  follows the order  $YF < Ku \leq MS < Ka < RS < NS$  for  $MgO$ ;  $YF < Ka < Ku \leq NS \leq RS \leq MS$  for  $Mg(OH)_2$ ;  $YF < Ku < RS < MS < Ka < NS$  for  $CaO$ ; and  $YF < RS \leq Ku \leq MS < Ka < NS$  for  $Ca(OH)_2$ .

### 3.3. Mg Concentration in Leachate

The Mg concentrations in the leachate,  $C_{Mg}$  (mg/L), obtained from the leaching tests in this study are shown in Figure 3. The  $C_{Mg}$  values for the spent Ca-based adsorbents are not included in this figure because they were not measured.

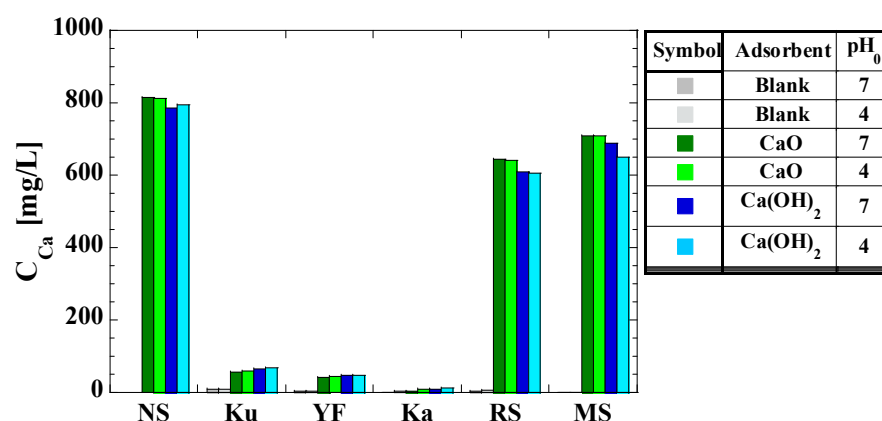


**Figure 3.** Mg concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In the leaching tests without spent adsorbent (Blank), the  $C_{Mg}$  values were approximately 2 mg/L in Ku and less than 1 mg/L in the other soils. These values were significantly lower than those observed for the spent Mg-based adsorbents. Therefore, it could be concluded that most of the Mg ions detected in the leachate were derived from the Mg-based adsorbents. In Figure 3, some differences exist in  $C_{Mg}$  between  $pH_0 = 4$  and 7 in some cases, but no significant difference is apparent for most cases. Therefore, the effects of  $pH_0$  on  $C_{Mg}$  seem to be relatively weak, similar to those of  $pH_f$ . Furthermore, in Figure 3, comparing the  $C_{Mg}$  values among the NS cases,  $Mg(OH)_2 < MgO$ , and this tendency is different from the abovementioned tendency of  $C_{AS}$ . Additionally, the  $C_{Mg}$  values obtained from testing the different soil types follow the order  $Ka, RS, MS \leq NS \ll YF < Ku$ .

### 3.4. Ca Concentration in Leachate

The Ca concentrations in the leachate,  $C_{Ca}$  (mg/L), obtained from the leaching tests in this study are shown in Figure 4. The  $C_{Ca}$  values for the spent Mg-based adsorbents are not included in this figure because they were not measured.



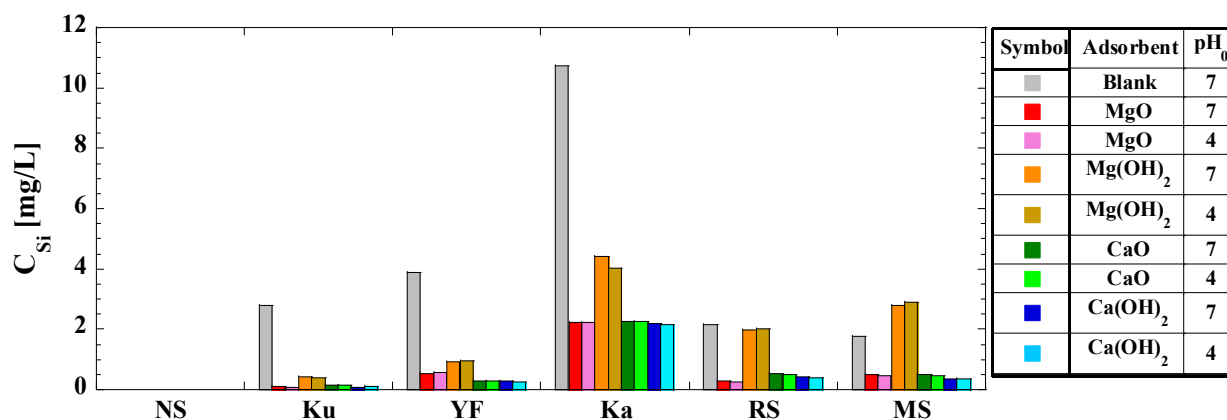
**Figure 4.** Ca concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In the leaching tests without the spent adsorbent (Blank), the  $C_{Ca}$  values were approximately 9 mg/L in Ku and less than 3 mg/L in the other soils. These values were much lower than those in the leaching tests with the spent Ca-based adsorbents. Therefore, it could be concluded that most of the Ca ions detected in the leachate derived from the Ca-based adsorbents. For the spent adsorbents containing As(III), as shown in Figure 4, a slight difference existed in  $C_{Ca}$  between  $pH_0 = 7$  and 4.



### 3.5. Si Concentration in Leachate

The Si concentrations in the leachate,  $C_{Si}$  (mg/L), obtained from the leaching tests in this study are shown in Figure 5.



**Figure 5.** Si concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

No difference in  $C_{Si}$  was observed depending on  $pH_0$ , similar to  $C_{AS}$ ,  $C_{Mg}$ , and  $C_{Ca}$ . Comparing the data in the leaching tests with only soil without the spent adsorbent,  $C_{Si}$  followed the order  $MS < RS < Ku < YF < Ka$ . In the leaching tests with both spent Mg-based adsorbent and soil,  $C_{Si}$  followed the order  $MgO < Mg(OH)_2$  among the Mg-based adsorbents and  $Ku < YF < MS \leq RS < Ka$  among the soils. Additionally, in RS and MS, the  $C_{Si}$  values were higher when the spent  $Mg(OH)_2$  adsorbent and soil coexisted than in the only-soil case. However, the  $C_{Si}$  values in all the soils were lower when the Ca-based adsorbent and soil coexisted than in the only-soil case, and  $C_{Si}$  followed the order  $Ku < YF < RS \approx MS < Ka$ . Additionally, a slight difference in  $C_{Si}$  existed between CaO and  $Ca(OH)_2$ . Furthermore, comparisons between the different spent adsorbents revealed that  $C_{Si}$  followed the order  $MgO < CaO \approx Ca(OH)_2 < Mg(OH)_2$ .

### 3.6. Fe Concentration in Leachate

The Fe concentration in the leachate,  $C_{Fe}$  (mg/L), was measured in all tests. In the leaching tests with only soil without the spent adsorbent, Fe was detected only in RS and MS (0.10–0.24 mg/L). In the leaching tests with both spent adsorbent and soil, most of the  $C_{Fe}$  values for Ka were slightly over 0.01 mg/L, whereas those for the other soils were significantly below 0.01 mg/L.

## 4. Discussion

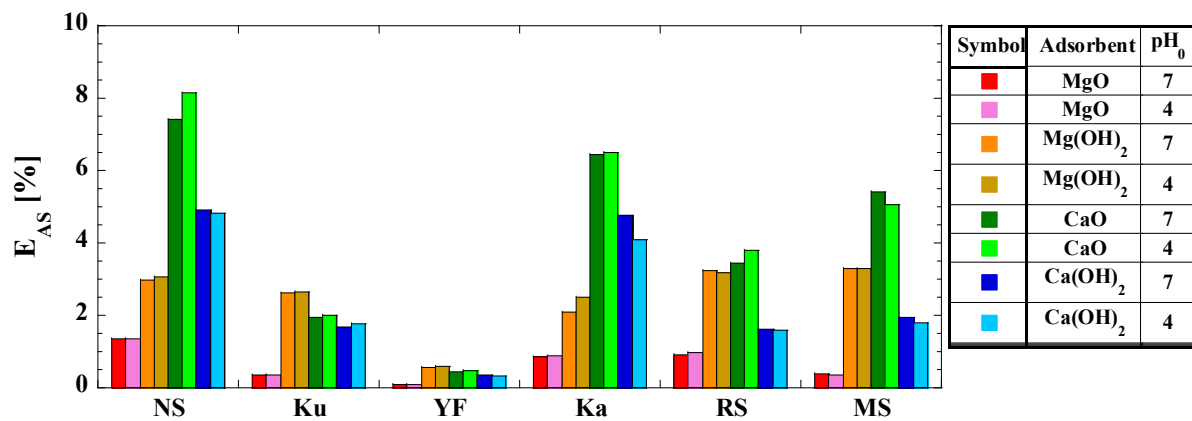
### 4.1. As Leaching Ratio

In this study, the As leaching ratio,  $E_{AS}$  (%), was calculated as follows:

$$E_{AS} = C_{AS} / (Q_{AS} \times W_{SP} / V) \times 100 \quad (6)$$

where the additional concentration of the spent adsorbent in the leaching tests was  $W_{SP} / V$  (g/L).

The  $E_{AS}$  values obtained from the above equation are shown in Figure 6 for each spent adsorbent type and initial pH value.



**Figure 6.** As leaching ratio versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

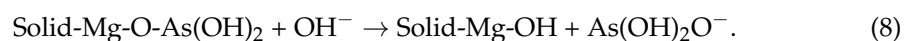
$E_{AS}$  followed various orders depending on the soil type:  $MgO < Ca(OH)_2 \leq CaO < Mg(OH)_2$  for Ku and YF;  $MgO < Mg(OH)_2 < Ca(OH)_2 < CaO$  for Ka;  $MgO < Ca(OH)_2 < Mg(OH)_2 < CaO$  for RS and MS. Although the ease of leaching As from the adsorbent differed depending on soil type, Figure 6 demonstrates that the spent MgO adsorbent had the lowest  $E_{AS}$  value for all soils.

Additionally, overall, the  $E_{AS}$  values shown in Figure 6 are clearly higher than for those containing As(V) reported in a previous study [39]. Therefore, the risk of As leaching in soil is higher for spent adsorbents containing As(III) than for those containing As(V). From the above results, it can be concluded that the environmental stability of spent adsorbents largely depends on the As valence as well as the type of adsorbent and soil.

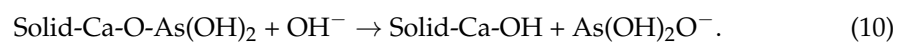
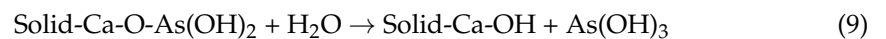
#### 4.2. Dissolved Forms of As in Leachate

The As(III) in the spent Mg- and Ca-based adsorbents is presumed to be adsorbed (immobilized) on the solid surface as “Solid-Mg-O-As(OH)<sub>2</sub>” and “Solid-Ca-O-As(OH)<sub>2</sub>”, respectively [40,41]. In addition, the reactions in which As(III) is desorbed from the adsorbent surface in a neutral or an alkaline solution are expressed by the following equations.

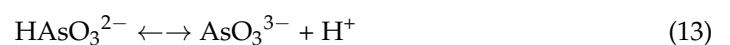
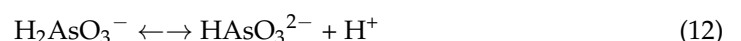
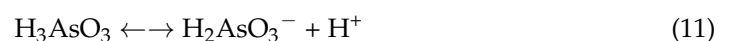
For the Mg-based adsorbents:



For the Ca-based adsorbents:



The dissolved forms of As(III) leached from the spent adsorbent containing As(III) are represented by the following dissociation reactions for arsenous acid:



where the acid dissociation constants of arsenous acid are  $pK_{a1} = 9.1$ ,  $pK_{a2} = 12.1$ , and  $pK_{a3} = 13.4$  (25 °C) [42], and the abundances of the dissolved arsenous acid species are determined by the following:

$$[\text{H}_2\text{AsO}_3^-]/[\text{H}_3\text{AsO}_3] = 10 \exp(pH_f - pK_{a1}) \quad (14)$$



$$[\text{HAsO}_3^{2-}]/[\text{H}_2\text{AsO}_3^-] = 10 \exp(\text{pH}_f - \text{p}K_{a2}) \quad (15)$$

$$[\text{AsO}_3^{3-}]/[\text{HAsO}_3^{2-}] = 10 \exp(\text{pH}_f - \text{p}K_{a3}). \quad (16)$$

The main dissolved forms in each leachate estimated using the above equations are shown in Table 3. No classification based on  $\text{pH}_0$  is included in Table 3 because a slight difference in  $\text{pH}_f$  was observed between  $\text{pH}_0 = 7$  and 4, indicating a small difference in the abundance ratio among arsenous acid species based on  $\text{pH}_f$ . In addition, when two forms are listed in a column, the one on the left is dominant.

**Table 3.** Dissolved forms of As leached from Mg- and Ca-based adsorbents containing As(III).

Soil	Blank	MgO	Mg(OH) <sub>2</sub>	CaO	Ca(OH) <sub>2</sub>
NS	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	HAsO <sub>3</sub> <sup>2−</sup> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	HAsO <sub>3</sub> <sup>2−</sup> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>
Ku	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>
YF	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	H <sub>3</sub> AsO <sub>3</sub> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>
Ka	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup> , H <sub>3</sub> AsO <sub>3</sub>	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup> , H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup> , H <sub>3</sub> AsO <sub>3</sub>
RS	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	HAsO <sub>3</sub> <sup>2−</sup> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	HAsO <sub>3</sub> <sup>2−</sup> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>
MS	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	HAsO <sub>3</sub> <sup>2−</sup> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>	HAsO <sub>3</sub> <sup>2−</sup> , H <sub>2</sub> AsO <sub>3</sub> <sup>−</sup>

NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

As shown in Table 3, for Blank, the main dissolved form of arsenite in all leachates is estimated to be H<sub>3</sub>AsO<sub>3</sub>. Also, in Ku, the main dissolved form is estimated to be H<sub>3</sub>AsO<sub>3</sub>, regardless of the type of the spent adsorbent. In YF, the main dissolved form is H<sub>3</sub>AsO<sub>3</sub> for the spent Mg-based adsorbents; in addition to H<sub>3</sub>AsO<sub>3</sub>, H<sub>2</sub>AsO<sub>3</sub><sup>−</sup> is estimated to be present in non-negligible amounts for the spent Ca-based adsorbents. In Ka, the main dissolved form is estimated to be H<sub>3</sub>AsO<sub>3</sub> for Mg(OH)<sub>2</sub>, whereas more H<sub>2</sub>AsO<sub>3</sub><sup>−</sup> than H<sub>3</sub>AsO<sub>3</sub> is present for MgO, CaO, and Ca(OH)<sub>2</sub>. In both RS and MS, the main dissolved form is estimated to be H<sub>2</sub>AsO<sub>3</sub><sup>−</sup> for the spent Mg-based adsorbents, and more HAsO<sub>3</sub><sup>2−</sup> than H<sub>2</sub>AsO<sub>3</sub><sup>−</sup> is present for the Ca-based adsorbents.

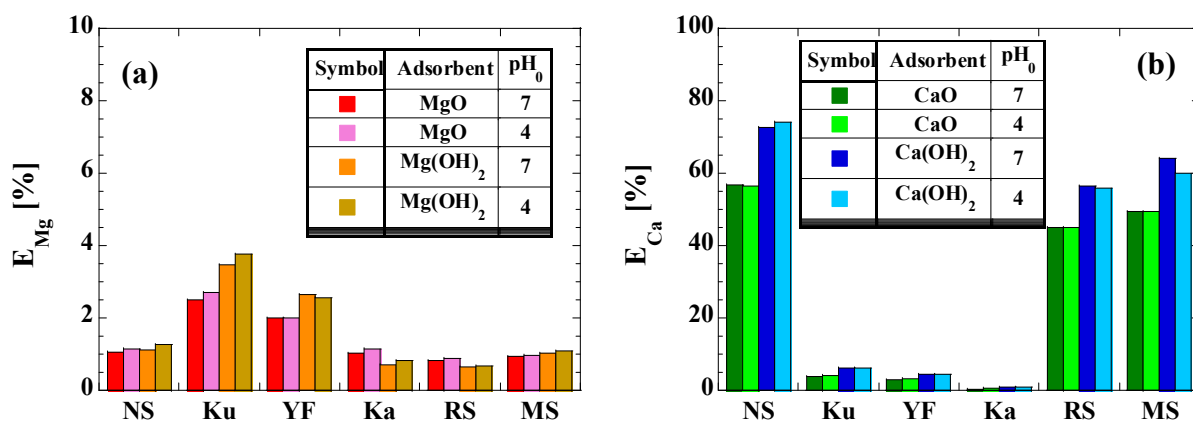
#### 4.3. Mg and Ca Leaching Ratios

In this study, the Mg and Ca leaching ratios,  $E_{\text{Mg}}$  (%) and  $E_{\text{Ca}}$  (%), were calculated as follows:

$$E_X = C_X / ((W_{\text{SP}}/V) \times 1000 \times \alpha_X / 100) \times 100 \quad (17)$$

where  $E_X$  is  $E_{\text{Mg}}$  or  $E_{\text{Ca}}$ .

Equation (17) is essentially the same as Equation (2). The  $E_{\text{Mg}}$  and  $E_{\text{Ca}}$  values obtained from Equation (17) for each adsorbent type and initial pH value are shown in Figure 7a,b, respectively.



**Figure 7.** Mg and Ca leaching ratios versus soil: (a) spent Mg-based adsorbents; (b) spent Ca-based adsorbents. NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

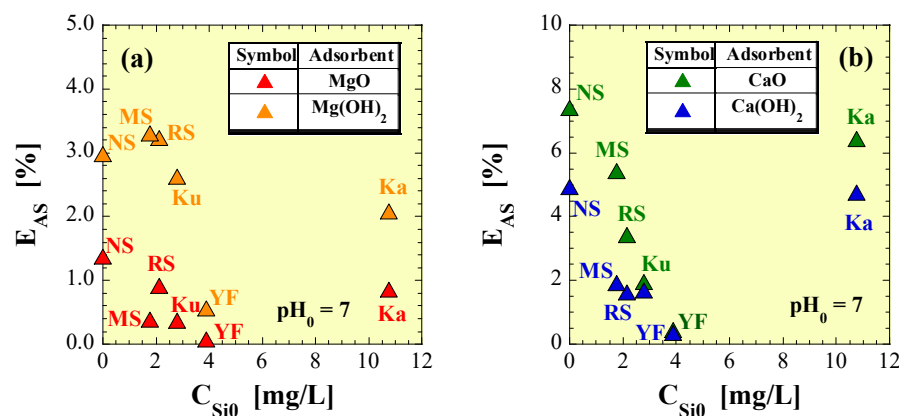
The  $E_{Mg}$  values in NS were clearly higher than those in Ku and YF, being almost equal to those in RS and MS. In Ka, the  $E_{Mg}$  values were comparable to those in NS. Moreover, as shown in Figure 7b, the  $E_{Ca}$  values were slightly lower in RS and MS than in NS but were significantly lower in Ku, YF, and Ka than in NS. Both  $E_{Mg}$  and  $E_{Ca}$  were the lowest in YF.

The residual ratio of each spent adsorbent after the leaching test was calculated by subtracting each value of  $E_{Mg}$  or  $E_{Ca}$  from 100. In all the soils tested in this study, the residual ratios of the spent Mg-based adsorbents were over 96%. However, although the residual ratios of the Ca-based adsorbents reached over 93% in Ku, YF, and Ka, they were less than  $\approx 60\%$  in RS and MS. Therefore, the environmental stability of spent Ca-based adsorbents was significantly reduced in sandy soils.

#### 4.4. Effects of Silicic Acid Leached from Soils

In the only-soil leaching tests without the spent adsorbent (Blank at  $pH_0 = 7$ ), Si components of more than 1.7 mg/L were leached from the soil in all soils, as shown in Figure 5. Although Si was not measured during the leaching test with only soil without the spent adsorbent at  $pH_0 = 4$  (Blank at  $pH_0 = 4$ ), Si components were expected to be leached to the same extent as in the Blank at  $pH_0 = 7$ . Previous studies have reported that the leaching behavior of As from spent Mg- and Ca-based adsorbents can be significantly influenced by the Si components present in a solvent [40,41]. These reports revealed that the presence of silicic acid slightly decreases the As leaching amount for spent Mg-based adsorbents containing As(III) [41]. They also reported that, for spent Ca-based adsorbents, the As leaching amount decreased with increasing initial silicic acid concentration [40].

In this study, to examine the effects of the Si components (silicic acid species) leached from soil, the  $C_{Si}$  value for the Blank (without adsorbent) in each soil was defined as the hypothetical initial Si concentration,  $C_{Si0}$ . In addition, due to the lack of  $C_{Si}$  data for the Blank at  $pH_0 = 4$  in this study, only data at  $pH_0 = 7$  were considered in this study.  $C_{Si0}$  increased in the order  $NS < MS \leq RS < Ku < YF \ll Ka$ . The  $E_{AS}$  values obtained from each leaching test are plotted in Figure 8 against  $C_{Si0}$  for each soil. Figure 8a,b correspond to the spent Mg- and Ca-based adsorbents, respectively.



**Figure 8.** As leaching ratios versus hypothetical initial Si concentration: (a) spent Mg-based adsorbents; (b) spent Ca-based adsorbents. NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

As shown in Figure 8a, for As(III)- $Mg(OH)_2$ , the  $E_{AS}$  values of MS and RS were slightly higher than that of NS, whereas the values in Ku, YF, and Ka were lower than that of NS. In particular, the  $E_{AS}$  value of YF was approximately one-fifth of that of NS, which is extremely low. Additionally, for As(III)-MgO, the  $E_{AS}$  values in all soils were lower than that in NS. The above findings demonstrate that for the Mg-based adsorbent containing As(III), the presence of silicic acid tended to lower  $E_{AS}$  overall, except in the cases of RS and MS for  $Mg(OH)_2$ . According to the above, for As(III)-MgO and As(III)- $Mg(OH)_2$ , the

effects of  $C_{Si0}$  on  $E_{AS}$  in the presence of soil in this study are in agreement with previous reports using silicic acid solutions [41].

As shown in Figure 8b, for the spent Ca-based adsorbents,  $E_{AS}$  tended to decrease as  $C_{Si0}$  increases, except in the plots of Ka. The  $E_{AS}$  values in Ka are slightly lower than those in NS for the spent Ca-based adsorbents containing As(III). Therefore, for the spent Ca-based adsorbents containing As(III), except for the Ka data, the effects of  $C_{Si0}$  on  $E_{AS}$  in the presence of soil in this study are in agreement with those reported in previous studies [40]. Additionally,  $Ca(OH)_2$  evidently has higher environmental stability than CaO, because overall the  $E_{AS}$  values were lower for  $Ca(OH)_2$  than for CaO. Furthermore, based on the test results, it seems reasonable to assume that the spent Ca-based adsorbents reduced the  $E_{AS}$  when coexisting with soil.

The results of this study demonstrate that, with the exception of some data, the As leaching from spent adsorbents is more likely to be reduced when the spent adsorbents coexist with soils than when soils are not present. This result introduces several possibilities, including (i) readsorption of As onto the spent adsorbent, (ii) adsorption of As onto the soil, (iii) incorporation of As in the process in which the Mg or Ca ions leached from the base material of the adsorbents produce magnesium or calcium hydroxide, and (iv) the incorporation of As in the process in which the silicic acid ions react with Mg or Ca ions leached from the base material of the adsorbent to produce magnesium or calcium silicate.

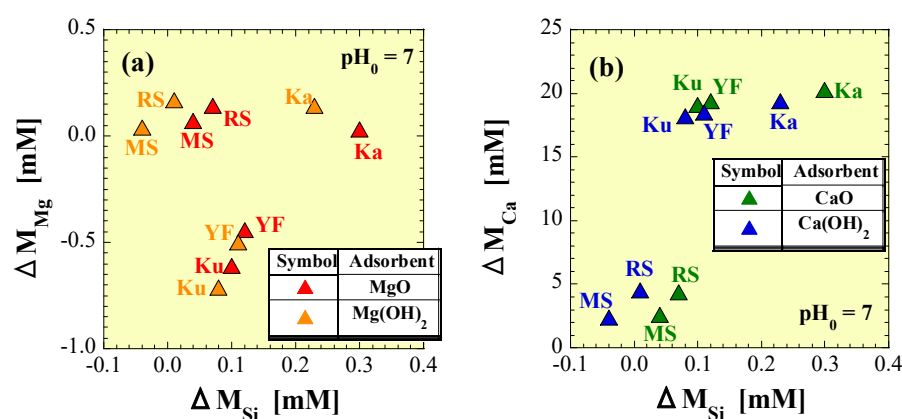
To verify these hypotheses, similar to previous studies [40,41], stoichiometric considerations were made using the values obtained by converting the mass-based concentration  $C_X$  (mg/L) to the molar-based concentration  $M_X$  (mmol/L). Thus,  $C_{Si}$  in mg/L converted to molar units is denoted as  $M_{Si}$ , mmol/L. The value of  $C_{Si}$  for the Blank is denoted as  $M_{Si0}$ . The difference between  $M_{Si0}$  and  $M_{Si}$ ,  $M_{Si0} - M_{Si}$ , is denoted as  $\Delta M_{Si}$ . The  $\Delta M_{Si}$  value is assumed to be the amount consumed for the formation of silicates or the adsorption on the spent adsorbent surface. Similarly,  $C_{Mg}$ ,  $C_{Ca}$ , and  $C_{AS}$  in mg/L converted to molar units are denoted as  $M_{Mg}$ ,  $M_{Ca}$ , and  $M_{AS}$  in mmol/L, respectively. Mg, Ca, and As may be leached from both the spent adsorbent and soil. Therefore, the values of  $M_{Mg}$ ,  $M_{Ca}$ , and  $M_{AS}$  for the Blank are denoted as  $M_{Mg(Blank)}$ ,  $M_{Ca(Blank)}$ , and  $M_{AS(Blank)}$ , respectively, and their values in NS are denoted as  $M_{Mg(NS)}$ ,  $M_{Ca(NS)}$ , and  $M_{AS(NS)}$ , respectively. Furthermore,  $M_{Mg(NS)} + M_{Mg(Blank)}$ ,  $M_{Ca(NS)} + M_{Ca(Blank)}$ , and  $M_{AS(NS)} + M_{AS(Blank)}$  are denoted as  $M_{Mg0}$ ,  $M_{Ca0}$ , and  $M_{AS0}$ , respectively.  $M_{Mg0} - M_{Mg}$  and  $M_{Ca0} - M_{Ca}$  are denoted as  $\Delta M_{Mg}$  and  $\Delta M_{Ca}$ , respectively.  $\Delta M_{Mg}$  and  $\Delta M_{Ca}$  are assumed to correspond to the amounts consumed in their silicate formation and directly adsorbed on the soil. Also,  $\Delta M_{Mg}$  and  $\Delta M_{Ca}$  do not include the amount readsorbed onto the spent adsorbents and the amount consumed due to Mg and Ca hydroxide formation, because  $\Delta M_{Mg}$  and  $\Delta M_{Ca}$  are the values obtained by subtracting  $M_{Mg(NS)}$  and  $M_{Ca(NS)}$ , respectively.  $M_{AS0} - M_{AS}$  is denoted as  $\Delta M_{AS}$ .  $\Delta M_{AS}$  is assumed to correspond to the amounts incorporated in the process of forming Mg and Ca silicates and directly adsorbed on the soil. Furthermore,  $\Delta M_{AS}$  does not include the amount readsorbed onto the spent adsorbents and the amount incorporated in the process of forming Mg or Ca hydroxides, because  $\Delta M_{AS}$  is the value obtained by subtracting  $M_{AS(NS)}$ .

In some cases, the  $\Delta M_{Si}$ ,  $\Delta M_{Mg}$ , and  $\Delta M_{AS}$  values obtained in this study were negative. A negative value of  $\Delta M_{Si}$  suggests that the amount of Si leached from the soil increases when it coexists with the spent adsorbent in relation to when only the soil is present. Negative values of  $\Delta M_{Mg}$  and  $\Delta M_{AS}$  indicate that the amount of Mg and As leached from the spent adsorbent increased when it coexisted with the soil in relation to those when only the spent adsorbent was present. Moreover,  $\Delta M_{Ca}$  never takes a negative value, regardless of the soil type.

Figure 9a,b show the plots of  $\Delta M_{Mg}$  for the spent Mg-based adsorbents and  $\Delta M_{Ca}$  for the spent Ca-based adsorbents against  $\Delta M_{Si}$ , respectively.

If the decreases in Si, Mg, and Ca in the presence of soil were caused only by the formation of magnesium silicate or calcium silicate species, positive correlations should be observed between  $\Delta M_{Si}$  and  $\Delta M_{Mg}$  or  $\Delta M_{Ca}$  in Figure 9. As shown in Figure 9a, for

Ku and YF, a weak positive correlation appears, but both  $\Delta M_{Si}$  and  $\Delta M_{Mg}$  have negative values. Thus, the leaching amounts of both Si and Mg increased. For Ka, RS, and MS, no regular trend was observed in the fluctuation in  $\Delta M_{Mg}$  with respect to that in  $\Delta M_{Si}$ . In Figure 9b, no regular trend exists in the fluctuation in  $\Delta M_{Ca}$  with respect to that in  $\Delta M_{Si}$ . In both Figure 9a,b, no regular trend can be observed even when focusing on the type of adsorbents. However, focusing on the soil types indicates that data for the same type of soil are plotted in adjacent positions. Even for data corresponding to the same soil type, the relative positions plotted in Figure 9a,b are different. However, in both images, RS is plotted adjacent to MS, and Ku is plotted adjacent to YF, whereas Ka is plotted at a location separate from them. These findings suggest that the soil properties that affect the spent adsorbents were similar for Ku and YF and for RS and MS, whereas those for Ka were quite different from those for the other soils.



**Figure 9.** Plots of (a)  $\Delta M_{Mg}$  for the spent Mg-based adsorbents and (b)  $\Delta M_{Ca}$  for the spent Ca-based adsorbents against  $\Delta M_{Si}$ . Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

The chemical composition of calcium silicate species is  $Ca_xSiO_{(x+2)}$ , where  $x = 0.5\text{--}4$  [40], indicating that the Ca/Si molar ratio of the average composition of the calcium silicate species produced should be between 0.5 and 4. Similarly, the Mg/Si molar ratio of the average composition of the magnesium silicate species produced should be between 0.5 and 4. Tables 4 and 5 show the values of  $\Delta M_{Mg}/\Delta M_{Si}$  and  $\Delta M_{Ca}/\Delta M_{Si}$  determined based on the data in Figure 9. Additionally, if either  $\Delta M_{Si}$  or  $\Delta M_{Mg}$  or  $\Delta M_{Ca}$  had a negative value, we assumed that neither magnesium nor calcium silicate was produced, and such a result was excluded. Tables 4 and 5 only present the ratios of the production amounts of silicates to the amounts of Mg and Ca adsorbed on the soil or to the amount of Si components adsorbed on the spent adsorbent; they do not indicate the produced amounts of silicates.

**Table 4.** Values of  $\Delta M_{Mg}/\Delta M_{Si}$  for spent Mg-based adsorbents at  $pH_0 = 7$ .

As	Adsorbent	Ku	YF	Ka	RS	MS
As(III)	MgO	-	-	0.09	59.1	-
As(III)	Mg(OH) <sub>2</sub>	-	-	22.0	2.05	1.58

Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

**Table 5.** Values of  $\Delta M_{Ca}/\Delta M_{Si}$  for spent Ca-based adsorbents at  $pH_0 = 7$ .

As	Adsorbent	Ku	YF	Ka	RS	MS
As(III)	CaO	203	152	67.1	77.6	59.2
As(III)	Ca(OH) <sub>2</sub>	190	144	66.6	75.3	48.7

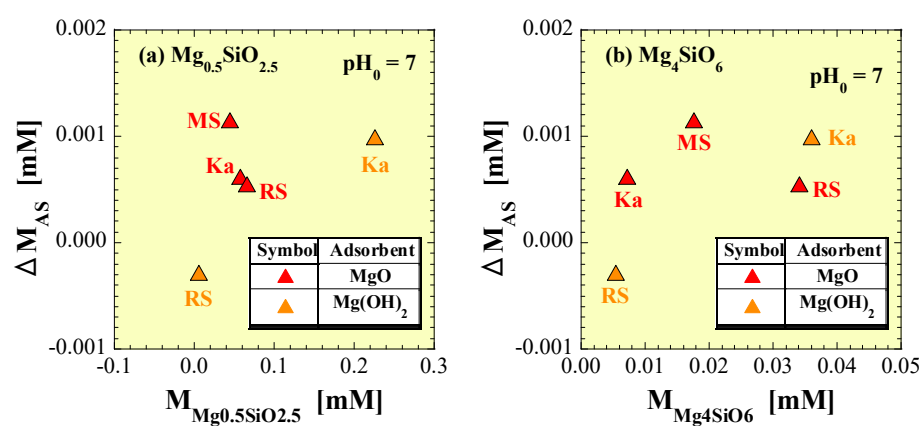
Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In Tables 4 and 5, the values exceeding four indicate a reduction in Mg or Ca beyond that consumed in silicate formation, which suggest that Mg and Ca leached from the spent adsorbent were directly adsorbed onto the soil. Conversely, values less than 0.5 indicate a reduction in Si beyond that consumed in the silicate formation, which suggest that silicic acid ions leached from the soil were directly adsorbed onto the spent adsorbent. As shown in Tables 4 and 5, the above analysis indicates that in Ku and YF, magnesium silicate was not produced for all Mg-based adsorbents. Additionally, for As(III)-MgO, magnesium silicate was not produced even in MS. Moreover, for the Ca-based adsorbents, calcium silicates could have been produced in all soils.

Subsequently, assuming that silicate was formed, the incorporation of As into the silicate was examined. The extreme (Mg or Ca)/Si composition molar ratios of the silicate species that can be produced are 0.5 and 4, as described above. Assuming the (Mg or Ca)/Si composition molar ratio of the generated silicate species is 0.5, if the value of  $\Delta M_{Si} - (\Delta M_{Mg} \text{ or } \Delta M_{Ca}) \times 2$  is positive, the amount of  $(\text{Mg or Ca})_{0.5}\text{SiO}_{2.5}$  produced is equal to  $(\Delta M_{Mg} \text{ or } \Delta M_{Ca}) \times 2$ , and, if negative, it is equal to  $\Delta M_{Si}$ . Assuming that the (Mg or Ca)/Si composition molar ratio of the generated silicate species is four, if the value of  $\Delta M_{Si} - (\Delta M_{Mg} \text{ or } \Delta M_{Ca}) \times 1/4$  is positive, the amount of  $(\text{Mg or Ca})_4\text{SiO}_6$  produced is equal to  $(\Delta M_{Mg} \text{ or } \Delta M_{Ca}) \times 1/4$ , and if negative, it is equal to  $\Delta M_{Si}$ .

The plots of  $\Delta M_{AS}$  against the production amount of silicate estimated based on these assumptions are shown in Figures 10 and 11. Figure 10 is a plot of  $\Delta M_{AS}$  against the estimated production amounts of (a)  $\text{Mg}_{0.5}\text{SiO}_{2.5}$  and (b)  $\text{Mg}_4\text{SiO}_6$  for the coexistence of the spent Mg-based adsorbents and soil. Figure 11 is a plot of  $\Delta M_{AS}$  against the estimated production amounts of (a)  $\text{Ca}_{0.5}\text{SiO}_{2.5}$  and (b)  $\text{Ca}_4\text{SiO}_6$  for the coexistence of the spent Ca-based adsorbents and soil. However, Figure 11a,b are exactly the same data plots, because  $M_{\text{Ca}0.5\text{SiO}_{2.5}} = M_{\text{Ca}4\text{SiO}_6} = \Delta M_{Si}$  was derived from the analysis based on the above assumptions.

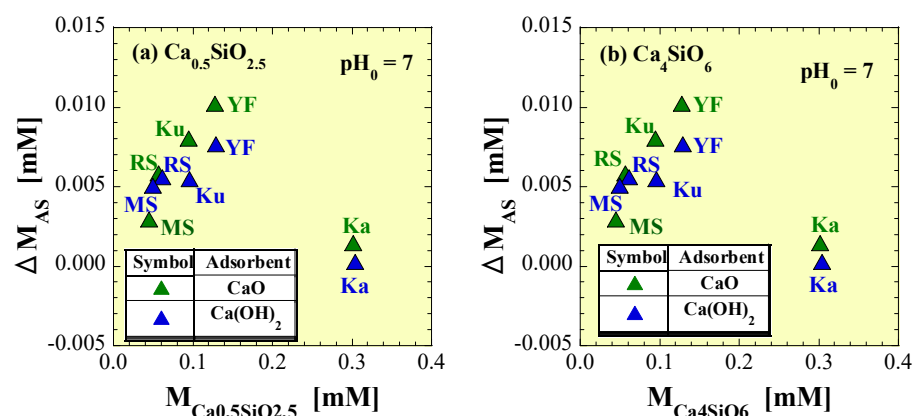
In Figure 10a,b, no correlation can be observed between the produced amount of magnesium silicate species and  $\Delta M_{AS}$ . However, because the amount of As leached from the spent Mg-based adsorbents was essentially low, even if the incorporation of As into the magnesium silicate species had occurred, it is possible that no clear trend could be observed.



**Figure 10.** Plots of  $\Delta M_{AS}$  against estimated production amounts of (a)  $\text{Mg}_{0.5}\text{SiO}_{2.5}$  and (b)  $\text{Mg}_4\text{SiO}_6$  for the coexistence of the spent Mg-based adsorbents and soil: Ka, Kanuma soil; RS, river sand; MS, mountain sand.

Comparing the values of  $\Delta M_{AS}$  in soils of the same type with different estimated production amounts of calcium silicate species can afford the amount of As adsorbed on the soil and the ratio of As incorporated into calcium silicate. However, in this study, such an analysis could not be conducted, because data for same soil types with significantly different estimated production amounts of calcium silicate species could not be obtained. However, in Figure 11, focusing on the data plots in which the type of adsorbent is the same, a positive correlation appears between the produced amount of calcium silicate species

and  $\Delta M_{AS}$ , except in the data plots of Ka. This result was attributed to the extremely low amount of As and the Ca ions leached from the spent adsorbents being directly adsorbed on Ka. The Ca ions were directly adsorbed before silicic acid ions were leached from Ka, forming calcium silicate species in situ. Additionally, CaO tends to have a slightly higher  $\Delta M_{AS}$  than  $\text{Ca(OH)}_2$ , which is attributed to the actual produced amount of calcium silicate species, which could be lower for  $\text{Ca(OH)}_2$  than for CaO. In other words, the proportion of silicic acid adsorbed on the spent adsorbent is inferred to be higher for  $\text{Ca(OH)}_2$  than for CaO.



**Figure 11.** Plots of  $\Delta M_{AS}$  against estimated production amounts of (a)  $\text{Ca}_{0.5}\text{SiO}_{2.5}$  and (b)  $\text{Ca}_4\text{SiO}_6$  for the coexistence of the spent Ca-based adsorbents and soil: Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

#### 4.5. Recommendations for Waste Disposal Considering Effects of Soil on Spent Adsorbents

As described in Section 4.4, in coexistence with soil, the effects of silicic acid species leached from the soil are thought to be quite significant. For Ca-based adsorbents in particular, the incorporation of As into the generated calcium silicate species is thought to prevent environmental pollution due to As leaching. However, the As adsorption capacity of the soil itself is assumed to contribute the most to the decline in  $E_{AS}$ , suggesting that the soil acts as a second adsorbent. If the soil itself has a high As adsorption capacity, most of the As leached from the spent adsorbents adsorbs onto the soil that is in contact with the spent adsorbents, which prevents the spread of As contamination over a wide area. Conversely, if the soil itself has a low As adsorption capacity, leached As does not readily adsorb onto the soil, and As contamination spreads over a wide area. Applying the abovementioned rationale to the soils tested in this study, Ku and YF are considered to exhibit the former behavior, and Ka, RS, and MS are considered to exhibit the latter. Thus, Ku and YF prevent the spread of As contamination, although the soil itself in contact with the spent sorbent is contaminated with As. Conversely, Ka, RS, and MS are less susceptible to contamination with As, but As contamination may spread over a wide area via soil pore water.

Furthermore, it may be possible to investigate the As adsorption capacity of individual soils and to use soils with a high As adsorption capacity as a natural adsorbent to prevent the spread of As contamination. However, the soil used as an As adsorption barrier must be risk-managed as As-contaminated soil, and trade-offs and risks must be considered to establish sustainable As treatment processes. Based on the premise that used adsorbents are appropriately processed and managed, examining the characteristics of the nearby soil when planning the location of a waste disposal site is very important to ensure sustainable safety, considering all steps from As purification using adsorbents to the disposal of spent adsorbents containing As.

Finally, among all the soils tested in this study, the spent adsorbents containing As(III) had lower environmental stability than those containing As(V) reported in a previous study [39]. This result indicates that oxidizing As(III) to As(V) before adsorbing As onto



adsorbents is advisable. Furthermore, MgO is strongly recommended as an adsorbent for As, because it exhibits high environmental stability for all soils.

## 5. Conclusions

Focusing on As(III), which is more toxic than As(V), leaching tests were conducted in this study involving four types of spent adsorbents containing As(III), five types of soil, and two types of ion-exchange water with different pH values. A slight difference was observed in  $E_{AS}$  due to solvent pH, whereas  $E_{AS}$  varied greatly depending on both type of adsorbent and type of soil. Focusing on the soil type,  $E_{AS}$  followed the order of  $MgO \ll Mg(OH)_2 \approx Ca(OH)_2 \approx CaO$  in Ku,  $MgO < Ca(OH)_2 \leq Mg(OH)_2$ ,  $CaO$  in YF,  $MgO < Mg(OH)_2 \ll Ca(OH)_2 < CaO$  in NS and Ka, and  $MgO \ll Ca(OH)_2 < Mg(OH)_2 < CaO$  in RS and MS. Focusing on the spent adsorbent type,  $E_{AS}$  followed the order of  $YF < Ku \leq MS < Ka < RS < NS$  for  $MgO$ ,  $YF < Ka < Ku \leq NS \leq RS \leq MS$  for  $Mg(OH)_2$ ,  $YF < Ku < RS < MS < Ka < NS$  for  $CaO$ , and  $YF < RS \leq Ku \leq MS < Ka < NS$  for  $Ca(OH)_2$ . For both the spent Mg-based and Ca-based adsorbents, the  $E_{AS}$  values were clearly higher for the spent adsorbents containing As(III) than for those containing As(V) reported in a previous study [39]. Therefore, the risk of As leaching in soil was evaluated as being higher for the spent adsorbents containing As(III) than for those containing As(V). Although the ease of leaching As from the adsorbent differed depending on the combination of soil type and As valence, the spent MgO adsorbent had the lowest  $E_{AS}$  in all the combinations. Finally, regarding environmentally friendly and sustainable As-removal treatment, disposal, and management, we recommend the following: (i) selection of MgO as an adsorbent and (ii) oxidation treatment of As(III) to As(V) before the step of adsorbing As onto adsorbents.

The amount of As leached from the used adsorbent is expected to vary depending on the ratio of the spent adsorbent to both soil and liquid. Therefore, as a near future challenge, it will be important to conduct leaching tests with these mixing ratios as experimental parameters. Additionally, to estimate the long-term stability of spent adsorbents, it will be necessary to investigate how the valence and state (mineralogy) of As incorporated into spent adsorbents change in soil.

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