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ARSENIC ADSORPTION CAPABILITIES OF SOIL-BENTONITE MIXTURES AS BUFFER MATERIALS FOR LANDFILLS

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ABSTRACT

Removal and fixation of As(III) and As(V) from aqueous solution by soil/bentonite mixtures were studied to develop reliable clay liners for waste landfill sites. One of two soils such as, Masatsuchi soil (weathered granite) and Murram soil (pumice) was used as a main body of the liner, and Wyoming bentonites were mixed with the soils because of its superior impermeability. As the result of batch experiments, it was shown that large part of As was removed by Masatsuchi soil without pH buffer, and the result was better than those of Murram soil. Both soils appeared to have best adsorption of As(V) and As(III) within pH ranges of 3–6.5 and 7–9.5 at where the dominant species in the aqueous solution were $H_2AsO_4^-$ and $H_2AsO_3^-$, respectively. A long-term leak test showed that Masatsuchi soil-Wyoming bentonite combination had the ability to remove all the As(III) from 4 ppm aqueous solution for more than 100 days.

Key words: As adsorption, Bentonite, Hydraulic conductivity, Clay

INTRODUCTION

Arsenic may exist in waste deposited to the landfills depending on the different origins of the wastes. Industrial wastes, especially from mining activities could have potentially high amounts of arsenic. Arsenic has been classified in Group 1 as 'carcinogenic species for human beings' by the international Research Centre for Cancer (Charlet et al., 2001). The WHO maximum permissible concentration in drinking water is 10 ppb. Thus, arsenic from landfill sites must be contained to prevent it's contamination to the groundwater system.

Some arsenic adsorption studies have looked into removal of arsenic from water using clay mineral (Manning and Goldberg, 1996 and 1997), natural solids (Chakravarty et al., 2002; Elizalde-González et al., 2001; Altundoğan et al., 2000), ion exchangers resins (Korngold et al., 2001 and Suzuki et al., 2000), aluminium loaded zeolite (Xu et al., 2002), and aluminium and ferric hydroxides (Gulledge and O'Connor, 1973). These studies have shown adsorption depend on pH and arsenic speciation at various magnitudes for the different materials studied. In laboratory studies it is possible to control pH and arsenic speciation, but in natural environments like in landfills it would be difficult to control these parameters. Therefore, a good arsenic adsorbent material should be one which has the ability of working at a wider pH range for adsorption of both As(III) and As(V). Generally, As(V) adsorption is favourable at pH 2–8 while As(III) is favourable at pH 6–10 with optimum pH depending on the adsorbent (Manning and Goldberg, 1996 and 1997; Suzuki et al., 2002).

Different countries have different regulations for hydraulic conductivity of the landfill barriers to prevent contamination of groundwater system from the landfill sites. These range from 5×10^{-8} for Germany to 1×10^{-4} for France, with other countries in between (Benson and Foose, 1999). Despite the low permeability and barrier thickness enforced by states, the landfill barriers are not completely impermeable. That means the permeation is slowed to different extents but not prevented. The landfill sites are therefore used to postpone the groundwater system contamination to later years and create problems for later generations. A secure landfill protection barrier will be the one with low permeability and additional function of adsorbing the contaminants such as arsenic from the permeation stream.

Landfill sites are constructed from soil bentonite mixtures with the bentonite having the functional role of ensuring lower hydraulic conductivity due to its ability to swell in water (Allen, 2001; Alawaji, 1999).

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TABLE 1. Composition of materials as determined by X-ray fluorescence (XRF)

Material Name	Loss on Ignition (%)	Al_2O_3 Al (%)	CaO Ca (%)	K_2O K (%)	MgO Mg (%)	SiO_2 Si (%)	Fe_2O_3 Fe (%)	Na_2O Na (%)	TiO_2 Ti (%)	MnO Mn (%)
WyomingA	5.081	15.909	1.273	0.405	1.783	69.531	3.885	1.96	0.125	0.048
WyomingB	5.783	20.890	1.324	0.706	2.732	62.243	5.198	0.965	0.140	0.018
Toyoura Sand	0.925	3.426	0.228	0.977	0.000	89.775	1.874	2.475	0.305	0.013
Masatsuchi	4.42	19.211	1.300	3.583	0.686	61.984	5.133	3.121	0.512	0.051
Murram	2.28	13.739	12.659	3.458	7.247	35.397	18.17	2.116	4.859	0.000

However it has been shown that, conventional soil bentonite landfill barriers do not effectively hinder diffusive transport of contaminants (Khandelwal and Rabideau, 2000). It is therefore important to search for proper soil bentonite mixtures which will have a dual role of both low hydraulic conductivity and a higher adsorption capacity of contaminants. The use of natural locally available materials for landfill barriers would be cost effective and therefore implementable by both the rich and the poor notions of the world.

The objectives of this study were to test the arsenic adsorptive abilities of soils and soil bentonite mixtures and evaluate their use as landfill barriers materials. Development of a multi-functional buffer material which is a good hydraulic barrier as well as a good adsorbent for harmful chemical species is the main goal.

MATERIALS AND METHODS

Materials used in this study were: standard sand and bentonite clay which were used to simulate hydraulic conductivity measurements. Two soils, one from Japan called Masatsuchi (weathered granite soil) and from Tanzania known as Murram (Pumice) were tested for there ability to adsorb As(III) and As(V) and their performance as landfill barrier materials. The compositions of these materials as determined by X-ray Fluorescence (XRF) are shown in Table 1. WyomingB and WyomingA are natural bentonites categorized into Na-montmorillonite clays while Toyoura sand (obtained from Yamaguchi, Japan) is standard sand with particles size less than 420 μm. The Masatsuchi and Murram soils were ground and sieved to particle size below 420 μm. The particle size distribution for Masatsuchi, Toyoura sand and Murram are shown in Fig. 1. All chemicals used in this study were prepared from analytical grade chemicals obtained from chemical suppliers.

Measurement of hydraulic conductivity was done according to ASTM D 5084-90 using equipment supplied by Hojun Co. Ltd. Falling-Head Tests with Increasing Tailwater procedure was followed.

Adsorption tests for As(V) and As(III) were done batch wise by shaking mixtures of adsorbents and the arsenic solution vigorously using Yamato SA 300 shaker. At the end of shaking the adsorbent was separated from the mixture by centrifuging at 15,000 rpm for 20 minutes. Concentrations of arsenic in the initial and supernatant solutions were determined by SEIKO

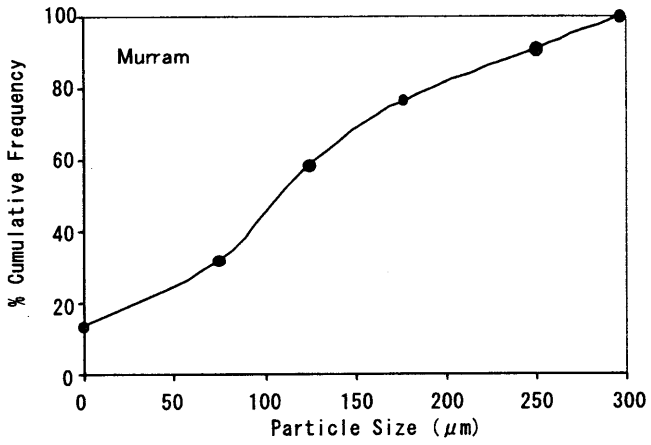

FIG. 1a. Particle size distribution for Murram soil.

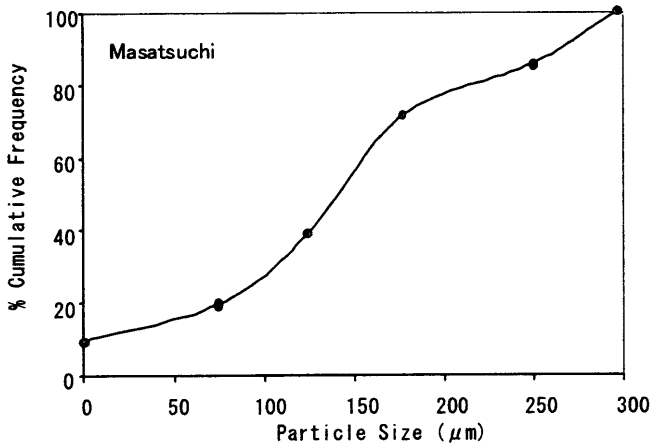

FIG. 1b. Particle size distribution for Masatsuchi soil.

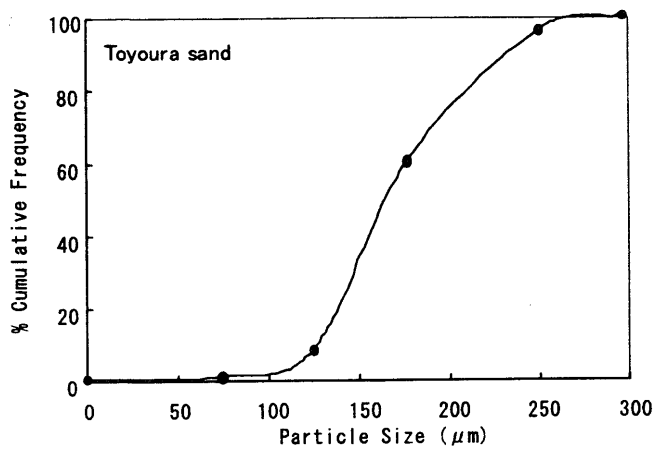

FIG. 1c. Particle size distribution for Toyoura sand.

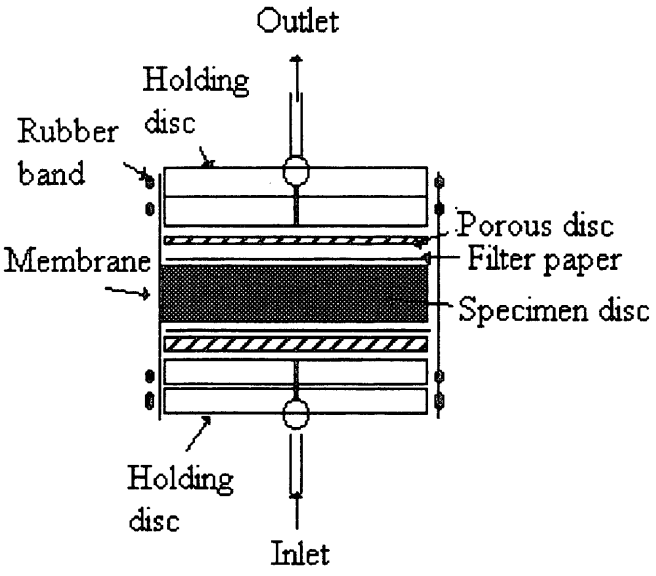

FIG. 2. Setup of permeation cell used to measure permeability and simulation of arsenic adsorption in compacted sand/soil-clay mixture.

TABLE 2. Permeability of sand/soil bentonite mixtures

Mixture	Mixing ratio	Hydraulic conductivity (cm s^{-1})
Toyoura sand/WyomingA	100/13	1.7×10^{-9}
Toyoura sand/WyomingB	100/13	1.3×10^{-9}
Masatsuchi/WyomingA	100/13	5.7×10^{-9}
Murram/WyomingB	100/13	1.5×10^{-8}

TABLE 3. Comparison of adsorption of As(III) and As(V) by different materials (Initial As concentration about 4 ppm)

Material	% As(V) adsorbed	% As(III) adsorbed	pH	Time (d)
Masatsuchi	99	83	5.3	1
Masatsuchi-WyomingB (100/13)	98	89	7.3	1
Murram	34	44	7.5	1
Murram-WyomingB (100/13)	5	45	8.5	1
Toyoura sand	—	6	8.5	1
Toyoura sand-WyomingB (100/13)	0	3	9.9	1
WyomingB	0	—	8.9	1

Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) model SPS-1500R. Variation of pH during arsenic adsorption was done by use of Good's Buffers and/or acetic acid, NaOH or HCl.

For simulation of arsenic adsorption in the landfills, arsenic solution was permeated through a compacted specimen assembled in the permeameter cell similar to one used for measurement of hydraulic conductivity of landfill barrier materials. A specimen with a diameter of 10 cm and a volume of 135 cm^3 was assembled as shown in Fig. 2. The specimen was prepared following exactly the procedure of ASTM D 5084-90 for preparation of hydraulic conductivity test specimen. The specimen was saturated first with distilled water before a solution containing about 4 ppm As(III) was permeated to the system. The permeation was forced from the bottom and nitrogen pressure was used to control the permeation rate. The permeated volumes as well as time were recorded. Arsenic concentrations were determined by ICP-AES.

RESULTS AND DISCUSSION

Hydraulic conductivity of soil/sand-clay compactions

The suitability of soil/sand-bentonite compaction for hydraulic conductivity barrier is its low permeability. For Japan, the hydraulic permeability has to be less than 1×10^{-6} cm s^{-1} while majority of other countries have enforced limit of at least 1×10^{-7} cm s^{-1} (Benson and Foose, 1999). The soil/sand materials in Table 1 were tested for their hydraulic conductivity when combined with WyomingB/WyomingA bentonite. Table 2 shows that using Toyoura sand-clay composite a superior hydraulic barrier material is obtained (permeability less than 2×10^{-9}). Masatsuchi-clay and Murram-clay compacted hydraulic barriers had permeability about 4 and 10 times faster than sand-clay compaction respectively. Using permeability as the only parameter, the sand-clay barrier would be the most suitable material for landfill protection. In the preceding sections evaluations will be made based on a second criterion of arsenic adsorption capabilities for the landfill protection materials.

Adsorption at natural pH

Table 3 shows adsorption of arsenic by different soils and soil-bentonite clay mixtures at natural pH of the materials when suspended in de-ionized water containing arsenic. The suspension of the various materials in pH unbuffered arsenic solutions was done in order to investigate arsenic adsorption of the two species As(III) and As(V) by the soils in their natural environment. Bentonite clays attain basic pH when they are suspended in water (pH 8.9 for WyomingB in deionised water).

The supernatants from a suspension of WyomingB bentonite with Masatsuchi soil in arsenic solution resulted in pH values higher than the pH obtained by the soil alone. The combination had little effect on arsenic adsorption. Addition of bentonite clay had improved removal of As(III) from 83% to 89% while maintaining removal of As(V) around 98%. On contrary the removal of arsenic with Murram was quite low as compared to removal by Masatsuchi. A mixture of bentonite clay and Murram led to the decrease of removal of As(V) to 5% from 34% while maintaining As(III) removal at 44%. The use of Murram in combination with clay did not give promising results as very low adsorption of As(V) was obtained. Similarly, sand-WyomingB system had almost no ability to remove any

of the arsenic species.

Combining the arsenic adsorption results in Table 3 and the permeability results in Table 2, Masatsuchi-clay materials had portrayed the best performance as landfill barrier system for meeting criteria of low permeability and good adsorption of both arsenic species.

Effect of pH

Figure 3 shows the effect of pH on adsorption of As(V) and As(III) using pH buffered arsenic solutions for Masatsuchi and Murram soils. Both soils showed similar trends for adsorption of As(III) and As(V) although Masatsuchi soil had better results. Removal of

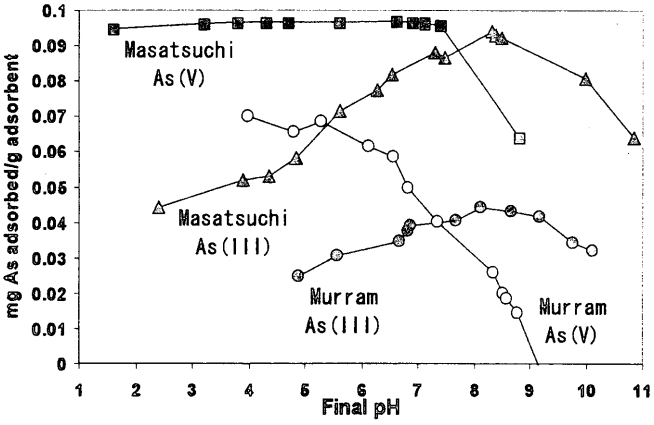

FIG. 3. Comparing removal of As(V) and As(III) as a function of pH for Masatsuchi and Murram soils. 10 ml of 8 ppm As(V) and As(III) solutions were mixed with 1 g and 0.8 g of Murram and Masatsuchi soil respectively and shaken for about 20 h at a temperature of about 293 K.

As(V) was favourable in the acidic pH range while As(III) adsorption increased with increasing pH up to around pH 9. The arsenic adsorption variation with pH was similar to the results found by other researchers (Altundoğan et al., 2000; Manning and Goldberg, 1997; Suzuki et al., 2000). From the results in Table 3, at natural condition Masatsuchi-WyomingB has pH around 7.5. At this pH Masatsuchi soil has a good adsorption of both species of arsenic (Fig. 3). On the other hand, Murram-clay mixture has pH around 8.5 at which adsorption of As(V) is very low. Despite having similar trends, Masatsuchi soil has more affinity to adsorb the two species of arsenic compared to Murram soil.

The reasons for the good adsorption properties of the Masatsuchi soil as compared to Murram soil can not be explained clearly from the composition of the soils as shown in Table 1. Masatsuchi has slightly more alumina than Murram while the Fe content in Masatsuchi soil is less than one third that in the Murram soil. The surface areas of both soils as determined by BET nitrogen adsorption were 3.85 and 13.35 m^2 for Masatsuchi and Murram soil respectively. The Murram average pore diameter and single point total pore volume for pores less than 1120 Å as measurement by BET method were 133.6 Å and 0.0446 cm^3/g respectively. The corresponding values for Masatsuchi were 102.3 Å and 0.0098 cm^3/g, respectively. With the high Fe content and large surface area of Murram soil it was expected to have better arsenic adsorption capabilities than the Masatsuchi soil. The fact that, Masatsuchi soil had higher arsenic adsorption than Murram means arsenic adsorption is controlled mainly by the surface chemistry of the adsorbent and not its bulk properties.

The XRD profiles of the soils shown in Fig. 4 indicate that Masatsuchi soil is more crystalline than

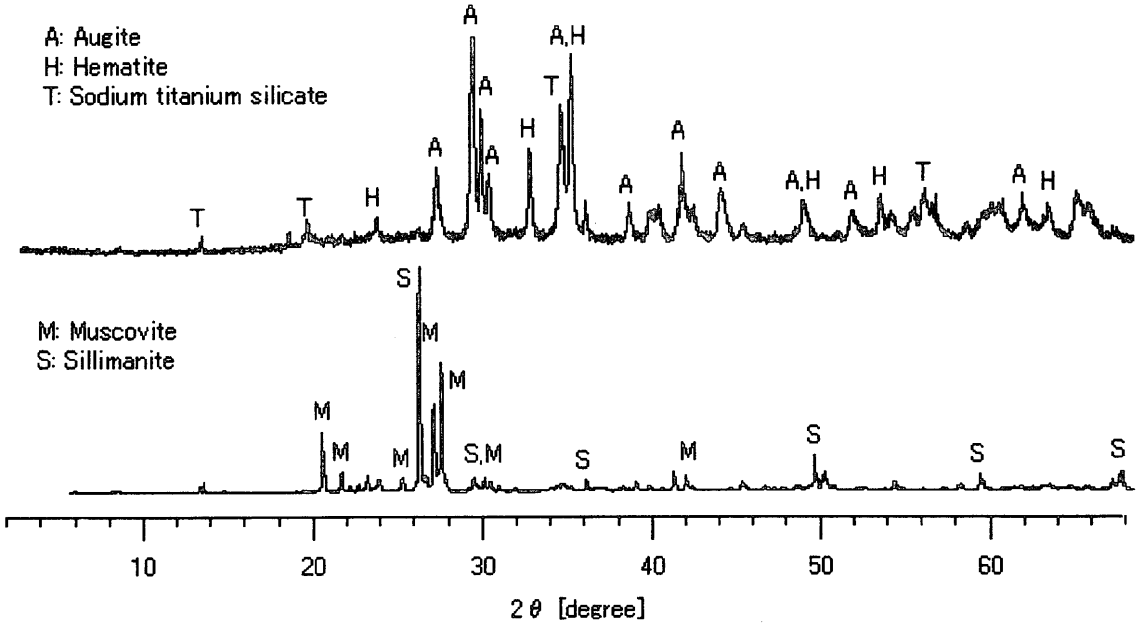

FIG. 4. XRD profile for Murram upper, Masatsuchi lower.

Murram soil as it has more intense peaks. Masatsuchi was obtained from Okayama prefecture and it is weathered granite. The XRD pattern in Fig. 4 for Masatsuchi had matches to muscovite and sillimanite although it was difficult to march all the peaks. Other researcher (Kagashima, 2002) had analysed granitic complex rocks and indicated the content as plagioclase, biotite, quartz and K-feldspar. The Murram XRD analysis has shown presence of mainly augite, hematite and sodium titanium silicate. By overlapping the two XRD patterns it showed the two soils have very little crystalline material in common. The most intense peaks for the two soils are at different location and very few peaks appear to have exact overlap.

Depending on the pH As(V) can exist in aqueous solution as various oxy-anions of arsenic acid ($H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) while the species of As(III) can be ($H_3AsO_3^\circ$, $H_2AsO_3^-$, and $HAsO_3^{2-}$) (Manning and Goldberg, 1997; Suzuki et al., 2000). Since for As(V) the predominant species in the pH range of 3–6.5 is $H_2AsO_4^-$ (Gulledge et al., 1973; Suzuki et al., 2000), then both soils appeared to have best adsorption of this species as the maxima performance for As(V) adsorption was observed within that pH range (Fig. 6). Adsorption of As(III) for both soils was at maxima around pH 7–9.5. The results are similar to those found by Manning and Goldberg, 1997 for clay minerals and amorphous $Al(OH)_3$. In the alkaline region the As(III) species responsible for adsorption is $H_2AsO_3^-$ (Suzuki et al., 2000).

Adsorption capacity

In Fig. 5, the adsorption capacities of Masatsuchi and Murram at various initial As(V) and As(III) concentrations were studied in pH unbuffered systems. Masatsuchi soil showed very high adsorption capacity for As(V) compared to As(III) and with better adsorption capacity for both species compared to the Murram soil. It had been indicated (Manning and Goldberg, 1997; Xu et al., 2002) that, As(III) is oxidized to As(V) in the presence of oxygen, therefore having a system which adsorbs both species and having a high adsorption capacity for As(V) in a wider pH range will ensure efficient removal of arsenic in landfills. While oxidative environment is more likely on surface waters, reductive environment is more likely in groundwater system and landfill sites and hence the chances of existence of As(III) in landfill barriers is more likely. As(III) is more toxic than As(V) (Xu et al., 2002), therefore materials which demonstrate ability to removal the two arsenic species will be more suitable than once which works for one arsenic species alone.

Simulation of arsenic adsorption in landfills

In landfill sites leachate will permeate through the landfill barrier materials, hence adsorption will also be controlled by the diffusion of adsorbent to the adsorbent sites. However with the low permeability employed for landfill barriers, diffusion is not expected to be the rate determining step for adsorption of As(V) and/or As(III). From the batch adsorption results obtained above, it was decided to evaluate adsorption of As(III) in a permeation used for measurement of permeability of compacted sand/soil and bentonite mixtures. Two rigs were used to monitor the permeated solution charged with As(III) concentration of about 4 ppm to a rig with Masatsuchi-WyomingB compaction and another one with Toyoura sand-WyomingB compaction. The compacted discs had a total weight of 215 g and a weight ratio of WyomingB to Toyoura sand/Masatsuchi soil was 13 to 100. The results showed continued about 100% removal of arsenic form the permeation through Masatsuchi-WyomingB compaction after a volume of 942 ml was colleted, Fig. 6. On the other hand permeate from sand-bentonite clay compaction showed fast deterioration in As(III) removal despite the slow permeation rate which was maintained. While 942 ml were collected within 95 days for the Masatsuchi-WyomingB

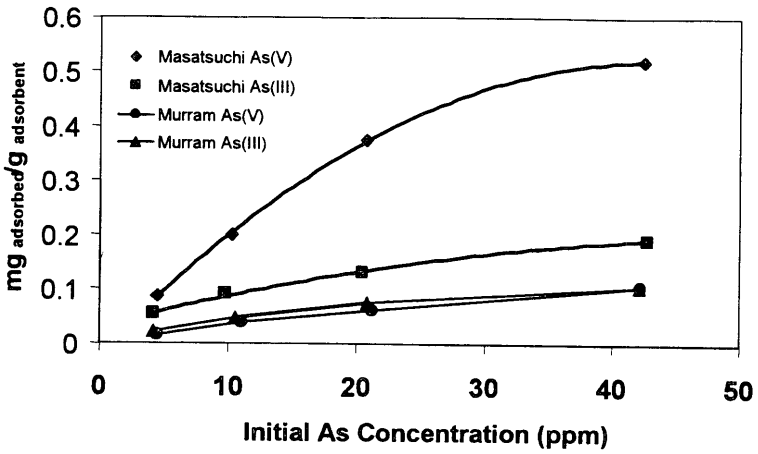

FIG. 5. Arsenic (V) and (III) adsorption capacity as a function of initial concentration after 3 days at temperature around 293 K. 20 ml of arsenic solutions were mixed with 1 g of adsorbent and shake vigorously all the time.

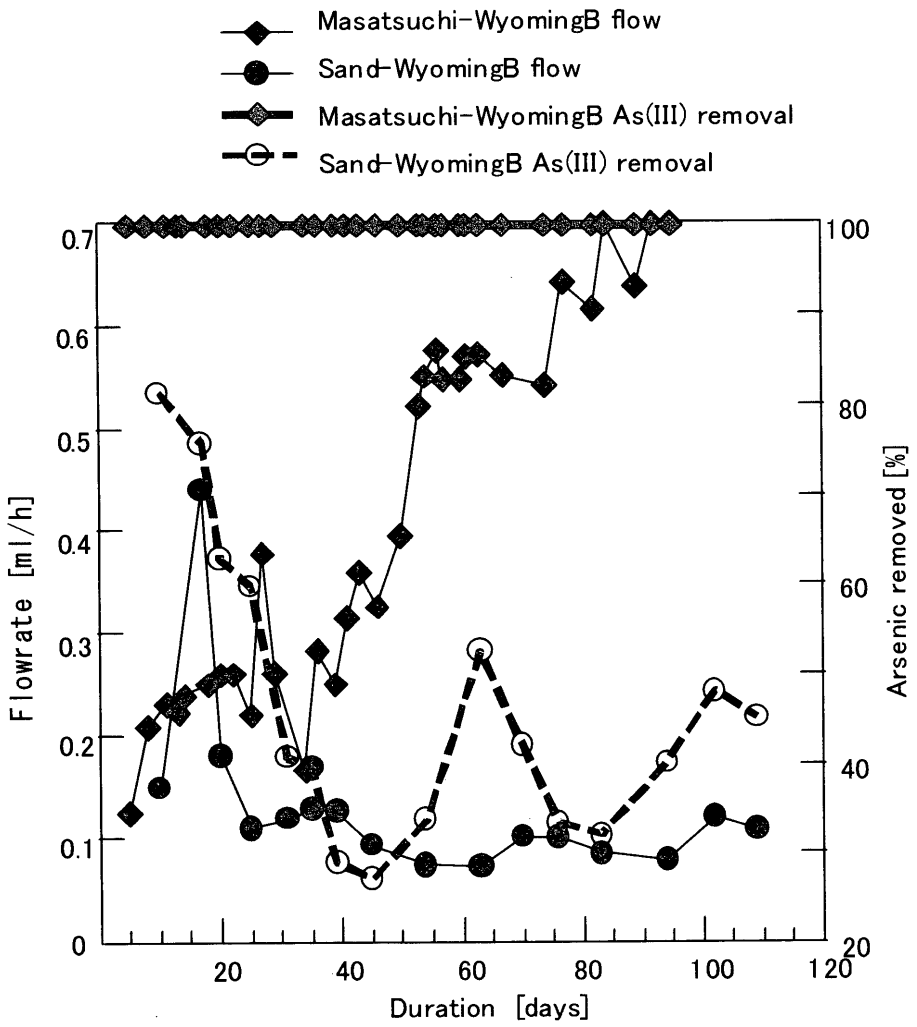

FIG. 6. Flow and As(III) removal profile for permeates through Masatsuchi-WyomingB and sand-WyomingB compactions.

compaction, only 248 ml permeated the sand-WyomingB compaction for 109 days. Increased permeation flow through the Masatsuchi-clay compaction did not alter its ability to adsorb arsenic. Using the capacity of the Masatsuchi soil's As(III) uptake of about 0.5 mg As(III) per gram of Masatsuchi soil, about 25 litres of a 4 ppm As(III) concentration can flow through before break-through. That is, for each ton of Masatsuchi soil employed in the landfill 0.5 kg of As(III) can be adsorbed.

CONCLUSIONS

The study has found that, Masatsuchi soil has a very high capacity for adsorbing As(V) as well as As(III) to a large extent. The soil arsenic adsorption capacity works quite well in a wider pH range. Murram soil has ability to adsorb arsenic but at lower capability compared to the Masatsuchi soil. The working pH range for Murram in adsorbing As(V) was rather small. Masatsuchi soil has also good advantage of maintaining its arsenic adsorption performance for both As(V) and As(III) species after mixing with bentonite clay. Murram As(V) adsorption dropped drastically after the soil was mixed with bentonite clay.

The main finding of this study was therefore, the possibility of applying multifunctional landfill protection materials without extra costs. Using soil-bentonite mixtures it was found that, Masatsuchi soil-WyomingB combination had the ability to remove all the As(III) from a concentration of 4 ppm when the solution was passed through a compaction similar to the ones employed into landfill sites. Similar compaction was tested for hydraulic conductivity, which was 5.7×10^{-9} cm s^{-1}. Compared to the enforced permeability limit of less than 1×10^{-7} cm s^{-1} for landfill barrier materials, Masatsuchi-clay is therefore a very good barrier material. The results are good news for the Japanese landfill companies which have been using Masatsuchi-bentonite mixture for landfill protection sites in Japan. By sampling soils and measuring both their permeability performance and adsorption characteristics, it is possible to

find suitable combination of soil-bentonite clay mixtures with desirable performance.

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