

TCLP Underestimates Leaching of Arsenic from Solid Residuals under Landfill Conditions

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Recent revision of the arsenic in drinking water standard will cause many utilities to implement removal technologies. Most of the affected utilities are expected to use adsorption onto solid media for arsenic removal. The arsenic-bearing solid residuals (ABSR) from adsorption processes are to be disposed of in nonhazardous landfills. The Toxicity Characteristic Leaching Procedure (TCLP) tests whether a waste is hazardous or nonhazardous; most solid residuals pass the TCLP. However, the TCLP poorly simulates the alkaline pH, low redox potential, biological activity, long retention time, and organic composition of mature landfills. These same conditions are likely to favor mobilization of arsenic from metal oxide sorbents. This study quantifies leaching of arsenic from Activated Alumina (AA) and Granular Ferric Hydroxide (GFH), two sorbents expected to be widely used for arsenic removal. The sorbents were subjected to the TCLP, the Waste Extraction Test (WET), an actual landfill leachate, and two synthetic leachate solutions. Up to tenfold greater arsenic concentration is extracted by an actual landfill leachate than by the TCLP. Equilibrium leachate concentrations are not achieved within 18 h (the TCLP duration) and an N₂ headspace and end-over-end tumbling increase the rate of arsenic mobilization. However, tests with actual landfill leachate indicate the WET may also underestimate arsenic mobilization in landfills.

Introduction

The Maximum Contaminant Level (MCL) of arsenic in drinking water was recently lowered from 50 µg/L to 10 µg/L. This will cause nearly 4000 US utilities to implement new or modified technologies for arsenic removal (1). Arsenic-bearing solid residuals (ABSR) from these operations are expected to be disposed of in landfills, where potential arsenic remobilization presents an obvious environmental concern. This potential is assessed by the Toxicity Characteristic Leaching Procedure (TCLP) (2, 3, 4, 5), although a few areas use the California Waste Extraction Test (WET) (6). The TCLP is designed to expose the waste to conditions more conducive to toxic leaching than landfill conditions and, by comparing the concentration leached to a toxicity characteristic (TC) regulatory limit, determine if the waste can be disposed in a nonhazardous landfill. Currently the residuals from most

arsenic-removal technologies pass the TCLP and are considered safe for disposal in nonhazardous, mixed solid-waste (MSW) landfills. The arsenic TC is 5 mg/L, although this regulatory limit is generally set at 100 times the MCL. However, even if the TC is lowered to 1 mg/L in line with the new arsenic MCL, the Environmental Protection Agency (EPA) believes that arsenic residuals would not be classified as hazardous waste and would remain suitable for nonhazardous landfilling (1).

Of the EPA-identified treatment options, adsorption onto solid media is favored for small facilities (those serving populations of less than 3301), which comprise over 92% of the impacted utilities (1). Activated alumina (AA) and granular ferric hydroxide (GFH) have been identified as solid adsorbents that will be widely used for arsenic removal. Although activated alumina is a best-available technology (BAT), GFH trials indicate it may be preferable due to a capacity more than 5x that of AA (3). A large number of other alternative sorbents have been developed (i.e., Bayoxide E-33, green sand, Aqua-bind, and iron-modified AA), but nearly all exhibit an alumina or iron oxy/hydroxide surface (7) and all will generate an ABSR. For other technologies (i.e., membrane filtration and ion exchange) that produce a liquid residual stream, the liquid residuals will typically need to be treated on site. The recommended process is adsorption/coprecipitation with amorphous ferric hydroxide (AFH, Fe(OH)₃·nH₂O) induced by addition of a ferric salt (typically FeCl₃). The residual for final disposal will be AFH, which like other ABSR, will be evaluated using the TCLP (8).

Most previous research has studied arsenic adsorption. Much less work is available on desorption. Because landfill disposal is characterized by long residence times, arguably sorption behavior will be near equilibrium and adsorption/desorption endpoints analogous. However, differences between adsorption and desorption kinetics may not be ignored in the design and interpretation of the shorter-duration leaching tests such as the TCLP and its surrogates. Myneni et al. (9) compared the adsorption and desorption of arsenate on Ettringite and found a similarity between adsorption and desorption equilibrium concentrations, but much slower desorption than adsorption kinetics. This is consistent with spectroscopic and pressure jump studies of arsenate sorption on goethite, which suggest a two-step adsorption process followed by slower relaxation to a more stable bidentate, inner-sphere bonding state (10, 11). A further convoluting factor may be surface precipitation. When the solution composition surrounding the ABSR changes (as with exposure to a test leaching solution or disposal in a landfill), the solid substrate surface layer may slightly solubilize and release ions that subsequently participate in surface precipitation reactions to form new solid phases and potentially incorporate arsenate or cover over previously sorbed arsenate (12, 9). This work only considers desorption, but some results are discussed with reference to adsorption results from other researchers. This does not imply that adsorption kinetics and mechanisms are the same as for desorption. Indeed, the porous nature of the sorptive media, AA and GFH, suggests hysteretic kinetics are likely. However, the kinetic differences between adsorption and desorption does not negate the utility of judiciously using equilibrium adsorption results to explain the direction of desorptive changes, keeping in mind that slow desorption kinetics may prevent equilibria from being achieved (or even approached) within the time frame of interest.

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TABLE 1. Characteristics of the Synthetic Extractants and Landfill Leachates

| test | pH | ORP (mV) | alkalinity (mg/L as CaCO ₃) | TOC (mg/L) | TDS (mg/L) | ionic strength (M) |
|-----------------|---------|----------|---|------------|------------|--------------------|
| TCLP | 4.95 | 103.5 | 766 | 38.6 | 1480 | 0.08 |
| WET | 5.05 | 74 | 7940 | 55.8 | 5160 | 0.10 |
| SL1 | 7.03 | 121.4 | 1500 | 1050 | 5200 | 0.03 |
| SL2 | 7.55 | -37 | 12 500 | 1310 | 8600 | 0.49 |
| LL ¹ | 6.82 | 36.1 | 1100 | 160 | 3600 | 0.33 |
| LL ² | 4.5-9.0 | N/R* | 300-11 500 | 30-29000 | 2000-60000 | N/R |
| LL ³ | 6.5-8.2 | N/R | 1250-8050 | N/R | 1960-16800 | N/R |
| LL ⁴ | 6.2-7.1 | N/R | N/R | 236-3160 | N/R | N/R |

N/R*: Values Not Reported. LL¹: Leachate collected from Tangerine Road Landfill, Tucson, AZ. LL²: Leachate composition reported in Christensen et al., (27). LL³: Leachate composition reported in Jang et al. (22). LL⁴: Leachate composition reported in Hooper et al. (5).

The arsenic in potable water supplies is in either the arsenite, As (III), or arsenate, As (V), oxidation states (8). In near-neutral waters arsenite is primarily fully protonated and uncharged as arsenous acid (H₃AsO₃) (pK_{a1} 9.2), whereas arsenate is predominantly in an anionic form (pK_{a1} 2.2, pK_{a2} 7.0 and pK_{a3} 11) (13). Metal oxy/hydroxide adsorption/desorption of ions is typically more efficient than of neutrals (14, 15, 16, 17). Thus, water containing a significant fraction of arsenite is recommended to undergo preoxidation prior to the application of an arsenic removal technology (1). Consequently, in this research, only leaching from residuals loaded with the arsenate ion is studied.

Besides pH, a number of other compositional characteristics of water or leachate influence arsenic sorption. In general, as ionic strength increases the fraction of contaminant sorbed decreases (14, 15). However, individual ions have differing affinities for surface groups and differ in their effectiveness in displacing sorbed arsenate. Added simultaneously, anions such as sulfate and phosphate directly compete with arsenate for surface sites (18, 19). However, they are much less effective (kinetically very slow) at displacing previously sorbed arsenate (10, 12). The concentration of Natural Organic Matter (NOM) may significantly decrease arsenate adsorption on metal oxide solids (20, 3). In addition, activated alumina sorption of arsenate is known to be more affected by the presence of other anions than iron oxide sorption (8). Finally, the iron oxide, ferrihydrite (Fe(OH)₃·nH₂O), has a much different sorption capacity than the iron oxide, goethite (FeOOH), into which ferrihydrite naturally ages by dehydration (21).

An appropriate leaching test must expose the waste to a solution in which the leach solution composition provides a more aggressive condition than a nonhazardous landfill leachate. Table 1 shows the composition of typical landfill leachates. In a landfill, pH, alkalinity, and TOC may be as high as 9.0, 11 500 mg/L, and 29 000 mg/L, respectively. The landfill residence time will range from days to months. In contrast, the TCLP specifies an acidic pH, an oxidizing and abiotic environment, and a short (18 h) contact duration. A component of this study exposed ABSRs to actual landfill leachate as well as to TCLP and WET-specified leachates. The results discussed are interpreted as abiotic tests due to their typically short duration, although microbe inhibitors were not added. This study does not intend to quantify all individual factors affecting the appropriateness of TCLP and WET protocols for evaluating ABSR leaching. It does attempt to answer whether these standard abiotic tests are appropriate for such evaluation and indicate whether an alternative, more appropriate protocol should be developed.

Materials and Methods

Sorbents. Conventional AA has been implemented for the selective removal of arsenic from potable water (22). Although it also removes other contaminants (i.e., fluoride and sulfate), it is somewhat selective for arsenic. The AA used is AA400G, manufactured by Alcan. The properties, according to the

manufacturer's product specifications, are particle size, 80-100mesh; specific surface area, 350-380m²/g; and pore volume, 0.50 cm³/g. This sorbent can be regenerated, although this is not expected to be frequently practiced (1, 23).

Granular ferric hydroxide (GFH) is a weakly crystalline β-FeOOH produced by conditioning previously compacted iron hydroxide slurry into irregular grains up to 2 mm diameter (19). To preserve its activity, the material must not be dried. GFH particles specifically adsorb As(V). Under comparable conditions, GFH is estimated to have fivefold or greater capacity than AA (3). GFH is manufactured by GEH and distributed in the United States by U. S. Filter. It is designed as a throw-away media.

Leaching Trials. Single batches of AA and GFH were preequilibrated with arsenate. For each, a solution was prepared with 150.0 g of sorbent in 1.00 L of solution. The initial concentration of arsenic added was 190 mg/L (as As) and 1080 mg/L (as As) for AA and GFH, respectively. After equilibration the aqueous concentration was 21.8 μg/L (as As) and 31.0 μg/L (as As) for AA and GFH, respectively. The sorbed concentrations were 1.27 mgAs/gAA and 7.2 mgAs/gGFH. All solutions were made using purified water (Milli-Q Water System by Millipore). Arsenate was added as Sodium Arsenate Heptahydrate (Na₂HAsO₄·7H₂O, KR Grade Aldrich Sigma). The solution ionic strength was adjusted to 0.1 M with NaCl (GR Grade EM Science). After 48 h of equilibration on a shaker table (Orbit, reciprocating speed 125 rpm), liquid samples were collected and analyzed. All subsequent leaching tests used GFH and AA from these single batches.

The TCLP specifies that samples be rotated end over end, whereas the WET specifies shaker table agitation. The duration of extraction is 18 ± 2 h and 48 h for the TCLP and WET, respectively. For all tests, the leaching temperature is 23 °C. Finally, the WET headspace is purged vigorously with N₂ prior to sealing and agitation, whereas the TCLP headspace is ambient air. For this study, all leaching tests were compared for both extraction durations (18 and 48 h), both agitation methods (shaker table and tumbler), and both headspace treatments (N₂ and ambient). Following leaching, the liquid for all samples was filtered through a 0.45μm glass fiber filter before analysis. The initial characteristics of the leaching solutions are shown in Table 1.

TCLP. The appropriate extraction fluid for both AA and GFH is extraction fluid #1 of the TCLP (2). This is prepared by adding 5.7 mL of glacial acetic acid (CH₃CH₂OOH) to 64.3 mL of 1N NaOH and bringing the mixture up to 1000 mL with deionized water. The pH is 4.93 ± 0.05. When a waste contains both solid and liquid phases, with the solid being more than 0.5 wt %, the TCLP prescribes a sample size of 100 g (solid plus liquid phase) and an addition of 1.950 L of extraction fluid to each sample. For this work, the TCLP was run at 0.05 scale, but checks on the reproducibility of results showed no drawback with this approach. The solids did not require size reduction.

TABLE 2. Composition of Simulated Leachate 1 (SL1) and Simulated Leachate 2 (SL2). the VFA Mixture in SL2 Is Identical to that in SL1

| SL1 | concentration (mg/L) |
|-----------------------------|----------------------|
| acetic acid | 576 |
| propionic acid | 192 |
| butyric acid | 422 |
| valeric acid | 163 |
| caproic acid | 232 |
| ammonium chloride | 2680 |
| sodium bicarbonate | 2520 |
| TOC | 1050 |
| pH | 7.0 |
| SL2 | |
| calcium carbonate | 1100 |
| sodium carbonate | 11 500 |
| ammonium chloride | 650 |
| TOC (VFA mixture) | 1310 |
| sodium citrate | 46 400 |
| hydroxylamine hydrochloride | 31.7 |
| pH | 7.5 |

WET. According to WET (6), the ABSRs studied are classified as Type (ii) substances. The solids and liquids are separated by vacuum filtration. The solids obtained passed through a No. 10 sieve, so no further milling was required. The WET extraction solution consists of 0.2-M sodium citrate at pH 5.0 ± 0.1, prepared by titrating analytical grade citric acid in Milli-Q water with 4-N NaOH. Five grams of the solid waste is placed in a glass container with 50 mL of the extraction solution.

Landfill Leachate (LL). Landfill leachate was obtained from the Pima County, Tangerine Road Landfill, Tucson, Arizona. The leachate was extracted from a cell containing mixed municipal waste. The composition of the actual leachate along with literature values (4, 24, 25) are shown in Table 1. Consistent with the TCLP protocol, 5.00 g of solid was treated with 97.5 mL of leachate.

Simulated Leachate 1 (SL1). A solution of volatile fatty acids (VFA) was prepared, consisting of 5 acids of low molecular weight in order to mimic the TOC concentration and approximate the makeup of landfill leachate (Table 2). Ammonium chloride and sodium bicarbonate were added to mimic the concentrations found in a mature landfill leachate. The pH was adjusted to 7.0 using 0.1-N NaOH. Analogous to the TCLP protocol, 97.5 mL of this solution was added to 5.00 g of the solid waste.

Simulated Leachate 2 (SL2). A second, more aggressive simulated leachate was prepared consisting of higher organic concentrations, ionic strength, and pH (Table 2). In addition to the 5 VFAs that were used in SL1, sodium citrate was added at the concentration used in the WET test. Hydroxylamine was added to create a reducing environment commensurate with the low ORP of mature landfills. The pH was adjusted to 7.5 using 0.1-M NaOH. To 5.00 g of the solid waste was added 97.5 mL of this solution.

Analytic Methods. Arsenic was measured using HPLC for pretreatment and species separation followed by Ion Coupled Plasma Mass Spectrometer (ICP-MS, Agilent 7500a) for detection. The system is an Agilent 1100 HPLC (Agilent Technologies, Inc.) with a reverse-phase C18 column (Prodigy 3u ODS(3), 150 × 4.60 mm, Phenomenex, Torrance, CA) maintained at 50 °C. The mobile phase (pH 5.85) contained 4.7mM tetrabutylammonium hydroxide, 2mM malonic acid, and 4% (v/v) methanol at a flow rate of 1.2 mL/min. The detection limit for this instrument was 0.1 µg/L for arsenic speciation, and 0.01 µg/L for arsenic totals. Analysis of replicates was within ± 5%. ORP measurements were made with a Platinum Single-Junction Electrode calibrated using ZoBell's solution (K₄Fe(CN)₆·3H₂O/K₃Fe(CN)₆ redox couple).

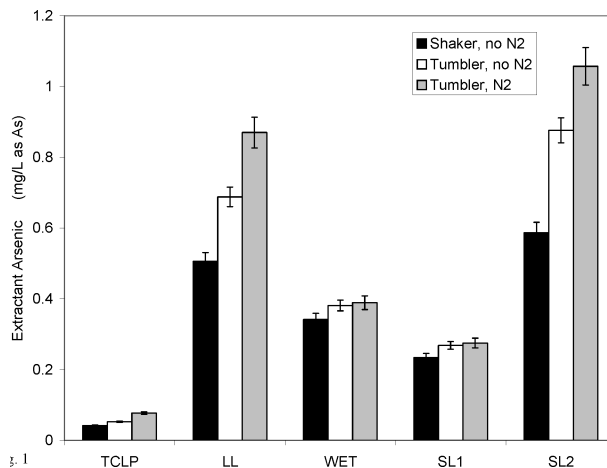


FIGURE 1. Concentration of total arsenic (arsenite + arsenate) in solution leached from AA after 18 h exposure using tumbler agitation with and without a N₂ headspace and shaker table agitation without a N₂ headspace. Error bars show one standard deviation for replicates. (TCLP: Toxicity Characteristic Leaching Procedure, WET: Waste Extraction Test, SL1: Simulated Leachate 1, SL2: Simulated Leachate 2, LL: Landfill Leachate).

The aluminum concentration was measured using a Graphite Furnace Atomic Absorbance Spectrometer (Perkin-Elmer, 4100ZL, detection limit 10 µg/L for Al), while iron was measured using the phenanthroline method.

Discussion and Results

Separate trials subjected arsenic-loaded AA to extraction by TCLP, WET, landfill leachate (LL), and simulated leachates (SL1 and SL2) under the standard conditions for both the TCLP (18-hour duration, end-over-end tumbler, ambient air headspace), WET (48-hour duration, shaker table, N₂ headspace) and variations thereof. Figure 1 shows arsenic concentrations for AA samples, agitated by tumbler for 18 h with and without an N₂ headspace. The TCLP, unlike the WET, does not introduce an N₂ headspace. The arsenic concentrations for all tests are above 21.81 µg/L, the aqueous concentration in equilibrium with the loaded AA. The TCLP test extracts the least arsenic, while the LL and the SL2 extract the greatest. The arsenic extracted by the LL is about 10x greater than that by the TCLP test. This alone suggests the TCLP is not a sufficiently aggressive test to conservatively predict arsenic (or likely other oxyanion) leaching from AA residuals exposed to landfill fluids. The high leachate pH (6.82) presumably contributes to the result, since the TCLP has a pH of 4.93 and arsenic mobilization increases as pH increases (17). In addition, the TCLP uses lower total organic concentrations than LL (albeit only by a factor of about four), which will decrease organic ion competition and oxide surface dissolution by organic complexes. The TOC of the LL in this study is at the lower limit of the range observed for typical MSW landfills (Table 1), although SL1 solution with a much higher TOC and comparable pH exhibits only about 1/3 the arsenic leaching of LL. However, some of the wide range of organic species present in LL, compared to the five VFAs in SL1, may more effectively compete with arsenate and enhance the leaching. This is consistent with previous work where 4 mg/L natural organic matter (NOM) decreased arsenate adsorption by 3x (3). Other factors, such as competition from other anions (phosphate, sulfate, etc.) in LL, also might enhance arsenic leaching.

In the AA trials, LL and SL2 generate As(III) in addition to As(V), whereas the WET and SL1 do not. This is consistent with the LL and the SL2 leachates being the most strongly reducing of the leachates (Table 1). However in the TCLP,

small amounts of As(III) were observed (about 12% of total As leached) and confirmed in duplicate tests, even though the ORP was not decidedly low (data shown in Supporting Information).

Differences in the standard TCLP and WET solid-to-extractant ratios hinder direct comparison of results. The TCLP prescribes a ratio of about 1:20 (w/w), while the WET prescribes 1:10 (w/w). The actual leachate and the two simulated leachates used ratios of 1:20, so the results could be compared to the TCLP test. Without knowledge of the isotherm for each fluid/solid mix, the exact impact of this disparity could not be quantified; qualitatively, as the fractional mass of solid decreases, the final leachate arsenic concentration should also decrease. Thus, the higher concentration of arsenic in solution for the WET versus TCLP test (Figure 1) is partially due to the higher solid fraction. However, the WET extracted only about half the arsenic of the LL, which has the same solid concentration as the TCLP.

Soluble aluminum was measured after the leaching tests in samples that were expected to have the most aggressive leaching. Both 18- and 48-hour samples were analyzed for all leaching tests conducted in the tumbler with an N₂ headspace. With the exception of LL, all samples analyzed had soluble aluminum less than 100 µg/L (data shown in Supporting Information). The LL sample was not analyzed for aluminum before the experiment, so it could not be concluded whether the high aluminum concentration in the leachate was due to leaching or its presence in the original LL. Concentrations of less than 100 µg/L are considered nonhazardous (the Secondary Maximum Contaminant Level (SMCL) is 200 µg/L). By this criterion, aluminum dissolution poses an environmental hazard in no test. Furthermore, based on a calculation (using the media density and particle size), the greatest dissolution of Al accounts for a fractional loss of surface area of about 2.5 × 10⁻⁴%, whereas the As release was up to 2.1% of the original sorbed mass. Consequently, dissolution of the activated alumina surface will not explain the observed leaching.

The three nonstandard leachates behave very differently (Figure 1), even though both simulated leachates show compositional similarities to the landfill leachate. SL1 is much less aggressive than LL, while SL2 is consistently more aggressive than LL (as well as the TCLP and WET). SL2 has a high organic concentration, high ionic strength, and, due to the hydroxylamine, a strong reducing character (although all are in the range observed for actual landfill leachates). The organic matter will enhance arsenic solubility although this is not likely a major factor since SL1 has a TOC close to SL2 and about 6x greater than LL. Both SL2 and LL have higher ionic strengths (a factor of 3 or greater) than any other leachates. A greater ionic strength will potentially produce two counteracting (although unlikely equal) effects. First, the greater concentration of anions (particularly multivalent) will lead to greater direct competition with arsenate for surface sites. Second, increasing ionic strength further compresses the electrical double layer (assuming nonspecific adsorption) and favors greater sorption. In both WET and SL2, there is a high concentration of citrate (0.2 M). The pK_as of citric acid are 3.13, 4.72, and 6.33 (26). At the pH of the WET and SL2 tests, there will be significant concentrations of doubly and triply charged citrate anions. Thus, if the interaction of citric acid with the sorbent surface is significant, its competition with AsO₄³⁻ could increase leaching in WET and SL2. However, the most likely explanation for the greater aggressiveness of the LL and SL2 lies in the lower *pe* of these leachates (Table 1). As (V) partitions much more strongly to AA than As (III) at acidic or near neutral pH (17). In both SL2 and LL, As (III) is found in the leachate, indicating arsenate reduction is occurring during exposure. The reductive natures of SL2 and LL mimic the highly reducing character of mature

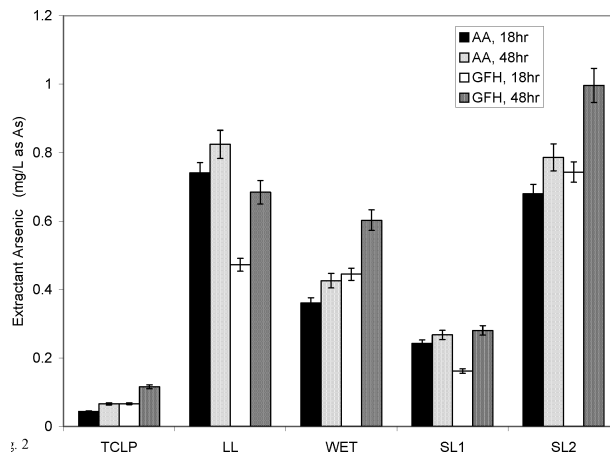


FIGURE 2. Concentration of total arsenic (arsenite + arsenate) in solution from AA and GFH run on the shaker table for 18 and 48 h with an N₂ headspace.

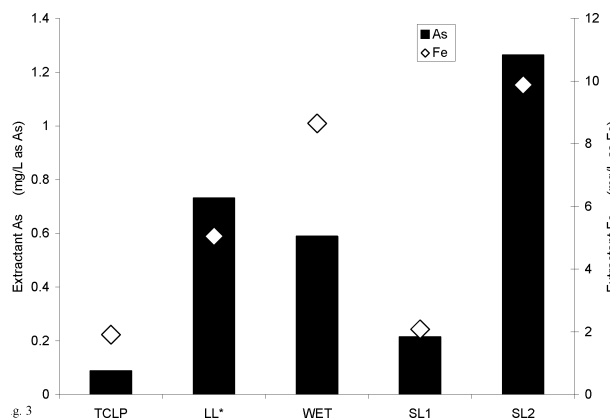


FIGURE 3. Concentrations of arsenate and iron in solution from GFH samples run on the tumbler for 18 h with an N₂ headspace. The background concentration of iron in the landfill leachate of 28 mg/L has been subtracted. The standard TCLP leached 45.5 µg/L.

MSW landfills and the mobilization of arsenic via reduction would be expected to be significant in landfill disposal. Although not studied, the anaerobic microbial activity characterizing mature MSW landfills is also expected to enhance arsenic mobilization from AA (27).

When all tests use 48 h exposure, shaker table agitation, and an N₂ head (the WET procedure), the results are amplified (Figure 2). Again, the WET leaches more than the TCLP, yet the WET results are only 60% of the total arsenic leached by LL. Furthermore, the 48-hour WET extracts about 8x the arsenic of the 18-hour TCLP test. In separate kinetic trials, it was found that the As concentration in the leachate increased in all tests between 18 and 48 h, and even beyond 48 h. Up to 10% more leaching was observed when the solutions were allowed to equilibrate for 6 weeks (data not shown). Some 48-hour trials with the LL and SL2 showed traces of methylated arsenic species, suggesting that microbial activity may be a factor with a longer leaching time.

The GFH results show similar (albeit amplified) trends to the AA results. Figure 3 shows arsenic and iron leaching from the GFH samples run on the tumbler for 18 h with an N₂ headspace. The leached arsenic concentration is highest in SL2, followed by LL, with the TCLP showing the least leaching. Although the WET better matches the LL results, it is still an insufficiently challenging environment for the leaching of arsenic from GFH to predict landfill disposal behavior. The TCLP is the least-conservative test for estimating the arsenic leaching from GFH expected in landfills.

For nearly all tests, the leached arsenic from GFH is higher than the corresponding concentration from AA. The GFH capacity for arsenic is much higher than that of AA. The GFH and AA at equilibrium with 31.0 and 21.8 $\mu\text{g/L}$ aqueous arsenic carried solid concentrations of 7.81 mg/g and 1.25 mg/g, respectively. Thus, similar percentages of leaching would result in about 6x-higher solution concentrations with GFH than with AA. Although the leached arsenic concentration from GFH is greater than from AA, the relative fraction of arsenic extracted (mass in solution/mass in solid) is less. For example, in the WET the fraction of arsenic extracted is 1.9×10^{-3} and 6.7×10^{-3} for GFH and AA, respectively.

A significant amount of iron was dissolved during the GFH leaching (Figure 3). This is expected, due to the propensity for iron to form soluble complexes with the conjugate bases of organic acids (particularly citrate in WET and SL2 (4)). The maximum dissolution accounts for about a 0.031% change in surface area (calculated based on manufacturer's reported surface area and density). For this same case (SL2, 48 hr, tumbler, and N_2 head), 0.47% of the sorbed arsenic leached. For the standard WET with GFH, 0.19% of the sorbed As leached, whereas iron dissolution accounted for an 0.031% loss of surface area. Thus, GFH surface dissolution could in some cases account for some, but not all, of the leaching observed. Any arsenic released from the surface due to iron dissolution would subsequently have to compete with the other ions and organics in the leachate for sites on the newly exposed iron surface. Thus, dissolution-related release would overcome desorption kinetic limitations caused by the potentially increased binding strength of adsorbed species with time (11).

In addition, for the more reducing leachates (SL2 and LL), iron may be being converted to the more soluble Fe(II) state. The standard electrode potential of the Fe(III)/Fe(II) couple is more positive than that of the As(V)/As(III) couple (28). However, there is no similar couple in the aluminum system. This explains the absence of As(III) in GFH trials, but not its presence in some AA trials (see Supporting Information).

Effect of Duration, Agitation, and N_2 . All tests were done for one of two durations: 18 or 48 h. For the leaching tests on the shaker table with an N_2 headspace (Figure 2), none reach equilibrium in 18 h. Arsenate adsorption on AA and GFH reached greater than 95% equilibrium in 48 h (unpublished data). Considering the small particle size, the disequilibrium at and beyond 48 h suggests that the leaching is not mass-transport limited, but is controlled by a slow reaction rate. For AA, the leached arsenic concentration increased 15 to 32% from 18 to 48 h, whereas for GFH the increase was 8 to 20%. The LL and SL2 have the greatest absolute value of concentration increase between 18- and 48-h periods. However, the fractional increase in concentration is the highest in the TCLP, although it exhibited the lowest absolute concentration of arsenic leached. This accentuates the conclusion that for the long fluid residence times characteristic of landfills, the 18 h TCLP will particularly underestimate arsenic leaching from both GFH and AA.

The TCLP prescribes agitation in an end-over-end tumbler, whereas the WET uses a shaker table. All protocols were evaluated using both agitation modes. Figure 4 shows results for 48-h, air-headspace tests. The concentrations in the tumbler were 25 to 65% higher than those obtained by the shaker table. The samples contain about 5 wt % of solid (10% for the WET case) and it was noticeable during shaker table agitation that the solids settled to the bottom, thus, hindering mixing of the bulk water with the solids. The GFH samples show a bigger difference in concentration between the tumbler and the shaker table than the AA samples (Figure 4). A possible explanation is that the end-over-end rotation tends to break up the relatively fragile GFH granules, in

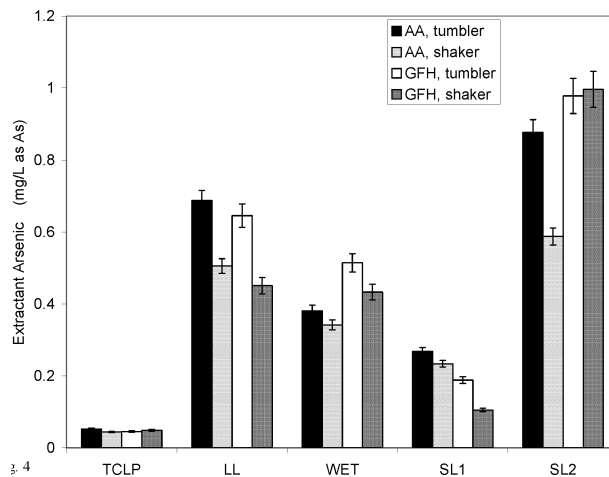


FIGURE 4. Concentration of total arsenic (arsenite + arsenate) in solution from AA and GFH samples run on the shaker table and tumbler for 18 h with no N_2 headspace.

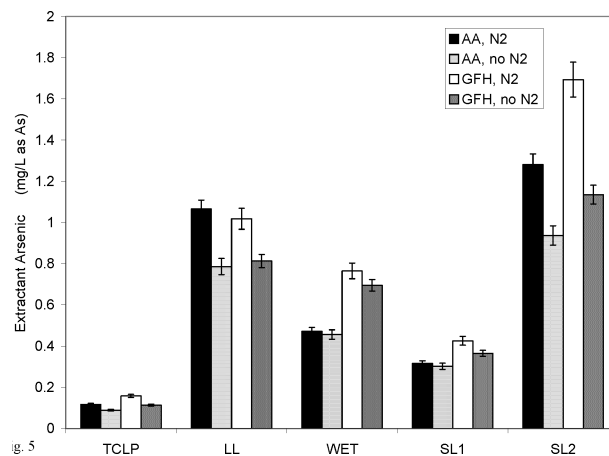


FIGURE 5. Concentration of total arsenic (arsenite + arsenate) in solution from AA and GFH samples run on the tumbler for 48 h with and without an N_2 headspace.

addition to mixing them. However, this was not verified by measuring particle size change during the trials.

The effect of N_2 was investigated by duplicating all of the tests in the presence and absence of an N_2 headspace on the tumbler for 48 h (Figure 5). An N_2 headspace always increased arsenic leaching. Also, the ORP of the solutions with an N_2 headspace was 20 to 60mV lower than that in the absence of N_2 (data in Supporting Information). LL and SL2 have the lowest initial ORP values while the TCLP, WET, and SL1 have much higher ORP values (Table 1). This confirms that the anoxic environment is more reducing and may aid arsenic mobilization. For both AA and GFH, the LL and SL2 exhibit 30–50% higher concentrations with N_2 , whereas the TCLP, WET, and the SL1 exhibit a 10–20% increase. For LL and SL2, the near absence of O_2 after N_2 purging preserves the reducing capacity. The sensitivity to redox potential of arsenate leaching from ferri-oxo/hydride sludges has been previously reported (29).

Aggressiveness of Protocols. The most aggressive physical leaching conditions (independent of leaching solution composition) were end-over-end tumbling, N_2 headspace, high solid-to-liquid ratio, and 48-hour duration. SL2 leached more arsenic under all conditions than the other tests. LL, SL1, and WET leach less aggressively, while the TCLP is the weakest extractant. SL2 was formulated with a high organic concentration comparable to that in a mid-strength landfill (as well as matching the citrate concentration of WET) and with a

higher ionic strength and pH than all the remaining solutions. In a number of cases, the arsenic solution concentration exceeded 1000 $\mu\text{g/L}$. This level is significant. If the toxicity characteristic limit is lowered to 100x the MCL, as is customary, some of the leaching tests (especially on GFH) would classify the residual as a hazardous waste. Overall, the study suggests the TCLP poorly predicts the stability of arsenic on AA and GFH and, in most cases, the WET procedure also under-predicts arsenic leaching. An ideal short-term leaching protocol would indicate the highest concentration of arsenic that could be expected under actual landfill conditions. For ease of application, an abiotic, short-term, batch test would be preferred to a biotic, long-term test, although the latter would most accurately mimic the landfill conditions. Of the protocols investigated, LL is obviously the closest analogue to the leachate from an MSW landfill, but it likely also underestimates actual landfill leaching, as it does not include the anaerobic microbial and long-term processes that would be expected to further increase arsenic leaching (29). Consequently, SL2, which produced arsenic mobilization greater than LL, is arguably the most appropriate of the protocols investigated. However, this would still require quantitative comparison with long-term, biologically active tests before it could be accepted as a conservative predictor of arsenic leaching from water treatment residuals under landfill conditions.

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Supporting Information Available

Six tables show the concentrations of arsenic species, aluminum, and iron, as well as the ORP at the end of the leaching trials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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