

# **Evaluating the Release of Arsenic from Drinking Water Adsorbents under Regulatory and Landfill Leaching Conditions Using X-ray Adsorption Fine Structure (XAFS) Spectroscopy**

Mengling Yi Stuckman<sup>1</sup>

## **Introduction**

Due to its known toxic and carcinogenic effects<sup>1</sup>, the presence of arsenic in drinking water is currently regulated in the United States at a level of 10µg/L<sup>2</sup>. In order to meet regulatory needs and protect public health, single-use adsorbents may be utilized to remove arsenic from impacted water systems in the US. Consequently, when saturated with arsenic, an estimated 10,000 tons of arsenic bearing solid residuals (ABSRs) from drinking water treatment systems will be discarded into landfills every year<sup>2-3</sup>. However, arsenic may be released into the liquid that percolates through the waste (landfill leachate) at a concentration several hundred times higher than that in the source water<sup>4</sup>. If improperly treated, released arsenic may cause secondary pollution to the discharged water bodies, some of which can be drinking water sources, resulting in possible ecological or human health concerns. Most ABSRs have been shown to pass regulatory leaching tests, such as the Toxicity Characteristic Leaching Protocol (TCLP) applied by USEPA and California Waste Extraction Test (CalWET) applied by California EPA, which determine their eligibility to be disposed of into a municipal solid waste (MSW) landfill. However, evidence

<sup>1</sup>: Environmental Science Graduate Program, The Ohio State University

Thanks for the advice from Dr. John Lenhart and Dr. Harold Walker from the Ohio State University, and helpful guidance with XAFS measurement and modeling from Dr. Kirk Scheckel at USEPA!

This project is sponsored by Ohio Water Department Authority. And special thanks to the PNC/XOR facilities at the Advanced Photon Source, IL. The research at these facilities, are supported by the US Department of Energy - Basic Energy Sciences, a major facilities access grant from NSERC, the University of Washington, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357.

exists to suggest that regulatory leaching tests fail to simulate the actual landfill conditions potentially favorable for arsenic release, such as elevated pH<sup>4-5</sup>, reducing conditions<sup>5-8</sup>, presence of competitive anions<sup>5</sup> and complex natural organic matter (NOM) that could dissolve the minerals comprising the adsorbent<sup>6, 9</sup>. Therefore, it is crucial to investigate mechanisms of arsenic release, especially information regarding binding transformations that directly determine As leachability from the ABSRs under different leaching conditions.

Data with respect to chemical binding structure at atomic level is often difficult to obtain by traditional analytical techniques for the following two reasons. First, they may not be *in situ* techniques, meaning that they may alter the original structure through additional sample preparation. For example, air-drying required before the actual measurements could potentially alter the binding status of the atom of interest with water molecule. Second, traditional techniques may not be sensitive enough to detect atomic energy oscillations. X-ray adsorption fine structure spectroscopy (XAFS) is the only technology available that is sensitive and selective enough to differentiate the oxidation state of the target element as well as the types, numbers and distance of the neighboring atoms under *in situ* conditions. The high-energy x-ray beamline necessary for this study is generated by one of the world's largest and most advanced synchrotron at Argonne National Laboratory, IL. The well-tuned incisive energy probe from the synchrotron is able to detect energy oscillations as small as 1eV<sup>10</sup>. Therefore, XAFS has been widely applied to study binding information of complex structured materials and natural processes, such as arsenic adsorption onto iron minerals. Previous studies conducted by Jing et al. (2005) and Sherman et al. (2003) have shown arsenic binding as an inner-sphere surface

complex on various adsorbent surfaces, including iron-based media such as granular ferric hydroxide. Research on commercialized iron adsorbents, however, is comparatively scarce. Data evaluating As speciation in media exposed over long periods of time to source waters of different composition, which could induce markedly different modes of As retention, is also lacking. Specific coordination and bonding information derived from XAFS would also help evaluate whether arsenic speciation in the spent commercialized adsorbents stays stable despite of the variation of chemical conditions in a landfill.

This research, therefore, represents one of the first studies utilizing both traditional chemical analysis and x-ray adsorption fine structure (XAFS) spectroscopy to evaluate As binding structures in ABSRs from long-term full-scale operations and associated binding strength differed from geographically diverse sources. Furthermore, this study also aims at providing direct binding transformation evidence to investigate leaching conditions favorable for As release.

## **Materials**

Five ABSRs from four different states, New Mexico (NM), New Hampshire (NH), Arizona (AZ) and Texas (TX1 and TX2), were collected from long-term arsenic removal operations (6 months to 30 months) initiated by the USEPA Arsenic Removal Technology Demonstration Program<sup>11</sup>. TX1 and TX2 are from the lag tank and lead tank respectively of the same test site<sup>11</sup>. All sites utilize Bayoxide E33, an iron oxide media, as the adsorbent in operation. Bayoxide E33 contains 90.1%  $\alpha$ -FeOOH (goethite). It has a high capacity for As(V), with 99% removal

efficiency, but is less effective at removing As(III), and thus pre-chlorination is required by the USEPA to promote As(III) oxidation<sup>12</sup>. As summarized in Table 1, each site had unique source water quality and operating conditions.

		New Mexico	New Hampshire	Arizona	Texas1	Texas2
<b>Elemental Composition of ABSRs<sup>a</sup> (mg/g)</b>	<b>As</b>	2.15	2.14	7.53	2.25	3.07
	<b>Mn</b>	2.25	21.65	1.69	3.34	9.91
	<b>S</b>	0.32	0.28	0.15	0.10	0.17
<b>Source Water Quality<sup>b</sup> (mg/L)</b>	<b>pH</b>	7.6	8.4	7.2	7.8	
	<b>Total As</b>	0.022	0.046	0.05	0.029	
	<b>Mn</b>	0.009	0.088	N/D	0.048	
	<b>SO<sub>4</sub></b>	158	38	13	2	
<b>Operation Time</b>		12 months	30 months	30 months	6 months	

**Table 1.** Comparison of sorbent characteristics and source water chemistry. All units are mg/L. Maximum relative error for elemental composition was 11.3%. a: elemental composition was obtained by chemical analysis. b: source water quality was reported from USEPA Final Performance Evaluation Report at NM<sup>13</sup>, NH<sup>12</sup> and AZ<sup>14</sup> and Six-Month Evaluation Report at TX<sup>11</sup>.

## Methods

The elemental composition of the ABSRs was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian Vista AX) after acid digestion<sup>15</sup>. Total As concentrations were measured with a graphite furnace atomic adsorption spectrometer (GFAA, Varian Spectr AA 880Z).

A basic synthetic leachate (SL) solution was prepared with the same major component composition as the landfill leachate collected from the Franklin County landfill, Ohio (all in mg/L: Mg<sup>2+</sup>, 100; Ca<sup>2+</sup>, 100; Fe<sup>3+</sup>, 1; NH<sup>4+</sup>, 200; HCO<sub>3</sub><sup>-</sup>, 1500; SO<sub>4</sub><sup>2-</sup>, 75; PO<sub>4</sub><sup>3-</sup>, 1.5; SiO<sub>3</sub><sup>2-</sup>, 50

and Total Organic Carbon, 400). The final pH of SL was adjusted using 1mol/L NaOH or 1 mol/L HCl to the desired value after the addition of the anions.

All ABSRs were subjected to three leaching tests: (1) regulatory leaching tests - TCLP<sup>16</sup> and CalWET<sup>17</sup>, and (2) leaching batch tests with synthetic leachate solutions varied by pH from 5.0 to 9.0. Details of the leaching conditions are summarized in Table 2. All leaching tests were conducted in duplicate at 23 °C. Post leaching solutions were subjected to elemental composition analysis, total As.

	Leachate composition	Liquid: solid	Agitation	Head-space	pH	Time
<b>TCLP</b>	Acetate, 0.1M	20:1	Rotator	Air	4.93±0.05	18h
<b>Cal WET</b>	Citrate, 0.2M	10:1	Shaker	N <sub>2</sub>	5.0±0.1	48h
<b>SL</b>	Synthetic leachate	10:1	Shaker	N <sub>2</sub>	5.0 – 9.0	48h

**Table 2.** Leaching conditions for different leaching tests.

The pre- and post-leaching solutions were subjected to traditional elemental composition analysis to evaluate the release of As and other compounds of interest using ICP-AES and GFAA. All pre- and post-leaching solid samples were transported to the Advanced Photon Source at Argonne National Laboratory, Argonne, IL for XAFS analysis to evaluate As speciation and binding information at the atomic level. Samples for XAFS analyses were mounted in Plexiglas plate multi-sample holders, and sealed with Kapton tape under N<sub>2</sub> in a glovebox. Arsenic K-edge (11,867 eV) spectra were collected at the 20-BM-PNC/XOR sector. Five scans were collected at ambient temperature in fluorescence mode with a solid-state 13-element detector. The collected scans for a particular sample were merged into one average scan and

pre-processed by ATHENA<sup>18</sup>. In WINXAS, the  $k^3$ -weighted extended X-ray absorption fine structure (EXAFS) spectra in  $k$ -space ( $\text{\AA}^{-1}$ ) were Fourier transformed (FT) to produce the radial structure function in  $R$ -space ( $\text{\AA}$ ). The experimental spectra were fit with single-scattering theoretical phase shift and amplitude functions calculated with the *ab initio* computer code FEFF6<sup>19</sup> using atomic clusters generated from the crystal structure of scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ). Final fits showed reasonable estimated values for radial distance ( $R$ ) and  $\sigma^2$  based on previous studies<sup>20-21</sup>.

## Results and Discussions

### 1. ABSR binding structures and initial As loadings from geographically diverse sources

Elemental compositions of ABSRs coincide with source water quality (Table 1). TX1 and TX2 were from the same water source location, and except for manganese, the elemental compositions were similar. Manganese in the source water was highest at the NH site and second highest for TX2 site (lead tank at TX site) while NH and TX2 spent media contain higher manganese than the other samples and the virgin media. ABSR at AZ has the highest initial As loading while the source water at AZ contains highest As. However, the initial As loading could also be affected by several factors that would be further discussed after EXAFS analysis.

Figure 1 depicts the  $k^3$ -weighted and Fourier transformed EXAFS for all five ABSRs. In all samples, the first coordination shell surrounding arsenic involves four oxygen atoms at an average distance of 1.69  $\text{\AA}$  (See largest peak in right figure in Figure 1). The second coordination shell surrounding arsenic involves two iron atoms at a distance of 3.30  $\text{\AA}$  (See line 2 in Figure 1).

This was very clear evidence of a bidentate binuclear (BB) complex in good agreement with the distance of 3.28 - 3.45 Å reported in the literature<sup>3, 20, 22-24</sup> (See Figure 2). Additional peaks that occurred in selected samples were also evident in the Fourier-transformed EXAFS spectra. For example, an As-Fe shell at a distance of 2.85 Å with a coordination number of 1 was found in samples NH, TX1 and TX2 (See line 1 in Figure 1). This feature, together with As-O at 1.69 Å (CN of 4), was consistent with the formation of mononuclear bidentate (MB) complexes<sup>6, 20, 24</sup> (See Figure 2). The fit for the sample NH could be further optimized by adding a fourth shell of As-Fe at 3.59 Å (See line 3 in Figure 1). This suggests that the coexistence of monodentate (MD) complex was possible in NH<sup>20</sup> (See Figure).

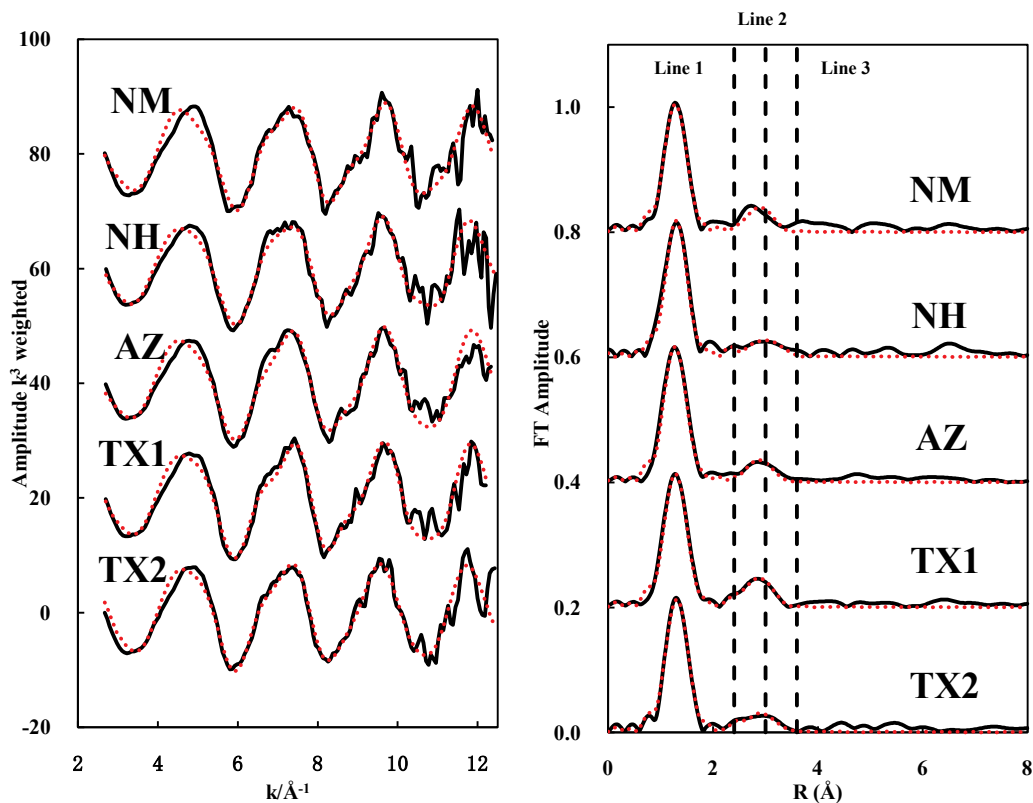


Figure 1.  $k^3$  weighted EXAFS and Fourier transforms for spent media. Line 1 represents MB complex at 2.4 Å; Line 2 represents BB complex at 2.8 Å; Line 3 represents MD complex at 3.6 Å. The peak positions are uncorrected for phase shift. Solid lines are measured spectra and dashed lines are model fits.

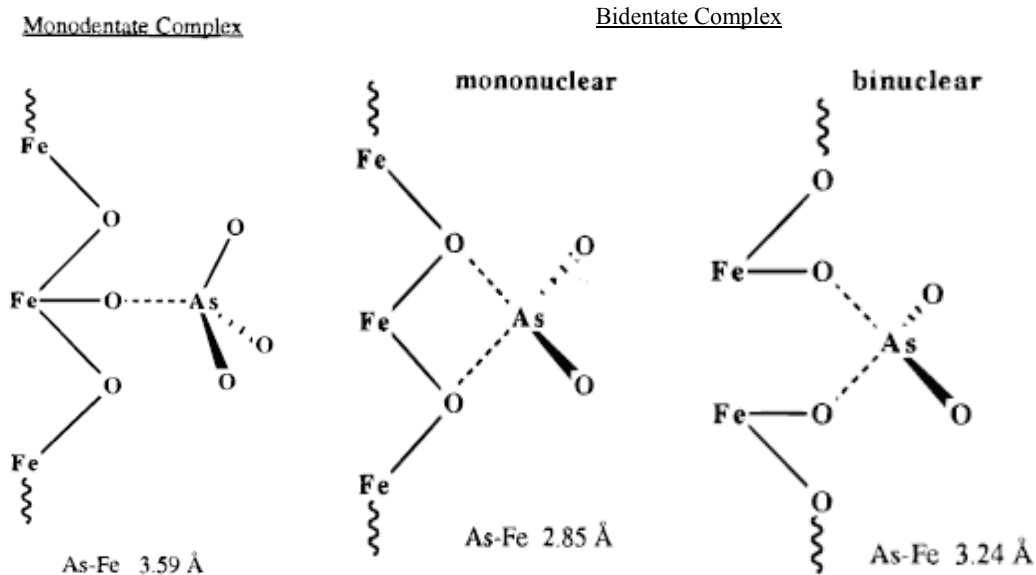


Figure 2. Schematic illustration of the surface structure of As(V) on goethite based on the local coordination environment determined with EXAFS spectroscopy by Fendorf et al.<sup>20</sup>.

XAFS analysis of the ABSRs demonstrates a binuclear bidentate (BB) complex was predominant in most spent media consistent with this structure being energetically favored over other structures (e.g., MB and MD). Sherman and Randall<sup>25</sup> predicted relative energies and geometries of  $\text{AsO}_4\text{-FeOOH}$  surface complexes using density functional theory (DFT) calculations and discovered that the MB structure is energetically unfavorable by 0.57 eV (55kJ/mol) relative to the BB structure. Most importantly, the energy of the transformation from MD complex to MB complex and to BB complex are -165eV and -95eV, respectively, implying that the monodentate complex cannot be significant but can still possibly exist. Ladeira et al.<sup>26</sup> used analogous DFT calculations to model surface complexation of  $\text{H}_2\text{AsO}_4^-$  on  $\text{Al}(\text{OH})_3$  and also concluded the BB complex was more stable than the bidentate edge-sharing and monodentate corner-sharing complexes.



Different structures reflect different environments encountered by the samples. With respect to time, Liu et al.<sup>27</sup> and Fendorf et al.<sup>20</sup> observed that the adsorption of arsenate on goethite followed a two step process. Initially, As (V) formed a MD inner sphere complex, but over time, a more stable binuclear, inner sphere bonding state was observed. Therefore, media subjected to more lengthy arsenic contact were dominated by BB complex. For example, AZ, sampled after operating for 30 months, had BB complex only in XAFS analysis and the highest initial As loading (See Figure 1). On the other hand, TX site which was operated for only 6 months had coexisting BB and MB complexes (See TX1 and TX2 in Figure 1). In water treatment, the kinetics of As adsorption can be slow due to the high porosity of the media within the column<sup>28</sup>, low As concentration in the source water and insufficient contact time, perhaps explaining the MB structure as well as lower initial As loading observed in the TX site.

The predominance of BB complexes and initial As loading could be affected by the source water chemistry as well as the operation conditions to which the media were exposed. At the NH site, manganese coated the media and inhibited As adsorption resulting in less As retention in the media (Table 1). The manganese coating resulted from MnO<sub>2</sub> coprecipitation after prechlorination and it possibly shields interactions between arsenic and the iron media surface, perhaps explaining the existence of MB complex, or even MD complex. In addition, unfavorable elevated operating pH further promoted coexistence of more unstable binding structures and less initial As loading. The source water pH at the NH site was 8.4 (See Table 1) which is out of the optimal operating range of pH (6-8) for the adsorption treatment. Moreover, the carbon dioxide (CO<sub>2</sub>) injection module prior to arsenic adsorption failed to adjust the pH to the target value of

7.0 due to CO<sub>2</sub> injection membrane fouling. Consequently, after 12 months, pH adjustment was not performed<sup>12</sup>. Studies have shown that the increase in pH significantly decreases the adsorption of arsenic on iron oxide minerals<sup>27, 29</sup>. At near neutral pH, arsenic after chlorination mainly occurs as the oxidized anionic forms (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> or HAsO<sub>4</sub><sup>2-</sup>) prior to adsorption treatment. As pH increases, the adsorbent surface will become more electrostatically repulsive towards anionic As species, creating larger energy barrier in the process of As adsorption. Therefore, failure of pH adjustment on top of manganese coating at NH site could have decreased adsorption of arsenic on iron oxide media.

## **2. High pH favors arsenic release**

Different chemical leaching environments demonstrate a significant impact on arsenic release as well as arsenic surface binding. In this study, we only focused on the pH effect on As release to provide direct evidence of the binding structure transformation in ABSRs to support the As release mechanism varied by pH. Figure 3 shows the effect of pH in leaching tests with synthetic leachate. Significant As release was observed with an increase of pH and the behavior is nonlinear and sample-specific. Because the pH<sub>PPZC</sub> (pristine point-of-zero charge) of goethite (α-FeOOH) is reported to be around 9<sup>30</sup>, as the pH increased from 5 to 9, the positive charge of the media surface decreases and the anionic arsenic species (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> or HAsO<sub>4</sub><sup>2-</sup>) were increasingly desorbed. The change was particularly evident in increasing the pH from 7 to 9, where As release from the NM, NH and AZ samples increase by 330%, 596% and 1100%, respectively (See Figure 3). Similar trends in the pH-dependence of As adsorption/desorption to

mineral surfaces has also been reported by Fuller et al.<sup>28</sup>, Anderson et al.<sup>31</sup>, Pierce and Moore<sup>32</sup>, Grafe et al.<sup>33</sup> and Hsia et al.<sup>34</sup>.

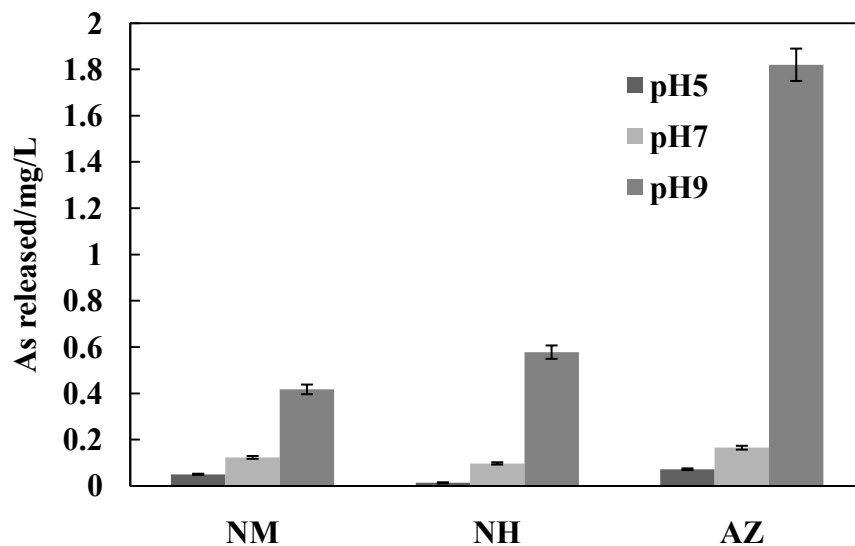


Figure 3. Effect of pH on arsenic release from different samples with synthetic leachate in 48h, shaker table and nitrogen headspace. Error bars set at 5%.

Accordingly, in the XAFS spectra, it was observed that as the pH increased, the binding structures in post-leaching samples transformed from stable forms into less stable ones that were more readily released. All post-leaching samples subjected to tests with synthetic leachate present binuclear bidentate complexes (See Figure 4 line2). Only samples at higher pH contained additional shells. For example, additional peaks were observed between 2.4 to 3.6 Å in the NM sample at pH 7 and pH 9 and the peak distance shifted further from the central As atom as pH increased indicating coexistence of MB and even MD complexes. This reflects that not only does the increased pH decrease the positive charge of the surface which inhibits adsorption of negatively-charged As species, it also facilitates the formation of weaker structure and As release.

Fendorf et al.<sup>20</sup> also reported that adsorbed As structures transform with pH, with monodentate complexes present at pH 9 shifting to binuclear bidentate complexes at pH 6. Fendorf et al.<sup>20</sup> attributed these changes to changes in surface coverage, defined as mass of As adsorbed vs. mass of Fe. In this work, an increase in As release as pH increases also indicates a decrease of As surface coverage. Therefore, variation in surface coverage could impact complex structure transformations and in some samples the results indicate a reduction in the number of complexation configurations.

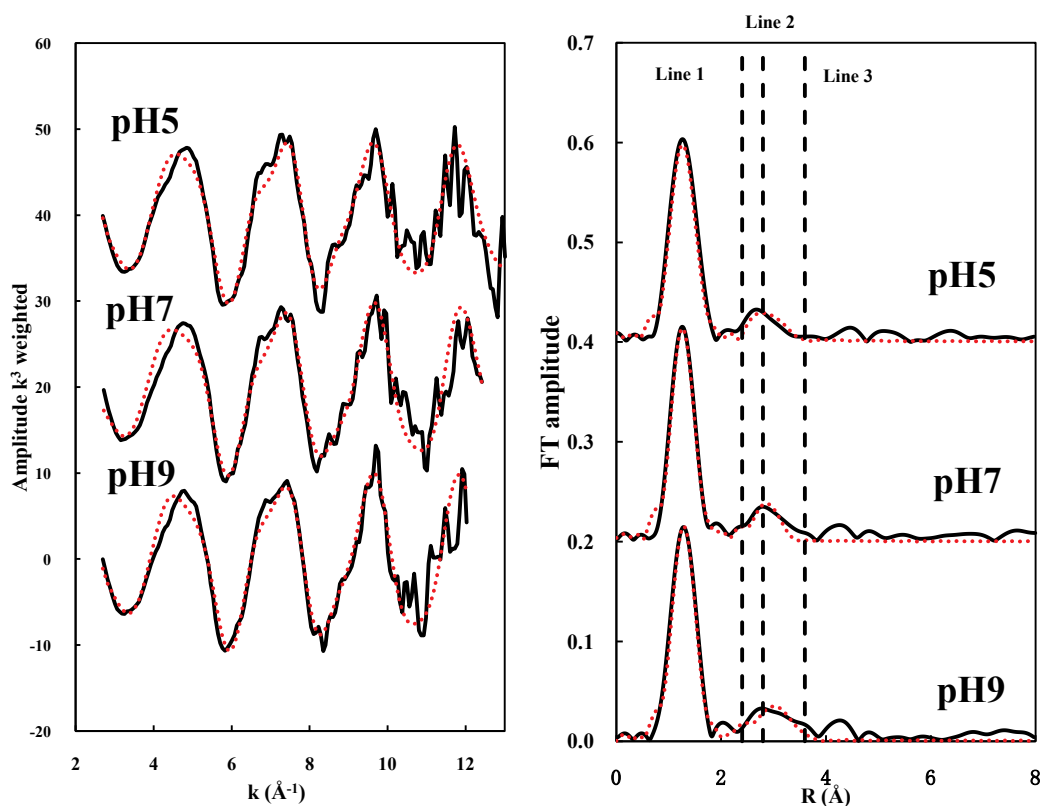


Figure 4.  $k^3$  weighted EXAFS and Fourier transforms for NM spent media subjected to leaching tests at different pHs. Line 1 represents MB complex at 2.4  $\text{\AA}$ ; Line 2 represents BB complex at 2.8  $\text{\AA}$ ; Line 3 represents MD complex at 3.6  $\text{\AA}$ . The peak positions are uncorrected for phase shift. Solid lines are measured spectra; dashed lines are model fits.

No change was observed in the AZ sample because the surface coverage was always high and the loss of surface coverage through the leaching tests was not sufficient to alter the mode of complexation. Even though the AZ sample possessed the highest surface coverage and was robust in surface complexation as leaching condition changes, it did release the most As. Therefore, for samples within high surface loading, complexation mode transformation may not be the main contributor to As release.

### **3. Iron dissolution is one of the main contributors to As release**

Regulatory tests not only determined the eligibility of ABSR disposal into MSW landfills, but also revealed the capability of certain carbon sources to dissolve iron accompanied by As release. Table 3 presents the As concentration in the regulatory tests. Noticeably, arsenic released from CalWET was approximately 100 times more than that from TCLP. All TCLP results were less than 0.120 mg/L which was far below the TCLP As limit (5mg/L). With respect to CalWET, The As release from the AZ sample during CalWET exceeded As limit (5mg/L) and was also 1000 times of the current drinking water standard. In addition, further tightening of the As limit would result in failure of four out of five samples to pass CalWET, because As release from those exceeded 100 times of the regulatory drinking water standards. The XAFS spectra didn't show significant binding transformations in post-leaching solids in both tests indicating the existence of other contributors to As release. This result aligned well with our previous observation that at pH as low as 5.0, BB complex was the dominant binding structure. Therefore, low pH was not favorable for the release of As in a way that it suppressed the formation of

weaker bindings which was the indication for subsequent As desorption from iron oxide surface. Similar experimental studies on pH effect on As desorption also revealed the insufficiency of regulatory tests to simulate landfill conditions with pH varied from 5 to 9<sup>4-5,7</sup>.

	NM	NH	AZ	TX1	TX2
<b>TCLP</b>	0.003	0.033	0.116	0.010	0.032
<b>CalWET</b>	0.6	1.81	10.3	1.71	2.38

**Table 3.** Final As concentration in regulatory leaching tests. Maximum relative error was 5.6%.

The widely reported explanation for such difference in As leachability from the two regulatory tests is that the citrate leachate used in CalWET promotes significant As release from ABSRs (See Table 2). Our previous research indicated that differences in leaching time, agitation methods or L:S ratio had only minor effects on As release. Citrate, which strongly binds iron<sup>35-36</sup> and competes with As for adsorption sites<sup>9,37</sup>, might dissolve the iron oxide based media accompanied by large amount of As release. As visualized in Figure 5, CalWET released 10.9 mg/L As and 253mg/L Fe in post leaching solution while TCLP released 0.085mg/L As with non-detectable Fe from the AZ sample. Shi et al.<sup>9,37</sup> also reported that in the presence of citrate, the adsorption of arsenate onto goethite in acidic media was significantly decreased due to citrate-promoted goethite dissolution and citrate competition with arsenate. Acetate, which is the TCLP leachate, did not decrease arsenate adsorption because of its inability to dissolve goethite and adsorb onto goethite<sup>37</sup>. It is also likely that citrate can complex arsenic through metal bridging complexes, particularly in the presence of Fe<sup>4</sup>. Shi et al.<sup>9</sup> observed enhanced

citrate adsorption at alkaline pH in the presence of arsenate supporting the formation of a complex between arsenate and citrate on the goethite surface. In this work, acidic environment (pH=5) was selected for CalWET test, thus, citrate-promoted goethite dissolution and citrate competition with arsenate were both considered the main contributors for As release. In real landfills, the major components of carbon sources are usually hard to identify and vary site by site. Therefore, the concern of citrate-like carbon-promote dissolution<sup>38-39</sup> and carbon competition<sup>5, 33, 40</sup> with arsenate still exist and have been reported in many studies. Furthermore, natural organic matter in the landfill could act as an electron-transfer mediator in redox reactions as well as carbon sources for microbial growth to promote biogenic As reduction and dissolution<sup>6, 38, 41-42</sup>.



**Figure 5.** Post leaching solutions from regulatory tests for the AZ sample subjected to TCLP (left) and CalWET (right).

## Conclusions and Implications

In sum, XAFS is a powerful *in situ* tool used to fill the gap between experimental phenomena and binding information to aid in understanding of As release. The coexistence of weaker As binding structures (MB and MD) is usually an indicator of less effective adsorption during drinking water treatment confounded by source water or treatment processes, such as less operation time, manganese coating and insufficient pH adjustment. Higher initial As loading would lead to larger As release in subsequent landfill disposal. Thus, drinking water facilities should consider the balance between the effective As treatment of the media and disposal cost in the future as the legislation tightens. Our results also presented no binding transformation after leaching tests at lower pH and transformation from stronger binding to weaker bindings as pH increases in the leaching condition. This could be utilized to directly support the idea that current leaching tests are not sufficient enough to simulate As release in landfill conditions with respect to elevated pH. TCLP was also shown to misrepresent the potential carbon-promoted iron dissolution or carbon competition with As on iron surface which would facilitate As release. The iron dissolution is found to be one of main contributors to As release in many recent studies.

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