

Leaching of Arsenic from Wastes of Arsenic Removal Systems

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Abstract

Arsenic in groundwater was first detected in Bangladesh at Chapai Nawabgonj district in 1993. Since then arsenic contamination problem has been reported from almost every parts of the country. It is estimated that approximately 27% of the wells are contaminated with levels above 50ppb, the current drinking water standard for arsenic in Bangladesh (Kinninburg, D. G., et al., 2001). It is also estimated that about 77 million people are at risk of arsenic poisoning. A number of technologies are now available for end-of-the-pipe treatment arsenic present in groundwater. These are primarily based on coagulation and filtration. Some of the technologies use alum or ferric chloride as coagulants followed by filtration through a sand column. Other technologies are based on sedimentation and/or filtration through activated/doubly activated column/granular ferric hydroxide column. Aggressive leaching adopted in the Toxicity Characteristic Leaching Procedure (TCLP) at pH 5 when applied to the wastes collected from different arsenic removal units has not produced leachate concentrations significant enough to term the wastes toxic as per the USEPA regulatory levels. However, TCLP may not be suitable for assessment of long-term leaching of arsenic from arsenic-rich waste, because such leaching may be kinetically restricted. Thus, modification of TCLP to represent the natural leaching environment comparable to real disposal conditions is necessary. Tests under modified TCLP may provide different results. The users are currently practicing a number of arsenic-sludge disposal options. The sub-aqueous disposal

and buried in mud or mixed with organic matters has been considered for studying the anaerobic leaching of arsenic from solids and multiphasic sludge. This option addresses the situation where the users dispose the sludge/waste into a nearby pond where it is mixed with mud and a small amount of domestic sewage. For both the solid wastes and the multiphasic sludge, the leaching of arsenic into the overlying aqueous phase showed similar trend where the arsenic concentration peaked within the first week and then tapered off and disappeared after twelve weeks. Absence of residual arsenic in the solids following anaerobic leaching indicate that a significant amount of arsenic is lost through biomethylation induced by the presence of organic matters used in the leaching experiment.

INTRODUCTION

In the early 1970's nearly one quarter of a million children died each year in Bangladesh and West Bengal from water borne diseases. In response to this problem, approximately 4 million tubewells have been drilled during the last 30 years to provide reliable, pathogen-free drinking water. This was initiated by the UNICEF and promoted by the DPHE in a move to motivate people to practice better hygiene. In addition to this government and international initiatives the non-government organizations and private entrepreneur also installed tubewells for rural water supply in Bangladesh.

Arsenic in groundwater was first detected in Bangladesh at Chapai Nawabgonj district in 1993. Since then arsenic contamination problem has been reported from almost every parts of the country. It is estimated that approximately 27% of the wells are contaminated with levels above 50ppb, the current drinking water standard for arsenic in Bangladesh (Kinninburg, D. G., et al., 2001). It is also estimated that about 77 million people are at risk of arsenic poisoning. Arsenic contamination may cause skin lesions and cancer of the bladder, kidney, lung and skin along with cardiovascular problems. Very recently the national steering committee on arsenic has informed that about 8500 arsenic patients have so far been detected across the country. It has been suggested in the popular media that this may be the largest mass-poisoning in the history [*New York Times, November 10, 1998*]. It is beyond the accidents at Bhopal, India in 1984 and Chernobyl, Ukraine in 1986.

A number of studies have been conducted to develop suitable techniques to treat arsenic laden groundwater. Most of these are aimed at developing household and small community level units. Although removal of arsenic from drinking water is possible through highly sophisticated

treatment methods, they are often expensive and are only applicable at a centralized treatment plants used in a distribution network. At present, steps are being taken by these organizations to build awareness among users and to identify suitable alternatives (e.g. surface water, rain water, deep tubewell water, etc). In addition, the Government of Bangladesh (GOB), the Non-Government organizations (NGOs), the donor agencies, private entrepreneurs, etc. are promoting locally and internationally developed household and community level arsenic removal units. The treatment alternatives currently being studied and promoted by different Government and Non-government organizations, Donor agencies and Private entrepreneur include:

- Passive sedimentation followed by filtration.
- Filtration through sand column.
- Filtration through activated alumina column.
- Alum coagulation followed by filtration.
- Ferric chloride coagulation followed by filtration.
- Filtration through iron coated sand bed, brick chips.
- Filtration through granular ferric hydroxide.

Almost all the materials used for filtration get clogged after prolonged use. Some of these units may be regenerated by washing with water or other reagents. However, after certain time the filter column has to be discarded. It should be mentioned here that these spent filter media are likely to contain very high level of arsenic following continuous accumulation. Also, some of the arsenic removal units generate liquid sludge containing high level of arsenic associated with iron flocs. Indiscriminate disposal of these spent media or sludge is likely to contaminate the surface water sources or may leach arsenic, which may be transported to the underlying aquifer.

Although the above may be a matter of grave concern, it should be noted that not all the arsenic trapped in the discarded used filter media is likely to leach out. Thus, a study should be conducted to estimate the amount of leachable arsenic present in a used filter media and in a specific amount of sludge generated from an arsenic removal system.

Major objectives of the present study are: (i) Determining the concentration of total arsenic present in a specific filter media and sludge generated by coagulation prior to final disposal; (ii) Estimating the concentration of leachable arsenic in these filter media and sludge through Toxicity Characteristic Leaching Procedure (TCLP) developed and followed by the USEPA; (iii) Determining the leachable arsenic from

adsorbed filter media and sludge under anaerobic conditions created by decomposing organic wastes.

MATERIALS AND METHODS

To perform the TCLP test, the test equipment was locally manufactured as per the specifications of the USEPA (Fig. 1). Another setup for analyzing the leaching characteristics of arsenic from sludge and contaminated media soaked in wastewater submerged in pond water to simulate the field condition (in anaerobic conditions) was also constructed.

Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. Following criteria is followed in determining whether the TCLP test is required or not:

- a) If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate USEPA regulatory levels could not possibly be exceeded, the TCLP need not be run.
- b) If an analysis of any one of the liquid fractions of the TCLP extract indicates that a USEPA regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.
- c) If an analysis of extract obtained using a bottle extractor shows that the concentration of any USEPA regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE (Zero Headspace Extractor) is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

Summary of the Method

- i) For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter is defined as the TCLP extract.

- ii) For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μ m glass fiber filter.
- iii) If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

Reagents and Acids

Reagent grade chemicals should be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. The following acids are essential in conducting TCLP: (a) Hydrochloric acid (1N), HCl, made from ACS reagent grade; (b) Nitric acid (1N), HNO₃, made from ACS reagent grade; (c) Sodium hydroxide (1N), NaOH, made from ACS reagent grade; (d) Glacial acetic acid CH₃CH₂COOH ACS reagent grade.

Extraction Fluid

Extraction fluid # 1 is prepared by adding 5.7mL glacial CH₃CH₂COOH to 500mL of reagent water and 64.3mL of 1N NaOH, and diluted to a volume of 1 liter. When correctly prepared, the pH of this fluid should be 4.93 \pm 0.05. Extraction fluid # 2 is prepared by diluting 5.7mL glacial CH₃CH₂COOH with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid should be 2.88 \pm 0.05.

These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid should be discarded and fresh extraction fluid be prepared. TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs. Extracts should be preserved according to the guidance given in the individual analysis methods.

Preliminary Evaluation for TCLP

Preliminary TCLP evaluation is performed on a minimum 100gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids; (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration; (3) determination of whether the solid portion of the waste requires particle size reduction; and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste.

Preliminary Determination of Percent Solids

Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

If the waste obviously yields no liquid when subjected to pressure filtration (i.e., is 100% solids) the extraction procedure should be followed without delay. If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required.

If the percent dry solids is less than 0.5%, the multiphasic analysis method should be followed for nonvolatile TCLP. Otherwise, if the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, particle size reduction analysis should be performed with a fresh portion of waste. Then the appropriate extraction liquid should be determined.

Determination of Appropriate Extraction Fluid

If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents, the appropriate fluid for the non-volatile extraction should be determined as below:

Weigh out a small sub-sample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500mL beaker. Add 96 .5mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, extraction fluid #1 should be used. If the pH from is >5.0, add 3.5mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes. Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2.

TCLP for Non-volatiles

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, weigh out a sub-sample of the waste (100 gram minimum) and extraction should be done directly as described later. Otherwise, if the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration as described earlier in the pre-evaluation steps.

Following filtration, if required, the material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. The filtrate should be weighed. The liquid phase may now be either analyzed (as described later) or stored at 4°C until time of analysis.

If the waste contains < 0.5 % dry solids then it should be considered the TCLP extract and be preserved for analysis by following the instruction described later. However, if the percent of solids is >0.5% then it should be determined whether particle size reduction is necessary. If not then TCLP extraction procedure should be followed. Amount of extraction fluid needs to be added in the extraction vessel is determined by:

$$\text{Wt. of extraction fluid} = [20 \times \% \text{ solids} \times \text{wt. of waste filtered}] / 100$$

This amount of appropriate extraction fluid is slowly added to the extractor vessel. It is then closed tightly, secured in rotary agitation device, and is rotated at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at $23 \pm 2^\circ\text{C}$ during the extraction period. It is important to note that as agitation continues, pressure may build up within the extractor bottle for some types of wastes (limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

Following the 18 ± 2 hour extraction, the material in the extractor vessel should be separated into its component liquid and solid phases by filtering through a new glass fiber filter. If compatible (e.g., multiple phases will not result on combination), the filtered liquid resulting from the above step should be combined with the initial liquid phase of the waste obtained. This combined liquid is defined as the TCLP extract.

Analysis of TCLP Extract

Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metal analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm 0.5\%$), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final analyte concentration} = [V_1C_1 + V_2C_2] / [V_1 + V_2]$$

Where,

V_1 = The volume of the first phase (L).

C_1 = The concentration of the analyte of concern in the first phase (mg/L).

V_2 = The volume of the second phase (L).

C_2 = The concentration of the analyte of concern in the second phase (mg/L).



Figure 1: TCLP Agitation apparatus constructed at BUET

Sample Collection

In order to achieve the objectives, a number of spent filter media and sludge samples have been collected, prior to disposal, from the arsenic removal units currently being used in different parts of Bangladesh. The DPHE/DANIDA units are currently being used at Noakhali. These are mainly coagulation-filtration based units. Ten sets of sludge samples have been collected from the Noakhali area. Some of these are semi-solid sludge samples and others are solid sludge samples collected from the filtration units. 10 more samples have been collected from the arsenic removal units developed by the Environmental Engineering Division of BUET under the BUET-UNU joint research program. These units have been installed at Barura, Comilla and are working without breakthrough for the past eighteen months. Sidko Ltd. supplied one sample from the granular ferric hydroxide based technology. Similarly, 17 multiphasic samples were collected of which 14 are of DPHE-DANIDA BTU at Noakhali, 2 from Stevens Institute of Technology units at Sonargaon and 1 from BUET Activated Alumina based unit (older model) at Sonargaon. During the sample collection process the methodology used, the condition of the unit and the length of use have also been recorded.

Sample Preparation

Twenty samples collected from the aforementioned treatment units have been analyzed for the determination of total arsenic content per unit weight of the dry sample. Standard Method 3050B (Clesceri, et al., 1998) was used to extract arsenic from the collected sludge and spent media for subsequent analysis using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS – Shimadzu, AA- 6800). Determination of

total arsenic content in the spent media and the multi-phasic sludge was performed to ascertain the fraction of arsenic leaching out of each medium following TCLP and anaerobic digestion. Simultaneously, solid samples from spent filter media were set up to perform the Toxic Characteristic Leaching Procedure (TCLP) following the USEPA method 1311 (USEPA, 1992).

RESULTS AND DISCUSSION

To conduct the TCLP tests a number solid and multiphase samples have been collected from different arsenic affected areas focusing on various arsenic removal technologies currently in operation. Fourteen solid samples comprising of 10 samples from Bucket Treatment Units (BTU) developed by the DPHE-DANIDA currently in operation at Noakhali. During the sampling operation information on the location, feed water arsenic concentration, volume of water treated during the period between last cleaning and the time of collection and the names of the owners of the units were recorded.

Following collection the samples were sorted into two groups: solid and multiphase (liquid/semi-liquid). This was done by filtering and weighing to determine the percentage of solids present. The type of extraction fluid to be used for the extraction process was determined as described in the earlier section. Subsequently, TCLP extractions were performed on the solid samples following the procedure described earlier using a locally constructed extraction apparatus as per the specifications of the USEPA. The solid samples were also digested using aqua-regia as described in the Standard Methods (Clesceri, et al., 1998) for total extraction of heavy metals. Following extraction, the amount of arsenic present in each extracted liquid was determined using an Atomic Absorption Spectrophotometer equipped with a graphite furnace (Shimadzu Model AA-6800). Figures 23 represent the results of the analysis of solid samples.

According to the USEPA, if the extract from a representative waste sample contains any of the listed contaminants at a concentration equal to or greater than the respective value, the waste itself is considered to be toxic. For arsenic this concentration is 5.0mg/L (USEPA, 1992). Since the arsenic concentration in the TCLP extract of the solid samples range between 2 – 220 µg/L, it is apparent that none of the solid sludge collected from different Arsenic Removal Units (ARU) exhibits toxicity as per the definition of the USEPA.

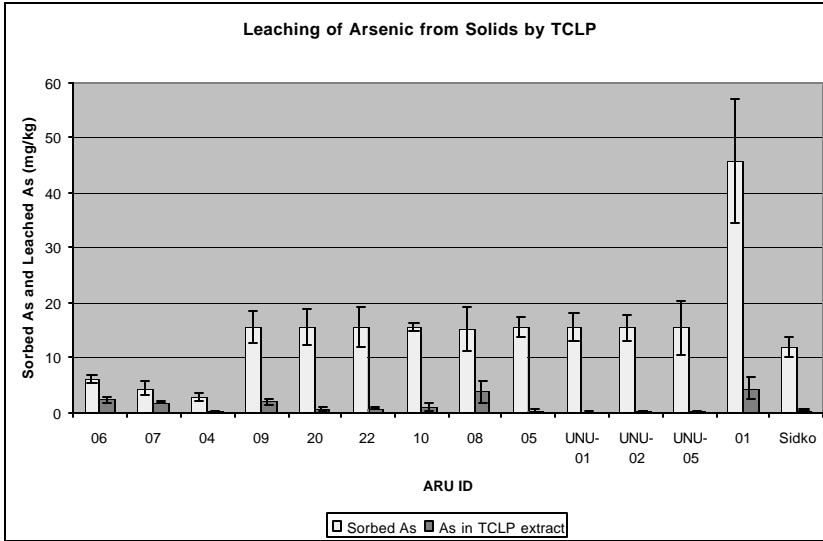


Figure 2: Comparison of arsenic sorbed on and extracted by TCLP conducted on solid samples

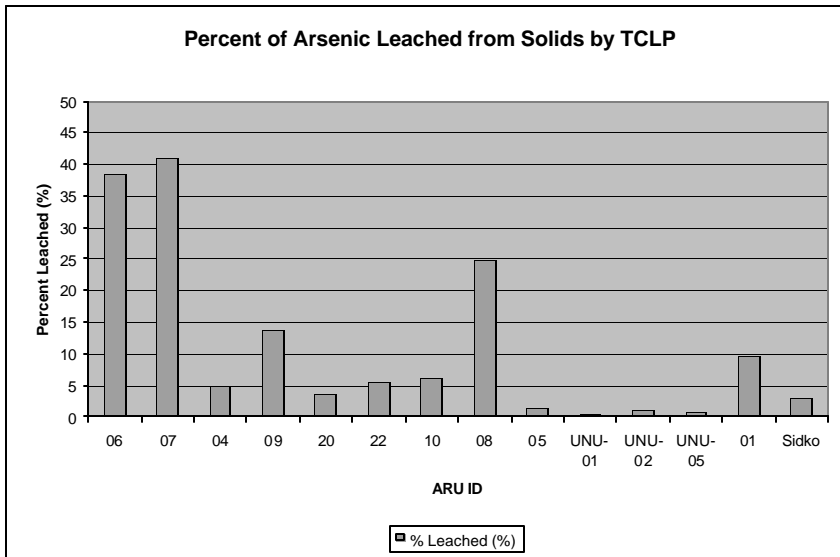


Figure 3: Percentage of arsenic leached from solids samples by TCLP

The total amount of arsenic accumulated during the period between the last washing of the sand filter and the time of collection was estimated to be the product of the volume of water treated during this period and the corresponding feed water arsenic concentration. However, the amount of arsenic sorbed on the sand particles is not uniform across the depth of the filter column and the adsorption sites may have been filled up in the top portion of the filter column. The ferric chloride based units leached the lowest amount of arsenic from the solid (sand) samples ranging between 0.05 – 0.2 mg/kg (0.3 – 1.2% by wt.). On the other hand, the bucket treatment units leached considerably higher amount of arsenic from sand under TCLP ranging between 7 – 220 mg/kg (1.6 – 41% by wt.)

As mentioned earlier, if the solids content in the sample is >0.5% the TCLP extraction procedure should be followed for the solids and the extracted fluid should be mixed with original filtered liquid for analysis only if they are compatible. The 17 multiphase samples collected during this study were first filtered. The solid contents of all these samples were found to be >0.5% (1-9.5%). Thus, the TCLP extraction was performed on these samples and the extracted liquids were then mixed with the corresponding filtrate for analysis. The amount of arsenic present in each extracted liquid was determined using an Atomic Absorption Spectrophotometer equipped with a graphite furnace (Shimadzu Model AA-6800). Figures 4 and 5 represent the results of the analysis of multiphase sludge samples.

It should be noted that in general the arsenic levels are very high in the TCLP extract of the multiphase sludge compared to the same of the solid samples. This is because of the fact that the multiphase sludge samples were collected primarily from the first bucket of the arsenic removal units where major portion of the arsenic present in the feed water is removed through coagulation. Figure 4 shows the relatively high levels arsenic per unit mass of the sludge. Since most of the arsenic is removed through coagulation relatively low level of arsenic is adsorbed on the solids as shown in Figure 2. Figure 5 shows a comparison of the arsenic levels in the feed water and the TCLP extract of the corresponding multiphase sample.

Leaching under Anaerobic Condition

The Toxicity Characteristic Leaching Procedure (TCLP) is primarily performed for screening of wastes for toxicity/reactivity and to determine the stability of the waste for the pollutants under consideration. Aggressive leaching adopted in TCLP at $\text{pH} \leq 5$ may not be suitable for analysis of arsenic laden wastes where arsenic is sorbed onto hydrous ferric oxy-hydroxides. These are less leachable at $\text{pH} 5$ relative to near

neutral pH values or alkaline conditions. Therefore TCLP testing at pH 5 would likely to show low leaching of ferric oxy-hydroxide wastes. In addition, leaching under natural conditions is not simulated in TCLP.

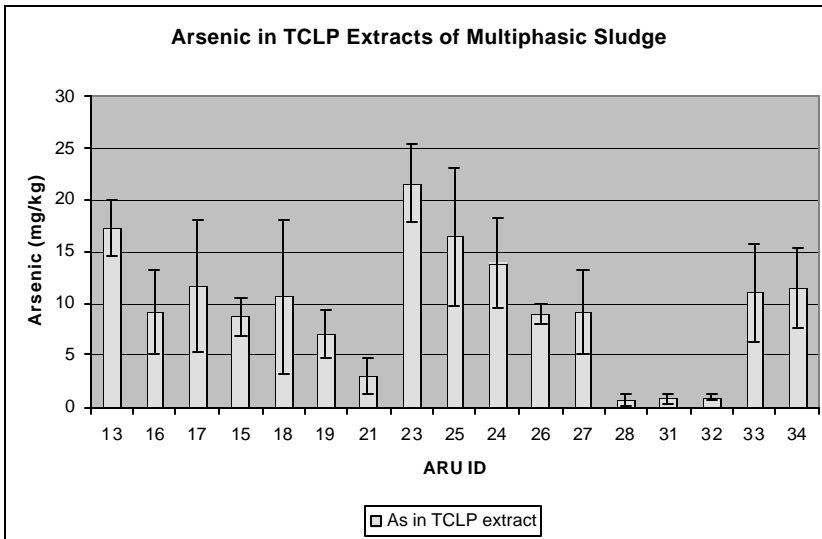


Figure 4: Leaching of arsenic from multiphasic sludge by TCLP

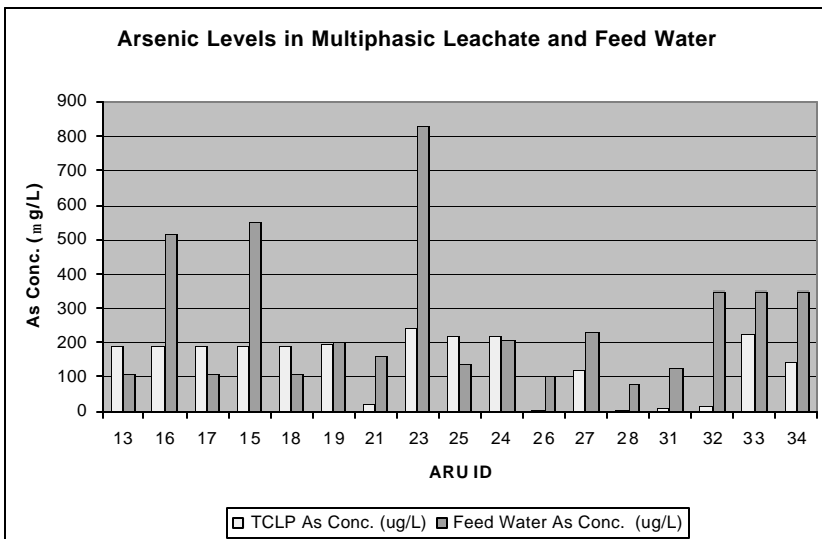


Figure 5: Comparison of arsenic levels in feed water and leachate of multiphasic sludge.

The expected natural disposal conditions in a rural household may include:

- On-land disposal in typical non-hazardous landfill dump or backyard,
- Sub-aqueous disposal,
- Sub-aqueous disposal and buried in mud or mixed with organic matters.

The first disposal depicts the situation where the users throw away the spent media or the liquid/multiphasic sludge in their backyard or the waste is centrally collected and disposed off at a local landfill. The second option depicts the situation where the users dispose off the waste and/or sludge into a ditch or nearby lowland, which is seasonally inundated. The third option addresses the situation where the users dispose the sludge/waste into a nearby pond where it is mixed with mud and/or cow dung or domestic sewage. Although its effectiveness in restricting the leaching of arsenic from wastes/sludge has not been extensively studied, the last option has been promoted in different forums. It is likely that the arsenic waste/sludge will be subjected to anoxic/anaerobic leaching under such disposal conditions.

Although all the three disposal options are likely to take place at all locations, due to resource constraints the study is focused on the third disposal option where leaching of arsenic sludge/waste mixed with organic matters in aqueous media is dominant condition. It is imperative that the experimental set-up simulates these conditions in the laboratory. A laboratory test procedure has been developed to simulate the anaerobic leaching conditions described above. Thus, an equal mass mixture of waste and organic mud collected from a local pond sediment bottom and a small amount of sewage and are placed in a large (preferably 2 litre) flask. The flask is filled up with pond water and is sealed with a liner that prevents oxygen penetration but allows insertion of a needle/syringe for sampling. The water column was made anoxic by bubbling nitrogen gas before capping. The top end had a hole for sampling, which was kept plugged, except for the time of sampling. Samples were collected using a syringe initially at one-week intervals and later one at four weeks interval. The experimental design for sub-aqueous disposal in an anoxic environment is provided in Fig. 6 and Fig. 7.

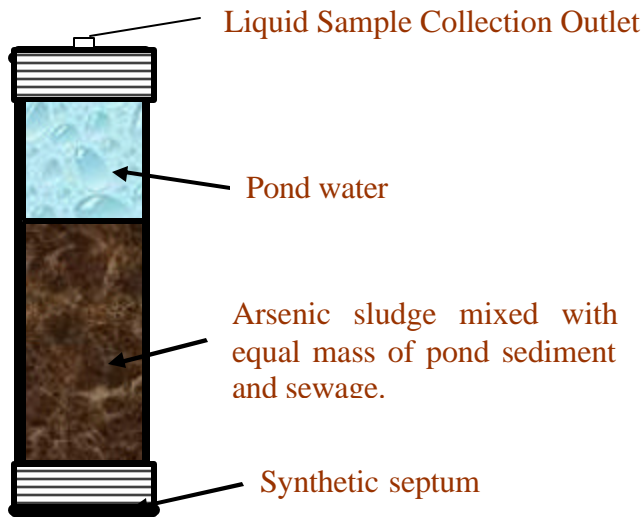


Figure 6: Schematic diagram of the anaerobic digestion chamber for the arsenic sludge



Figure 7: Setup of anaerobic digestion chamber for the arsenic wastes developed at BUET

Analyses of Anaerobic Leaching Results

Anaerobic leaching of arsenic from arsenic removal units has been studied in two phases. Continuous monitoring of the arsenic concentrations in the supernatant water has been performed for one year. Initially sampling was done once a week for three months, then once a month for two months and then once in two months till the end of one year. Samples were set in two groups: one set for the solid waste and the other set for the multiphasic sludge.

The BUET-UNU developed ferric chloride based ARU leaches out the lowest level of arsenic from the solids into the overlying water column under anaerobic condition. These had also produced the lowest levels of arsenic in the leachate following TCLP. At the initial stage, one of the BTUs developed by DPHE-DANIA has recorded the highest level of arsenic in the leachate from its solid wastes under anaerobic condition. However, rest of the BTUs have produced very low levels of arsenic comparable to the BUET-UNU units. On the other hand, the solid wastes from granular ferric hydroxide based technology supplied by Sidko Ltd. produced moderately high level of arsenic in the leachate under similar conditions. It should be noted that by the end of the 12th week the arsenic concentrations in the overlying water column for all the solid waste samples reduce to zero indicating that the end of the leaching process (Fig. 8).

The second set of anaerobic leaching columns containing multiphasic sludge samples showed a trend similar to those of the solids, where the arsenic levels in the overlying water column increased to the highest level during the first week and then tapered off to zero by the end of the 11th week. The arsenic level in the water columns of the DPHE-DANIDA BTUs showed the lowest values, whereas the activated alumina based unit of BUET (Older Model) and the Stevens Institute of Technology showed high levels of arsenic under the anaerobic leaching condition (Fig. 9).

Total extraction of arsenic following the completion of the anaerobic leaching experiment revealed negligible amount of arsenic sorbed on the solids. It is evident that significant portions of the arsenic initially sorbed on the solids have been lost to the environment during the course of the experiment. This loss may be attributed to the loss due to bio-methylation with the organic present in the mud and sewage. Preliminary results of a BUET research project currently being conducted on anaerobic leaching of arsenic under different environmental conditions have shown similar trends. Similar kinetics has been cited in a number of studies (Rodriguez, R. R., et. al., 1999).

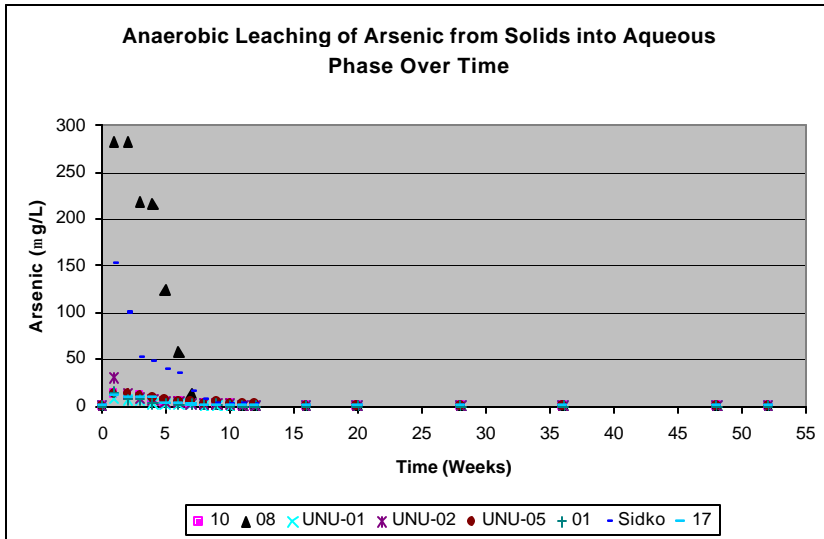


Figure 8: Anaerobic leaching of arsenic from solids into overlying water column

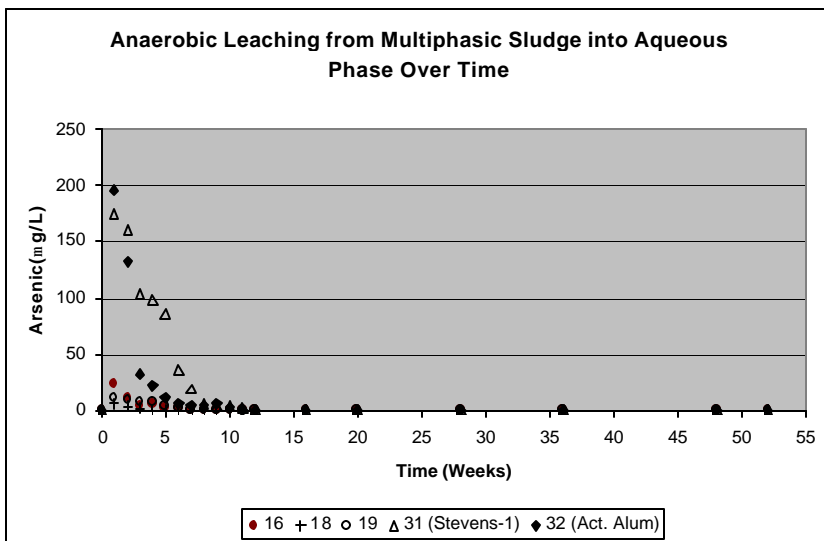


Figure 9: Anaerobic leaching of arsenic from sludge into overlying water column

CONCLUSIONS

A number of technologies are now available for end-of-the-pipe treatment arsenic present in groundwater. These are primarily based on coagulation and filtration. Some of the technologies use alum or ferric chloride as coagulants followed by filtration through a sand column. Other technologies are based on sedimentation and/or filtration through activated/doubly activated column/granular ferric hydroxide column.

The Toxicity Characteristic Leaching Procedure (TCLP) is primarily performed for screening of wastes for toxicity/reactivity and to determine the stability of the waste for the pollutants under consideration. Aggressive leaching adopted in TCLP at $\text{pH} \leq 5$ when applied to the wastes collected from different arsenic removal units has not produced lechate concentrations significant enough to term the wastes toxic as per the USEPA regulatory levels. However, TCLP may not be suitable for assessment of long-term leaching of arsenic from arsenic-rich waste, because such leaching may be kinetically restricted. Thus, modification of TCLP to represent the natural leaching environment comparable to real disposal conditions is necessary. Tests under modified TCLP may provide different results. Initial results of some studies conducted at BUET where continuous flow of water was passed through a column of solid waste show very high levels of leachable arsenic compared to the TCLP.

Although a number of disposal options are currently being practiced by the users, the sub-aqueous disposal and buried in mud or mixed with organic matters has been considered for studying the anaerobic leaching of arsenic from solids and multiphasic sludge. This option addresses the situation where the users dispose the sludge/waste into a nearby pond where it is mixed with mud and a small amount of domestic sewage. For both the solid wastes and the mutiphasic sludge the leaching of arsenic into the overlying aqueous phase showed similar trend where the arsenic concentration peaked within the first week and then tapered off and disappeared after twelve weeks. Absence of residual arsenic in the solids following anaerobic leaching indicate that a significant amount of arsenic is lost through bio-methylation induced by the presence of organic matters used in the leaching experiment.

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