

## **The minimization of wastes produced during the treatment of arsenic contaminated drinking water**

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### **Abstract**

Arsenic in potable groundwater is a major concern in the United States and many remediation strategies are being utilized to reduce arsenic levels to below the Environmental Protection Agency's maximum contaminant level of 10 µg/L. The most popular technology is adsorption, where the arsenic species in the groundwater are adsorbed onto a solid metal oxide phase which is ultimately disposed of directly into a landfill. Standard adsorptive media are generally not regenerated due to poor mechanical strength and huge volumes of solid waste are generated annually, typically with arsenic contents of a few milligrams per gram of material. These wastes, which usually pass the Environmental Protection Agency's (EPA) Toxic Characteristic Leaching Procedure (TCLP), are disposed of as non-hazardous wastes. Recent research has indicated that the adsorbed arsenic is mobilized under reducing landfill conditions and can migrate back into the groundwater supply. Consequently, the current method of disposal of large volumes of arsenic-bearing wastes may have a major environmental impact in the future. This paper discusses the advantages of regenerating a more durable iron-based adsorbent media using a strong caustic solution to strip and concentrate the arsenic in a small volume of liquid and return the media to service. The stripped arsenic is then precipitated to generate a much smaller volume of solid and disposed of as a hazardous waste. This greatly reduces the total volume of solid waste generated during the arsenic treatment process.

*Keywords: arsenic, drinking water, landfill, adsorption, regeneration, solid waste disposal, TCLP.*



## 1 Introduction

Arsenic occurs in groundwater in many parts of the USA at levels above the Maximum Contaminant Level (MCL) of 10 µg/L which was implemented in January 2006. An effective method to remove arsenic from potable water is to use adsorptive media which display a high affinity for arsenic over other common anions found in water, such as sulfate, chloride and bicarbonate [1]. This selectivity means that fixed beds of granular adsorptive media may remain in operation for many months before they are exhausted, which results in concentrations of arsenic in the media of several milligrams per gram. (The exact concentration will depend upon the water chemistry and the initial concentration of the arsenic in the water being treated). Once the media has been saturated with arsenic, it is thrown away and replaced with fresh media. Although the adsorbed arsenic can easily be stripped by treating with a solution of sodium hydroxide, the relatively poor physical strength and low resistance of the media to attrition means that this is not routinely performed. The act of sluicing the media into and out of columns during the regeneration procedure causes the granules to be destroyed or greatly reduced in size making the regenerated media unsuitable for further use in a packed bed column. Thus, as regeneration is not an economically viable option, the materials have to be used on a 'once through' basis leading to the generation of large volumes of solid, arsenic-laden wastes that need to be disposed of in a safe and environmentally conscious manner.

The fate of arsenic-bearing wastes in the environment has recently become a concern. Research by Ela and others has shown that although most arsenic adsorbents pass the TCLP test, the arsenic is released from the media under landfill conditions [2-5]. The disposal of large volumes of spent media produced from water systems that have used adsorption to comply with the EPA's drinking water arsenic MCL may potentially cause environmental problems in the future if the arsenic migrates from the landfill back into the groundwater or causes the landfill leachate to require further treatment. A possible solution to this problem would be to use adsorptive media that can be regenerated and reused. This would allow the arsenic to be stripped from the spent media and concentrated into a small volume of solid for a more controlled disposal as hazardous waste. The regenerated media could then be reused which would reduce the solid waste volumes sent to the landfill.

This study compares the relative amounts of solid, arsenic-bearing waste residuals generated using a media on a single use basis compared to the amounts of waste produced by regenerating the media and subsequently concentrating the arsenic waste into a small volume.

## 2 Materials and methods

ArsenX<sup>np</sup> is a hybrid inorganic/organic sorbent that was developed and commercialized by SolmeteX for the removal of arsenic from drinking water [6]. The media consists of hydrous iron oxide nanoparticles impregnated into 300 – 1200 µm durable anion exchange resin beads and is currently manufactured



under license by The Purolite Company in Philadelphia, USA. The small size of the hydrous iron oxide particles and the high porosity of the polymer substrate ensure that reaction kinetics associated with arsenic uptake are rapid and the arsenic removal capacity is high. The field arsenic capacity and service life is similar to many commercial granular adsorption media [7].

The elemental iron content of ArsenX<sup>np</sup> is typically around 25% dry weight. The crystallographic form of the iron oxide has yet to be conclusively determined since the material is poorly crystalline which makes the precise identification of the iron compound(s) via X-Ray Powder Diffraction (XRD) difficult [8]. Weak reflections in the XRD pattern suggest that the form of the hydrous iron oxide may be goethite, FeOOH, but the peaks are rather broad and limited in number. The polymer component of the media means that it has an appreciable crush strength, similar to standard ion exchange resins. This is in stark contrast to the bulk of the commercially available granular adsorption media which readily crush when exposed to pressure.

The greater physical strength of ArsenX<sup>np</sup> means that it can be easily regenerated using a caustic solution followed by a wash to reduce the pH of the resin to neutral. The vast majority of the adsorbed ions (e.g. arsenate, phosphate) are rapidly eluted from the resin in a small eluant volume which can be further treated to produce a minimum of solid waste for disposal. The regenerated media is then reused for further water treatment with only a small decrease in arsenic capacity.

### 3 Regeneration process

ArsenX<sup>np</sup> can be successfully regenerated in a column configuration by slowly passing 10 bed volumes of a caustic solution through the media followed by a wash with carbon dioxide-saturated water or brine to return the pH of the media to neutral. The precise conditions used for the regeneration process are proprietary and were developed at SolmeteX to maximize the regeneration efficiency and produce the minimum volume of waste for disposal. Once the regeneration process has been completed, the caustic solution contains almost all of the arsenic and other adsorbed species and needs to be treated prior to safe disposal. The wash solution only contains trace levels of toxic species and is generally suitable for direct disposal to sewer without further treatment or can be reused if required. The regeneration process has been certified by the Water Quality Association (WQA) allowing the regenerated media to be reused for potable water treatment.

#### 3.1 Laboratory study

A sample of ArsenX<sup>np</sup> that had been used in a field trial was regenerated at SolmeteX using a caustic brine solution and this spent solution was then neutralized with hydrochloric acid. Selected analytical data is summarized below in Table 1. This sample of ArsenX<sup>np</sup> was used in a groundwater containing arsenic and vanadium. Both ions were adsorbed by the media and subsequently



released during the regeneration process. The major anion present in solution after neutralization was chloride (originating from the initial regenerant solution and the hydrochloric acid) which had a concentration in excess of 10,000 mg/L. Sodium was the major cation present (originating from the regenerant solution), though mg/L levels of other metals, such as iron, calcium, uranium and barium have been detected in laboratory studies at SolmeteX. The exact composition of the trace components is highly dependent upon the trace composition of the water that was treated.

Table 1: Selected components in the neutralized spent regenerant solution.

Component	Arsenic	Vanadium	Sulfate	Initial pH
Concentration / mg/L	50.0	3.48	2280	6.06

The addition of 0.05 mL of a 40% (w/v) solution of  $\text{FeCl}_3$  to 20 mL of the waste solution was found to be sufficient to reduce the vanadium and arsenic concentrations via a precipitation and adsorption mechanism to below the detection limit. If all of this iron reacts to form  $\text{Fe}(\text{OH})_3$ , the total mass of iron hydroxide produced would be 0.66 g. Assuming the sludge after filtration will contain 90% water, the mass of solid waste for disposal as a hazardous waste is approximately 6.6 g per liter of regenerant solution.

This calculation of sludge production is specific for this particular sample of  $\text{ArsenX}^{np}$  that was used in the regeneration studies.  $\text{ArsenX}^{np}$  that contains a greater concentration of arsenic and other species would produce higher concentrations of arsenic in the regenerant waste stream. This would subsequently require a greater mass of ferric chloride to achieve a low enough concentration of toxic species left in solution to allow the liquid to be suitable for discharge to sewer.

### 3.2 Full scale application

The regeneration process developed in the laboratory was scaled up at the Mobile Process Technologies (now Basin Water) plant in Memphis, Tennessee and used to regenerate 1,330 liters of arsenic-laden  $\text{ArsenX}^{np}$  media from field installations. A total of 11,350 liters of arsenic-bearing caustic regenerant waste was produced which was neutralized using hydrochloric acid and then treated with sufficient ferric chloride solution to remove all the soluble arsenic and other species that had been eluted from the  $\text{ArsenX}^{np}$  by the caustic. The ferric hydroxide floc was allowed to settle under gravity and the aqueous phase decanted. The waste liquid was then analyzed for arsenic and other metals and discharged to the sewer once it was confirmed that it met discharge criteria. The major ions in this solution were  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  with concentrations in the hundreds or thousands of milligrams per liter. The floc suspension was then passed through a filter press to reduce the moisture content and minimize the volume for ultimate disposal.

The total volume of concentrated iron sludge produced following the ferric chloride treatment was 170 liters which was sent for disposal at a hazardous



waste landfill, even though it almost certainly passed the TCLP test. The water content of this sludge was not determined making direct comparison to earlier laboratory data impossible. Thus, the total solid arsenic-bearing waste for disposal was reduced from 1,330 liters to just 170 liters, approximately one eighth of the waste volume that would have been produced if the media was used on a once-through basis. A picture of the sludge cake is shown in Figure 1. The amount of sludge produced will primarily depend upon the total concentration of arsenic in the regenerant caustic solution which will in turn depend upon the concentration of arsenic on the spent media. (ArsenX<sup>np</sup> that was used in low pH waters ( $\text{pH} < 7$ ) may have arsenic levels at exhaustion that are several times higher than the levels found on ArsenX<sup>np</sup> that was used in high pH waters ( $\text{pH} > 8$ )).



Figure 1: Ferric hydroxide sludge after filter press. (White particles are precoat used to coat the filter press.)

The relative volume of solid waste generated to the volume of regenerated ArsenX<sup>np</sup> in this full-scale regeneration run was similar to the laboratory scale regeneration study described in Section 3.1. The 170 liters of ferric hydroxide sludge that was generated from 11,350 liters of spent regenerant solution is equivalent to approximately 15 mL of waste produced per liter of solution treated. The laboratory study produced an estimated 6.6 g of sludge (a volume of probably 4-5 mL) for a regenerant solution with a much lower concentration of

arsenic. Differences between the two numbers are likely to be due to variations in the moisture content of the sludge and the concentrations of arsenic and other contaminants in the spent regenerant solution.

## 4 Discussion

### 4.1 Landfill conditions and arsenic leaching

The TCLP (and the more stringent California Waste Extraction Test (WET) test) are designed to determine whether a solid waste is suitable for disposal in a non-hazardous waste landfill. The tests are carried out under slightly acidic conditions and are more appropriate to determine the leachability of heavy metals, such as lead and copper, which tend to become more mobile as the pH decreases. By contrast, the capacity of adsorptive media for arsenic is greater at the pHs of the TCLP and WET tests than under most groundwater conditions and thus these tests are not really appropriate to assess arsenic leachability. Critically, both of these tests are under oxidizing or neutral conditions and thus favor the formation of the more strongly adsorbed As(V) species rather than As(III) which is far more mobile in the environment. Some of the key parameters of natural landfill conditions, TCLP and the California WET test are shown below in Table 2.

Table 2: Comparison of landfill conditions, California WET test and TCLP.

Parameter	TCLP	California WET Test	Mature Landfill
<b>pH</b>	4.95	5.05	7-9
<b>Bioactivity</b>	Abiotic	Abiotic	Biotic
<b>Contact Time</b>	18 hrs	48 hrs	Weeks/months
<b>Active component</b>	acetate	citrate	Organic/inorganic mixture
<b>Redox condition</b>	Oxidizing	Neutral	Reducing

It is clear that landfill conditions are very different from the test conditions and recent research has demonstrated that under anaerobic reducing conditions, arsenic is rapidly released from arsenic-laden adsorptive media and naturally occurring iron oxides. Conditions including the pH of the landfill, the Redox conditions, competing anions (e.g. phosphate) and the presence of organic compounds in landfill leachates have all been shown to influence arsenic mobility [9–11].

The stability diagrams of iron oxides and arsenic (Figure 2) show that landfill leachate conditions fall into a region where the stable form of iron is soluble Fe(II) and the thermodynamically favored oxidation state of arsenic is As(III). This is in contrast to the iron sludge formed by the precipitation of iron(III) hydroxide and arsenate (As(V)). Consequently, if this waste sludge is placed in a landfill, it can be expected that the iron would be reduced to soluble Fe(II) and



the arsenate reduced to the more mobile As(III) form. Typical granular iron media and ferric hydroxide sludges generated by the treatment of potable water would be expected to behave in a similar manner. Consequently, such media may be better classed as a hazardous waste and disposed of as such.

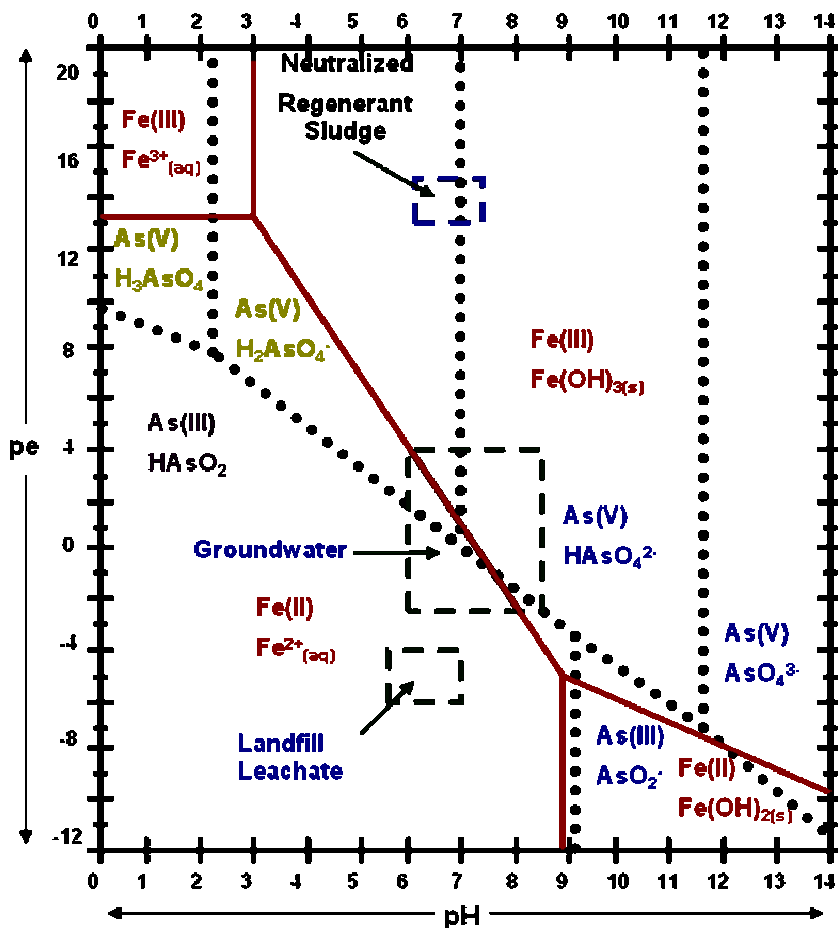


Figure 2: Stability diagram for arsenic and iron [12].

## 5 Conclusions

The use of adsorptive media to remove arsenic from drinking water is an effective method to meet the arsenic MCL but leads to the generation of large volumes of arsenic-laden solid wastes for landfill disposal. Recent research has raised concerns regarding the mobility of arsenic adsorbed onto metal oxide substrates under landfill conditions and has questioned the validity of TCLP and

the California WET tests as appropriate tests to determine suitability of this solid waste for non-hazardous landfill disposal. Laboratory-scale trials on regenerating ArsenX<sup>np</sup>, a commercially available media for arsenic adsorption, demonstrated that the media could be successfully regenerated leading to a large reduction in the volume of solid waste requiring disposal. This regeneration process has now been proven on a commercial scale.

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