# US EPA's TCLP Test
# Fails to Predict the Leaching Risk of
# Water Treatment Arsenic Residuals

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For centuries arsenic has been best known for its use as a poison. It has been suggested, however, that low levels of arsenic could be beneficial as a nutrient.[1] Arsenic in the form of Fowler's solution, Asiatic pills, Donovan's solution and DeValagin's elixir, were commonly used into the nineteen fifties as a therapy for anorexia, neuralgia, rheumatism, asthma, cholera and many other conditions.

The ancient Romans, however, used arsenic as a way to resolve personal matters or conflicts, since arsenic contamination or poisoning of food and/or water can result in illness and in death.

Arsenic does cause significant health concerns. Recent US EPA tests should be repeated due to there being no definitive test to predict the stability of arsenic residuals under landfill conditions and over long periods of time.

## Health effects

Arsenic is one of the most toxic elements on earth. Its toxicity has been confirmed by many cohort studies, such as the one conducted in Millard County, Utah, which concluded that drinking water with dissolved arsenic as low as 14 µg/L was linked to increased mortality.

Exposure to arsenic may occur through skin contact and/or drinking/ingesting water or food that contains arsenic. Exposure to significant levels of arsenic has been implicated in causing various health effects such as irritation of the stomach, intestines, skin, lungs and lymphatic system as well as development of lung and liver cancers. The visible effects of acute arsenic exposures are often evident (Figure 1).

Acute exposure to inorganic arsenic has been implicated in causing DNA mutations, infertility and miscarriages. It also has been implicated in reduced immunity to infections, heart disruptions and brain damage.

## Sources

Arsenic can be found in rocks, soil, animals, water, etc. The presence of arsenic in groundwater can be attributed to weathering and subsequent dissolution of arsenic-bearing minerals.

Since mineral dissolution is a very slow process, high arsenic concentrations are normally associated with groundwater rather than surface water. This is due to much longer contact of water with arsenic-bearing minerals in a subsurface environment.

Commonly, arsenic concentrations in groundwater are a result of up flow of geothermal waters, dissolution of arsenic-rich minerals (such as arseno pyrite) or evaporative concentrations.[2]

## Global occurrence

In Europe, arsenic problems are most prevalent in Hungary, Serbia and Croatia, with levels several times higher than the World Health Organization (WHO) and US EPA limits of 10 µg/L. In the Americas, the US, Mexico, Argentina and Chile are most affected by arsenic problems.

Bundschuh[3] estimated that in Latin America alone, more than four million people are exposed to arsenic levels > 50 µg/L. In Argentina, levels as high as 5,000 µg/L have been documented, and in some cases, reaching alarming levels as high as 11,500 µg/L in some water sources in Cordoba Province. (Figure 2 shows global arsenic distribution.)

## Occurrence within the US

Within the US, naturally occurring arsenic in groundwater will vary from region to region as a result of the unique climate and geology. The western US generally has a higher concentration of arsenic, with values frequently above 10 µg/L.

Recent USGS reports, however, suggest that states such as Maine, Michigan, Minnesota, South Dakota, Oklahoma and Wisconsin have water sources with arsenic concentrations exceeding 10 µg/L. Further, these sources are more common than previously suggested.[2] (Figure 3 shows the distribution of arsenic in groundwaters of the US.)

Elevated arsenic levels are generally found in groundwater in the arid southwest of the US. This region, unfortunately, primarily depends on groundwater as a drinking water source. Therefore, it is not surprising that it is particularly impacted by the recently implemented arsenic standard of 10 µg/L.

**Figure 1. Health effects of arsenic-induced skin cancer. Such visible effects have been observed in Bangladesh, India and many other places in the world.**

**Figure 2. The prevalence of arsenic throughout the world, with countries in orange indicating arsenic presence.**



## Chemistry of arsenic

Arsenic in potable water supplies is almost entirely in either the arsenite, As (III), or arsenate, As (V), oxidation states.[4] In near neutral waters arsenite is primarily fully protonated and uncharged as arsenous acid ($H_3AsO_3$) ($pK_{a1}$ 9.2).

In contrast, arsenate is predominantly in an anionic form in the neutral pH range of typical waters[5] ($pK_{a1}$ 2.2, $pK_{a2}$ 7.0 and $pK_{a3}$ 11). Metal-based sorption, as a treatment technology of ions, is more efficient for charged ions than for neutral species. Therefore, water containing a significant fraction of arsenite is recommended to undergo pre-oxidation from arsenite to arsenate prior to the application of an arsenic-removal technology.[6]

## Treatment technique overview

As a requirement of the *Safe Drinking Water Act (SDWA)*, US EPA recommended different best available technologies (BATs) to comply with the new arsenic maximum contaminant regulation.[6] These technologies include precipitation/coagulation, adsorption and ion exchange.

The technologies available and under development for arsenic removal by small utilities depend primarily on adsorption of arsenic onto a throwaway or regenerable solid media. Arsenate adsorption on metal oxy/hydroxide solids is a strong function of electrostatic attraction. The electrostatic effect responds to the amphoteric nature of surface functional groups, whereby pH adjustment tends to increasingly protonate or deprotonate surface functional groups (i.e., hydroxides) and decrease or increase, respectively, the surface attraction for anions, such as arsenate.[7]

Adsorption also occurs due to non-electrostatic attraction (termed specific adsorption), which explains some sorbents' (e.g.: iron, manganese) increased selectivity for arsenate over other equally charged anions. In this case, a stronger chemical bond (termed specific or chemical sorption) occurs between the sorbate and sorbent.[8]

Of the US EPA-identified treatment options, adsorption onto solid media is strongly favored for small treatment facilities (those serving populations of less than 3,301), which comprise over 92 percent of impacted utilities.[6] A brief description of each of these technologies is described below.

## Precipitation/coagulation

Soluble arsenic is most commonly removed by co-precipitation with ferric salts. This method has been designated as the best demonstrated available technology (BDAT) for the removal of dissolved arsenic by US EPA. Precipitation/coagulation technology is based on growth and aggregation of particles in water.

**Figure 4.**
**GFH Bayoxide® B E33 Media C ArsenX$_{np}$ and AA**
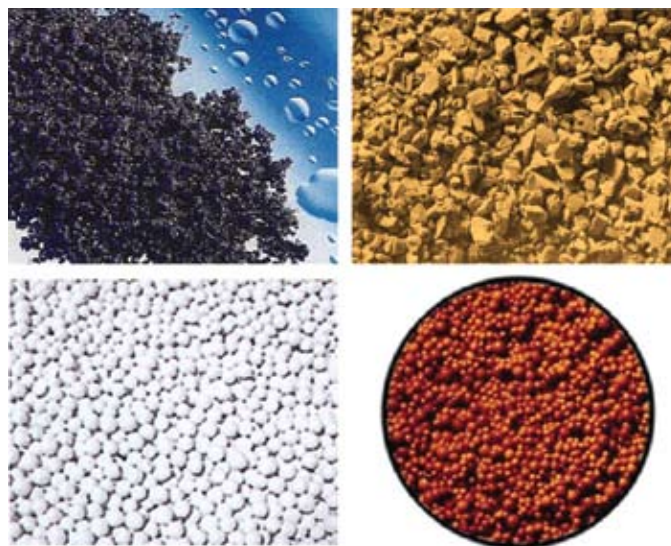


A single process can involve both coagulation and co-precipitation. Co-precipitation refers to the formation of an insoluble complex by an inorganic complex and coagulant. In all forms of coagulation, soluble arsenic is converted to insoluble particles, which can then be removed by sedimentation or filtration. Ferric chloride and ferric sulfate are the most common coagulants used.

The best arsenic removal rates are obtained in a pH 6.5 to 8.5 range. A variety of practical coagulation systems are based on similar principles and display short-term results, ranging from 50 to 98 percent removal of detectable arsenic contamination.

In all cases, however, disposal of the sludge from these approaches remains a significant pollutant trade-off issue. This is because the most efficient available arsenic removal technologies with high-adsorption capacities generate large amounts of solid residuals, which require disposal.

## Adsorption techniques

Adsorption techniques are designed to concentrate arsenic solutes on the surface of a sorbent, resulting in reduction of their concentration in the bulk water phase. This technique employs adsorptive media such as activated alumina (AA),

**Figure 3. Arsenic concentrations in US groundwater (USGS, 2000)**



Concentration of arsenic
▲ At least 50 ug/L
▲ 10–50
▲ 5–10
▲ 3–5
▲ 1–3

Source: USGS
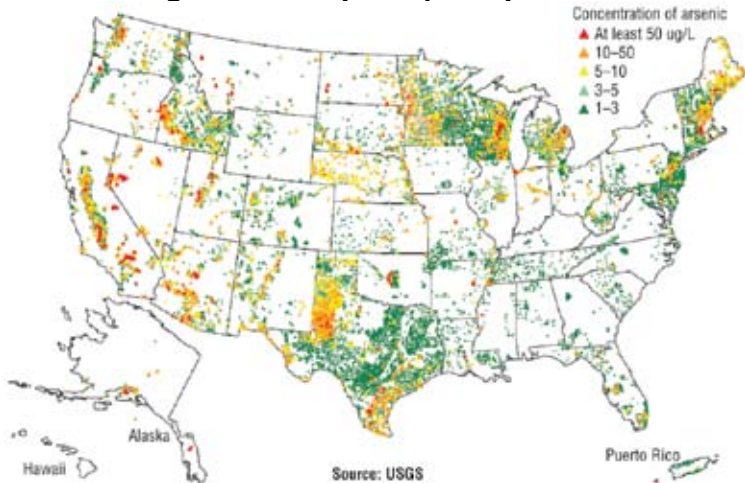
granular ferric hydroxide (GFH), and many other commercially available products such as Bayoxide E-33 (Figure 4). Most of the commercially available media differ in their relative capacity and abilities to remove arsenic.

### Ion exchange treatments

Ion exchange treatments produce a liquid residual brine stream, which must be either treated onsite or discharged to a sanitary sewer (US EPA, 2001). Technically based local limits (TBLL), however, dictate sewer limits due to increased TDS (salt content) accompanying arsenic treatment.

Consequently, it is expected that liquid (brine) stream residuals will need to be treated onsite. The recommended process in this case is adsorption/co-precipitation with amorphous ferric hydroxide, AFH [$Fe (OH)_3 \cdot nH_2O$], induced by the addition of ferric chloride, and corresponding pH adjustment above the solubility product.

### Membrane filtration

The efficiency of membrane technologies (such as RO, MF and UF) for arsenic removal is highly dependent on the size distribution of arsenic-bearing particles found in the source water. Considering the fact that a greater majority of arsenic in groundwater is in the dissolved fraction, this makes RO most suitable compared to MF and UF.

Practically all of the above arsenic-removal techniques produce arsenic-bearing, solid residuals. Such would be evaluated using the toxicity characteristic leaching procedure (TCLP), and may allow disposal in non-hazardous landfills.

### Limitation of treatment technologies

All the above-mentioned treatment technologies have limitations. The concentration and nature of other anions in solution affects the fraction of arsenic sorbed, as ions compete for the surface sites. In general, as ionic strength increases, the fraction of contaminant sorbed decreases. However, individual ions have differing affinities for surface groups, so the effectiveness of competing ions in displacing a target ion depends not only on relative concentrations of the ions, but also on the identity of both the ions and the surface.

For instance, sulfate competes effectively with arsenate for most anion exchange resin sites, whereas it has much less effect on arsenate adsorption by activated alumina.[9] Likewise, phosphate concentration is observed to strongly influence arsenate adsorption on granular ferric hydroxide, GFH.[10]

Concentration of natural organic matter (NOM) is also expected to impact the degree of arsenic adsorption. The effect of NOM on sorption is much harder to predict than the effect of pH or ionic strength, and only a few studies have been conducted on anion sorption in the presence of variable concentrations and types of NOM.

Natural organic matter may directly compete with the ion of interest for surface sites,[8] or may sorb to the surface and create additional surface attraction and enhanced sorption.[11] It also may act as a complex ion agent to bind with the ion and keep it in solution, or may directly react with the sorbent surface to enhance dissolution of the surface and cause loss of sorption sites.[11]

Xu[12] found the presence of NOM to significantly decrease anion adsorption on metal oxide solids. Amy[13] confirmed this observation for arsenic sorption on ion-exchange resins, iron

oxide-coated sand and activated alumina.

Not only does composition of the water affect ion sorption by solids, but so also does the nature of the sorbent. This effect is manifested both as a difference between sorbents, as well as the difference between different mineralogical forms of the same metal oxide. For instance, AA has a lower sorption capacity than GFH, and ferrihydrite [$Fe (OH)_3 \cdot nH_2O$] has a sorption capacity which is over 10 times higher than goethite ($FeOOH$), even though ferrihydrite naturally ages by dehydration to goethite.

As previously mentioned, practically all arsenic-removal techniques produce arsenic-bearing solid residuals, which must be evaluated using TCLP and may allow disposal in non-hazardous landfills. According to US EPA, once a solid residual passes TCLP (non-hazardous), arsenic will potentially not leach out of the landfills, and will not migrate into and contaminate groundwaters. A detailed description of this test will be discussed in the subsequent sections.

### Treatment residual production

US EPA estimates that implementation of the recently enacted arsenic drinking water standard (10 µg/L) will lead to the generation of over eight million pounds of arsenic-bearing solid residuals every year, containing over 30,000 pounds of arsenic.[6] This number does not include residuals currently generated from mines and other industrial operations.

The state of California uses a different leaching method called the waste extraction test (WET). Both TCLP and WET are currently being used to simulate landfill-leaching conditions and predict the risk posed by landfill disposal of arsenic residuals.

### US EPA's TCLP test

US EPA's TCLP is a method required for determination of characteristic waste properties for solid waste under the *Resource Conservation and Recovery Act (RCRA)*. It has been used as a reference method in determining the mobility of arsenic in contaminated soils or other materials.

TCLP determines whether a waste is considered hazardous or non-hazardous. It requires that arsenic concentration in the extracting solution during testing must be less than five mg/L in order to be considered a non-hazardous waste and safe for municipal solid waste (MSW) landfill disposal.

The validity of this test in predicting the leaching risk posed by water treatment arsenic residuals remains questionable (Table 1).

### California waste extraction test (WET)

The state of California's WET method,) is used to determine regulatory threshold (same as the TCLP limit: 5.0 mg/L arsenic in the leachate). However, WET uses a longer extraction period and different extractants than TCLP; citrate is used in the WET method rather than acetate because it is a stronger chelating agent.

It should be noted that both TCLP and WET were designed to simulate landfill-leaching conditions. Therefore, the following section briefly describes landfill characteristics and how they compare to the leaching test (particularly the TCLP).

**Table 1: Characteristics of leaching protocols and actual landfill conditions**

| Test | TCLP | WET | Actual landfill |
|------|------|-----|-----------------|
| Chelator | acetic acid | citric acid | multiple |
| Duration | 18 hr | 48 hr | weeks–years |
| pH | 4.95 | 5.05 | 6.5-9.0 |
| Bioactivity | abiotic | abiotic | biotic |
| ORP (mV) | -68.2 | -101 | anoxic, variable |

### Overview of landfill conditions

Landfills have long residence time (years) allowing for accumulation of concentrated landfill leachate, which is conducive

Figure 5. Picture of a modern-day landfill fitted with a liner (adapted from the Web)
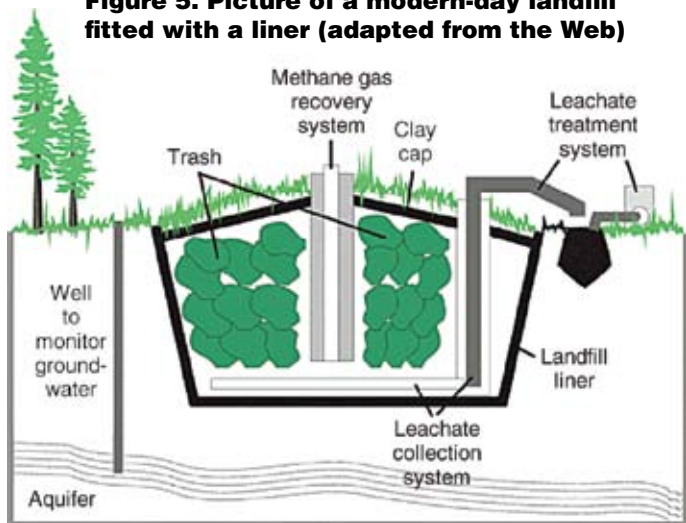
to arsenic leaching. The continuous generation of landfill leachate explains why the design of modern-day landfills have liners. (Figure 5). Such liners are meant to protect under-groundwater sources from contamination.

Landfill leachate has neutral to alkaline pH ranging from 6.5 to 9.0 (Table 1). High concentrations of anions (carbonate, phosphate and sulfate) favor arsenate extraction from arsenic-laden solid residuals.

Landfill leachate is also high in readily biodegradable substrates reflected in very high biochemical oxygen demand (BOD) loadings. In the acidic phase, high BOD values are accounted for largely by volatile fatty acids (VFAs). These VFAs can serve as electron donors to support microbial reduction of arsenate and iron sorbents like ferrihydrites. Landfill leachates support a diverse population of microorganisms that have recently been proven to contribute to arsenic leaching through geochemical cycling.[10]

## Inadequacy of assessment for leaching risk

TCLP may be inadequate at representing mobilization of arsenic in landfill conditions. Evidently, conditions used in TCLP are very different from typical conditions prevalent in a landfill. High pH, a reducing environment, long residence time and anaerobic microbial activity are landfill characteristics that are not simulated by TCLP.

For instance, in an actual landfill, the pH can be as high as 9, alkalinity as high as 11,500 mg/L and TOC 29,000 mg/L. More so, landfill disposal involves liquid and solid residence times on the order of months and decades, whereas TCLP tests are completed in a short (18-hour) contact duration.

TCLP conditions include an acidic pH of 4.9, and an oxidizing and abiotic environment, whereas landfills are characterized by reductive environments. Long residence times of more than five years normally result in creation of alkaline pH (Table 1), which is particularly conducive to leaching of arsenic metals, but such conditions are not replicated by TCLP.

It has been widely established that landfill conditions often promote both changes in redox potentials and also biochemical processes, which can potentially cause transformation of arsenic-bearing solid residuals, resulting in the liberation of arsenic into the leachate. Such processes can result in reduction of arsenate As (V) to arsenite As (III) and, in some cases, to dissolution of the solid onto which the disposed arsenic was previously bound.

As (III) has been proven to be more toxic and mobile than the form onto which it was disposed in the landfills. Such changes

as described above are significant in that they often pose a contamination risk to drinking water sources.

Because of dissimilarities in physicochemical conditions, which occur between TCLP and landfills (Table 1), many residuals from most arsenic-removal technologies pass TCLP. Consequently considered safe for disposal in non-hazardous MSW landfills, characterization of arsenic mobility in samples using TCLP may be inadequate.

## Contradicting evidence

It is, therefore, not surprising that a mounting body of studies have shown that leaching of arsenic from arsenic-bearing solid residuals under simulated landfill conditions is much faster than what would be expected by TCLP characterization.[10] Research compared the effect of different leachates (TCLP, California WET and actual landfill leachate collected from a landfill) on arsenate desorption from common water treatment sorbents.

The conclusions from these studies were that both California WET and TCLP methods mobilized much less arsenic than actual leachates collected from the landfill. The TCLP method mobilized the least amount of arsenic compared to other California WET analyses and actual landfill leachate.

Many residuals from most arsenic removal technologies pass TCLP and are considered safe for disposal in non-hazardous, MSW landfills. There are, however, distinct dissimilarities in physicochemical conditions between TCLP and landfills.

Currently, there is no definitive test to predict the stability of arsenic residuals under landfill conditions and over long periods of time. The development of such a protocol would be useful.

## References

1. F. Frost. 2000. *Dose-Response of Arsenic and Health Effects: Perhaps We Know Too Much*. AWWA Albuquerque Conference.

2. USGS, 1998. Arsenic in Ground-Water Supplies in the United States. *http://co.water.usgs.gov/trace/pubs/segh1998*

3. Bundschuh, J., García, M.E. and Bhattacharya, P.: Arsenic in groundwater of Latin America — A challenge of the 21st century. Geological Society of America Annual Meeting, Philadelphia, 22–25 Oct. 2006, *Geological Society of America Abstracts with Programs* 38:7, 2006, p. 320.

4. US EPA, 2000. "National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Proposed Rule," *Federal Register*, 65:121-38888.

5. Wagman, C., Evans, H., Parker, V., Schumm, R., Harlow, I., Bailey, S., Churney, K. and Butall, R. 1982. *Journal of Physical Chemistry* Ref. Data II, Suppl., 2, 392.

6. US EPA, 2001. "National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Final Rule," *Federal Register*, 66:14-6976.

7. T. Lin, *et al.*, 2001b. Adsorption of Arsenite and Arsenate within Activated Alumina grains: Equilibrium and Kinetics. *Water Research*, 35: 2049-2057.

8. Parks, G., 1990. "Surface Energy and Adsorption at Mineral/Water Interfaces: An Introduction", in *Mineral-Water Interface Geochemistry, Review in Mineralogy*, ed. by M. Hochella and A. White, Mineralogical Society of America, Washington, D.C.

9. D.Clifford, *et al.*, 1999b. *Ion Exchange and Inorganic Adsorption in Water Quality and Treatment*, 5th ed., American Water Works Association, McGraw-Hill, Inc., New York, NY.

10. Amlan Ghosh, Mo Mukiibi and Ela Wendell 2006. Leaching of Arsenic from Granular Ferric Hydroxide Residuals under Mature Landfill Conditions. *Environmental Science and Technology*, 19: 6070-5.

11. R. Schwarzenbach, *et al.*, 1993. *Environmental Organic Chemistry*, John Wiley & Sons, Inc., New York, NY.

12. H. Xu, *et al.*, 1991. Effects of Acidification and Natural Organic Materials on Mobility of Arsenic in the Environment, *Water, Air, and Soil Pollution*, 58:269-278.

13. Amy, G., M. Edwards, P. Brandhuber, L. McNeill, M. Benjamin, F. Vagliasindi, K. Carlson, and J. Chwirka, 2000. *Arsenic Treatability Options and Evaluation of Residuals Management Issues*. AWWA Research Foundation, Denver, CO.

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