

FINAL REPORT

Date covered in this report: 10/14/2005-7/29/2008

PROJECT TITLE: The feasibility of removing inorganic arsenic from landfill leachate via sorption to mineral oxide surfaces.

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COMPLETION DATE: 7/29/08

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KEY WORDS: Arsenic, arsenate, arsenite, mineral oxide, landfill, leachate, sorption, selenite.

ABSTRACT

Arsenic in landfill leachate poses a potential problem to landfills in Florida during final leachate disposal when concentrations are above allowable limits. From a list of 68 solid waste directors in Florida, 26 responded to our email or telephone queries and 7 identified arsenic as a problem during final leachate disposal. These sites included Alachua County, Lake County, Marion County, Martin County, Orange County, Polk County and Santa Rosa County. For all, leachate was treated offsite at either a waste water treatment plant or by deep well injection. These sites paid hauling and disposal fees and faced surcharges due to leachate characteristics like concentrations of arsenic and BOD. Mineral oxides sorbents that have been gaining wide use in arsenic removal during drinking water treatment were examined in this study for their potential to remove arsenic from landfill leachate, an onsite treatment option. Though physical characteristics of Bayoxide E33 (iron oxide), ADSORBSIA GTO (titanium oxide) and Kemiron (iron oxide) were done in this study, emphasis was placed on Kemiron which has a local distributor in Florida that was interested in this application. BET surface area of Kemiron is 39.8 m²/g and Electron Dispersive Spectroscopy (EDS) studies found Kemiron to be 40.37% iron and 42.25 % oxygen by mass. Leachate (filtered) obtained from Polk County's North Central Landfill did not affect the sorption of 800 ppb arsenate (As(V)) onto 1 g/L Kemiron between pH 5 and 9. Batch systems for arsenate (As(V)), arsenite (As(III)) and selenite (Se(IV)) removal from aqueous solutions as a function of pH, ionic strength, and particle size (< 38 μ m and between 250 and 425 μ m) were investigated and showed typical anionic behavior whereas As(III) sorption showed a maximum around pH 8. Langmuir isotherms best described the As(V) and Se(IV) removal at pH 7 with maximum adsorption capacity of 82 mg/g and 52 mg/g respectively. As(V) and Se(IV) sorption decreased as pH increased and both anions were unaffected by sodium nitrate (NaNO₃) background electrolyte. As(V) sorption decreased in the presence of Se(IV), increased in the presence of Ca and remained unchanged in the presence of sulfate or carbonate. Though Bayoxide E33 had a higher surface area (95 m²/g) than Kemiron, its sorption capacity for As(V) under similar conditions was significantly lower. Rate of uptake experiments show that the capacity of 250-425 μ m particles to sorb As(V) to be significantly lower than the 38 μ m particles.

EXECUTIVE SUMMARY

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Initially, only a relatively small portion of the Los Angeles Basin was affected, but a tremendous influx of new residents and new industrial growth CCA-treated wood or its combustion products in landfills in Florida are potential sources of arsenic which may become a part of the landfill leachate stream. Arsenic in landfill leachate solutions raises concerns over groundwater contamination for unlined landfills and proper disposal or management for lined landfills. Arsenic is toxic with a drinking water Maximum Contaminant Level of 10 ppb. There are options for treating landfill leachate to remove arsenic. For example, some landfills use membrane processes to remove arsenic whilst some ship the leachate offsite to a wastewater treatment facility. Costs associated with leachate disposal/treatment could potentially be high and in some cases is directly linked to the arsenic concentration in the leachate. This study examined the conditions under which arsenic can be removed from leachate on site through sorption processes using mineral oxide surfaces. This could potentially be a cost effective and efficient treatment alternative for arsenic in landfill leachate.

OBJECTIVES: 1) To identify Class 1 landfills in Florida with potential leachate disposal problems due to arsenic and select experimental conditions based on leachate characterization information, 2) To determine the influence of geochemical conditions pH, ionic strength, and the presence of competing ions on the removal of arsenic from landfill leachate solutions using commercially available mineral oxides, and 3) To model arsenic sorption to commercially available mineral oxides.

METHODOLOGY: Attempts were made to contact 68 solid waste directors on a master list provided by the Florida Department of Environmental Protection (FDEP). They were asked about arsenic concentrations in leachate and whether it posed a disposal problem to determine the scope of the problem due to arsenic in landfill leachate in Florida. Available leachate records from the landfills with problems were examined to identify contaminants and conditions for conducting further laboratory studies on arsenic removal from landfill leachate. Three different commercially available mineral oxide sorbents (Bayoxide E33, ADSORBSIA GTO and Kemiron) were characterized for surface area, porosity, mineralogy, and elemental make up. Kemiron, an iron oxide based sorbent, has a local distributor in Florida and was used for the majority of the studies done in this report. These experiments included batch equilibrium sorption and rate of uptake laboratory studies of As(V), As(III) and Se(IV). Se(IV) was chosen not only to serve as a co-contaminant, but also because its concentrations in leachate also approach regulatory limits though not as close as arsenic. The influence of geochemical conditions like pH (4-10), contaminant concentration, ionic strength (0.001 N and 0.1 N NaNO₃), and the

presence of selenite, calcium, carbonate and sulfate on arsenic (As(V)) removal were examined in the laboratory. Arsenic removal in the presence of actual landfill leachate was characterized for Kemiron and ALCOA DD660, an aluminum based mineral oxide for which much As(V) and As(III) sorption has already been done.

RATIONALE: CCA-treated wood or its combustion products in landfills in Florida are potential sources of arsenic. Arsenic in landfill leachate solutions raises concerns over groundwater contamination for unlined landfills and proper disposal or management for lined landfills. Figure 1 depicts a typical lined landfill in which leachate in which some leachate is recycled through the landfill to assist with biodegradation processes. Waste distributed throughout a landfill releases heavy metals like arsenic which collect in leachate solution. That leachate solution is either hauled to an offsite treatment plant or recycled back into the landfill. If recycled into the landfill, the leachate containing the heavy metal of concern is sprayed throughout the landfill, thereby possibly contaminating a larger area of the landfill. Unlike organic compounds, heavy metals like arsenic do not degrade. An opportunity exists to capture the heavy metals released to leachate in an onsite treatment step that minimizes the volume occupied by the heavy metal, making it easier to recycle it or easier to dispose of it in a controlled environment. It should be noted that if leachate is sent to a waste water treatment plant, the heavy metals will more than likely return to the landfill in the biosolids waste from the treatment facility.

One option for collecting the heavy metals in the leachate involves passing the leachate through fixed beds of adsorbent particles consisting of mineral oxides. Under the right conditions these particles can accumulate the heavy metals through sorption processes. For example, the approximate surface area of Phase I and Phase II at Polk County North Central Landfill is $4 \times 10^6 \text{ ft}^2$. In 2004, 7.9×10^6 gallons of leachate was produced. If we assume an average arsenic concentration in leachate of $100 \text{ } \mu\text{g/L}$, then the landfill would produce $\sim 3023 \text{ g As/yr}$. If we assume that a sorbent has a capacity of $40 \text{ mg As/g sorbent}$, then, the amount of sorbent required to treat the arsenic would be $(3023 \text{ g As/yr} \times 1000 \text{ mg/g})/40 \text{ mg As/g sorbent} = 76,000 \text{ g sorbent/yr}$ or 167 lbs/yr . Hence, the arsenic that was leached in a year from a landfill surface area of 424 ft^2 , can be collected in a small footprint fixed bed reactor on mineral oxide sorbents weighing no more than an average man. The arsenic collected on the sorbents can either be recycled, fixed via some addition process, or stored in a smaller landfill site where it can be better managed to prevent leaching and contamination of a larger landfill area once again.

Processes to Consider in a Lined Landfill "Bioreactor"

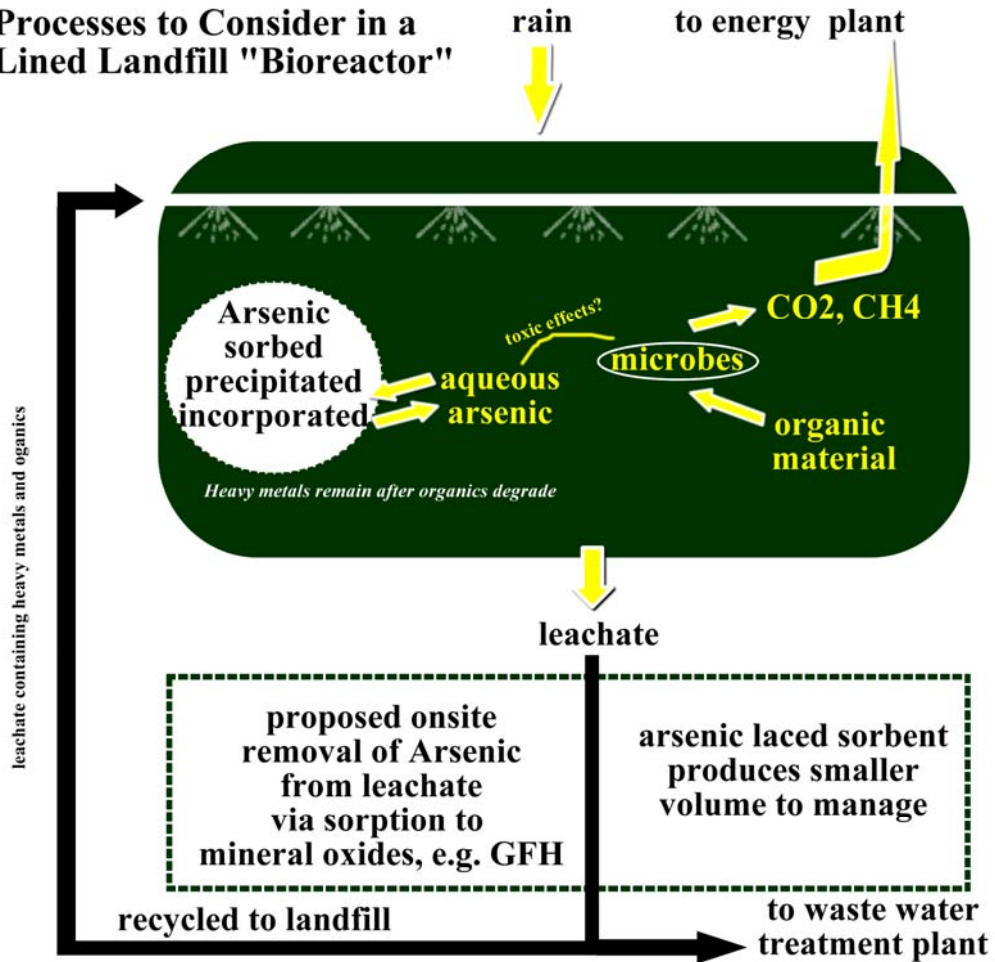


Figure 1 Schematic of rationale for on-site treatment of landfill leachate.

RESULTS: We attempted to contact 68 Florida landfills (not only active Class 1 landfills) via email and phone to learn about their leachate disposal practices and total arsenic concentrations. Of the 68 landfills on the list, we got 26 responses and of those 26 responses we identified 7 landfills in Florida that would benefit from this study. Landfills with leachate that had arsenic concentrations greater than 10 ppb combined with a disposal issue related to arsenic were identified. The seven landfills identified were:

- Alachua County
- Lake County
- Marion County
- Martin County
- Orange County
- Polk County
- Santa Rosa County.

These seven landfills paid for offsite leachate disposal and sometimes had an additional surcharge fee because arsenic concentrations were above permissible limits. Though

leachate contained a list of other heavy metals, arsenic concentrations were closer to or above permissible limits. Arsenic speciation was not provided by the various landfills and this study examined both As(III) and As(V) sorption.

Mineral oxides sorbents that have been gaining wide use in arsenic removal during drinking water treatment were examined in this study for their potential to remove arsenic from landfill leachate, an onsite treatment option. Though physical characteristics of Bayoxide E33 (iron oxide), ADSORBSIA GTO (titanium oxide) and Kemiron (iron oxide) were done in this study, emphasis was placed on Kemiron which has a local distributor in Florida that was interested in this application. BET surface area of Kemiron is 39.8 m²/g and Electron dispersive spectroscopy (EDS) studies found Kemiron to be 40.37% iron and 42.25 % oxygen by mass. Leachate (filtered) obtained from Polk County's North Central Landfill did not affect the sorption of 800 ppb arsenate (As(V)) onto 1 g/L Kemiron between pH 5 and 9 though it did reduce the sorption of 800 ppb As(V) on ALCOA DD660. Batch systems for arsenate (As(V)), arsenite (As(III)) and selenite (Se(IV)) removal from aqueous solutions as a function of pH, ionic strength, and particle size (< 38 µm and between 250 and 425 µm) were investigated using Kemiron. Langmuir isotherms best described the As(V), and Se(IV) removal at pH 7 with maximum adsorption capacity on Kemiron of 82 mg/g and 52 mg/g respectively. As(V) and Se(IV) sorption decreased as pH increased and both anions were unaffected by sodium nitrate (NaNO₃) background electrolyte. As(V) sorption decreased in the presence of Se(IV), increased in the presence of Ca and remained unchanged in the presence of sulfate or carbonate. The presence of calcium in a molar ratio of approximately 2:1 compared with As(V) enhanced As(V) removal from Kemiron. As(III) sorption onto Kemiron showed a maximum around pH 8 and was also not affected by ionic strength. Freundlich isotherms better described As(III) sorption to Kemiron and for the conditions studied in the lab, loadings of ~ 90 mg As(III)/g Kemiron were seen at pH 7.

The results of this research show that arsenic can be removed from landfill leachate via sorption to mineral oxide surfaces, however, more studies have to be completed to fully assess the feasibility of using this system in the field. Based on laboratory experiments, a pre-treatment step is necessary to filter leachate prior to interaction with mineral oxide surfaces. Membrane bioreactors are an example of a pretreatment step that not only reduces the solids loading, but also removes COD. Whilst such a system would change the overall make up of the leachate solution owing to the removal of organic compounds, it would not affect the total metal concentrations. Hence, the work initiated in this project would still be applicable in terms of assessing arsenic removal from complex matrices. Once developed fully this project will benefit landfill operators whose costs associated with disposal of their arsenic containing leachate are high.

This project directly supported Douglas Oti, a PhD student and provided research opportunities for undergraduate students Ryan Locicero and Austin Roe and high school teacher Ann McNicol. The following papers/presentations were made as a part of this project:

1. Oti, D. and M.A. Trotz. (2008) Characterization and Adsorption of Arsenate and Selenite onto Kemiron. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substance and Environmental Engineering*, 43 (10).
2. Oti, D.; Roe, A.; Trotz, M. A. Arsenic removal using Kemoxide, a commercially available iron oxide sorbent. Poster presentation to be made by Douglas Oti at the 2006 Florida AWMA conference on 9/22/2006.
3. Trotz, M. A. Arsenic removal from drinking water and landfill leachate via sorption to commercially available mineral oxides. Presented at the Florida Section of the American Chemical Society, FAME Environmental Chemistry symposium, Orlando, FL. Invited Presentation on 5/11/2006.
4. Locicero, R. Oti, D., Roe, M., and M. Trotz. Removing arsenic from Class 1 Florida landfill leachate using commercially available mineral oxides. Undergraduate posters were also presented at the USF REU poster symposium 4/2006.
<http://reu.eng.usf.edu/Symposium/Symp2006/symposiumS2006.asp>
5. Oti, D., Thomas, K., and M.A. Trotz. Understanding the solid/liquid interface and its importance to arsenic mobility. Poster presented at the USF interdisciplinary graduate poster symposium (3/2007).

The original project website, landfillinfo.net, was replaced by landfillinfosite.com because of high fees associated with the expiration of the original domain name and hosting shifted to the USF server under the PI's account.

CONCLUSIONS: Onsite treatment of landfill leachate can potentially be economically more feasible than hauling to a treatment facility which incurs surcharges depending on concentrations of contaminants like arsenic and BOD. In Florida, seven landfill sites identified arsenic as a problem in leachate because concentrations were above limits acceptable to treatment facilities resulting in disposal surcharges. There may be more landfills in Florida facing this problem, however, of a list of 68 solid waste directors, project personnel were only able to reach 26 as a part of this project. This study showed that arsenic could be removed from leachate using commercially available mineral oxides, however, a pretreatment step was used to filter leachate through a 0.45 μm filter. In the field, this pretreatment step could take the form of a membrane bioreactor that not only reduces turbidity, but also removes BOD and COD.