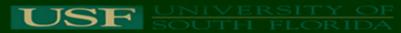
# The feasibility of removing inorganic arsenic from landfill leachate via sorption to mineral oxide surfaces.

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5/1/06



Presentation made to Technical Advisory Group USF, Tampa, FL



## **Outline**

- Introductions
  - TAG members
- Project Background
  - The scope of the Florida Center Proposal
- Research Progress
- The next 6 months of research

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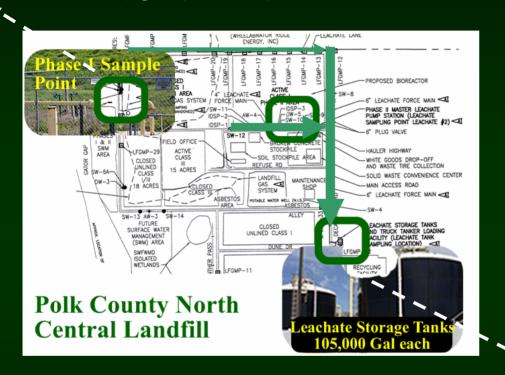
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## Leachate Collection System

Total As: 157 μg/L (4/12/05)



2004 Leachate				
Quantity	Quantity (gallons)			
Phase I	1,730,400			
Phase 2	6,418,206			
Tank then hauled to Treatment	7,986,529			

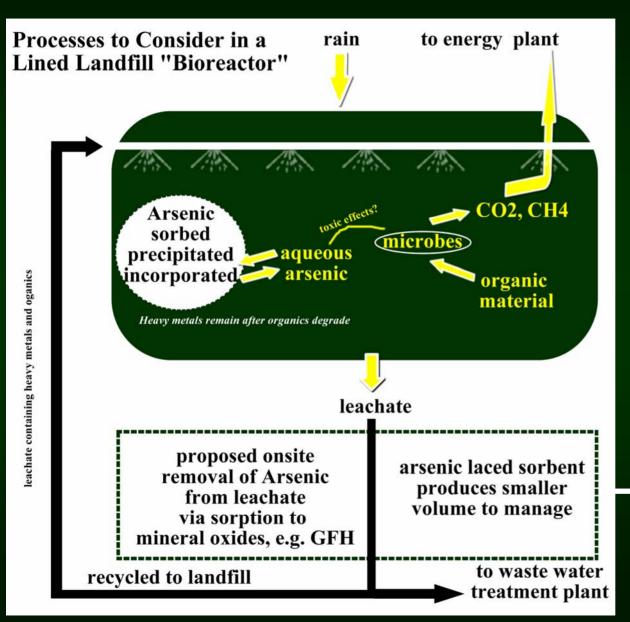
Total As: 89 μg/L (4/12/05)

Filtrate: 66 ug/L

Let, average As in tank = 100 μg/L

Leachate produced: 7,986,529 gals/yr x 3.785 L/gal \* 100E-6 g As/L = 3023 g As/yr

### Rationale for on site removal of As from leachate



Approximate surface area of Phase I and Phase II at Polk County North Central Landfill is 4 x 10<sup>6</sup> ft<sup>2</sup>.

In 2004, 7.9 x 10<sup>6</sup> gals leachate produced. Assume average As conc. in leachate was 100 µg/L, produced ~ 3023 g As/yr

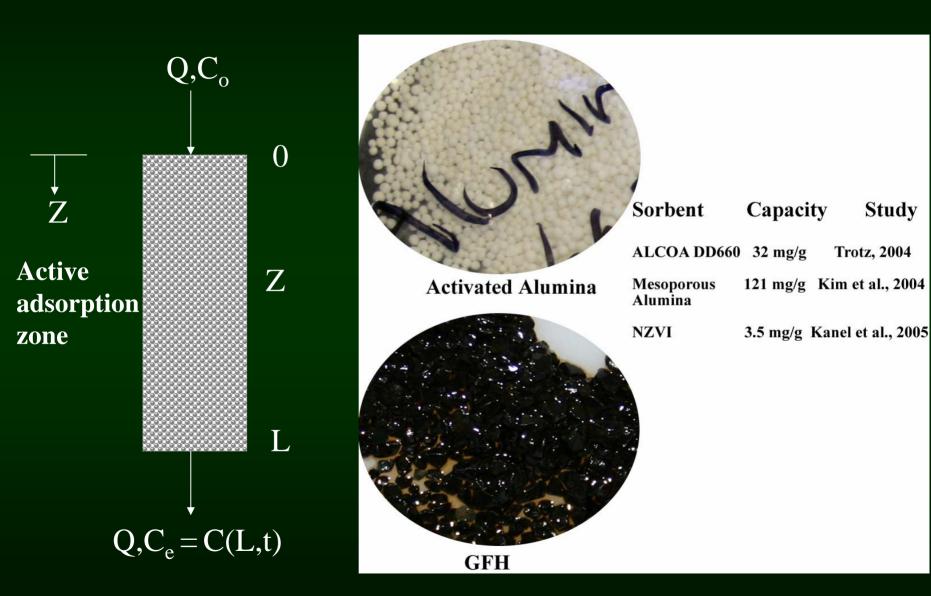
Assume sorbent Capacity: = 40 mg As/g sorbent

3023 g As/yr x 1000 mg/g 40 mg As/g sorbent

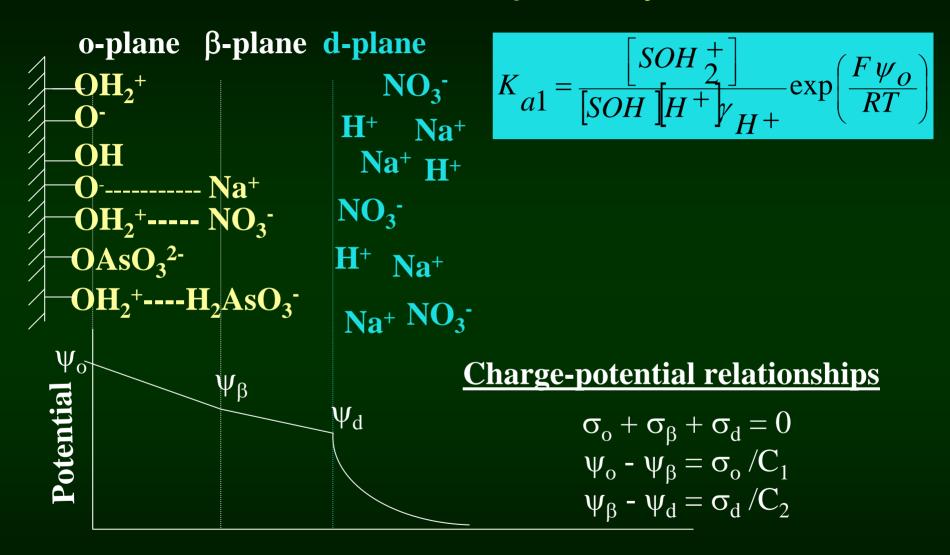
= 76,000 g sorbent/yr

## Sorption Processes

Study



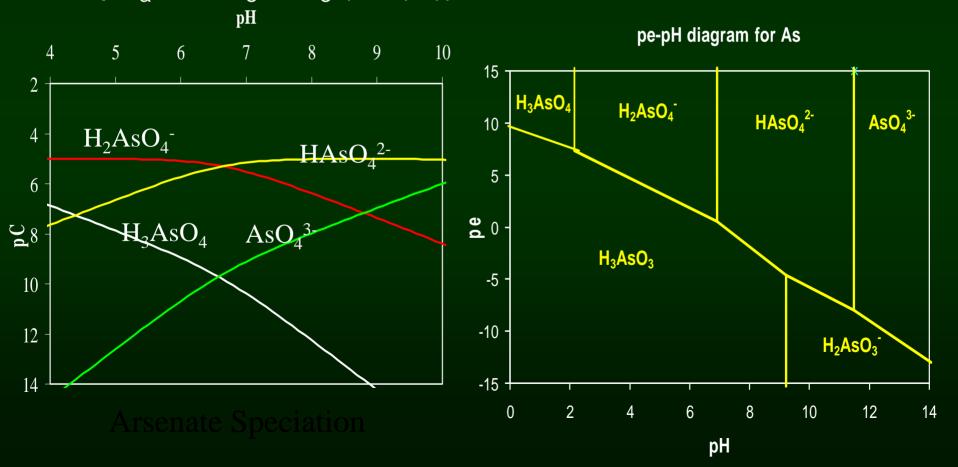
## Schematic of the Triple Layer Model



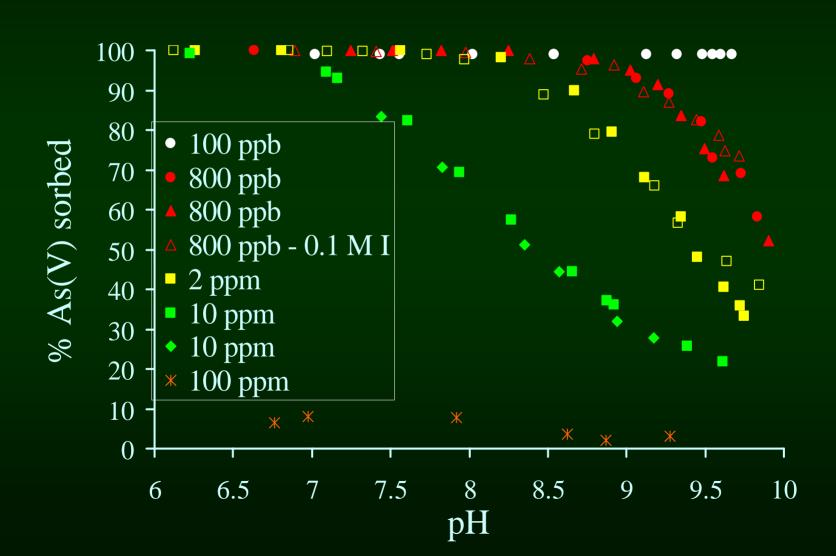
Distance from surface

## **Arsenic Chemistry**

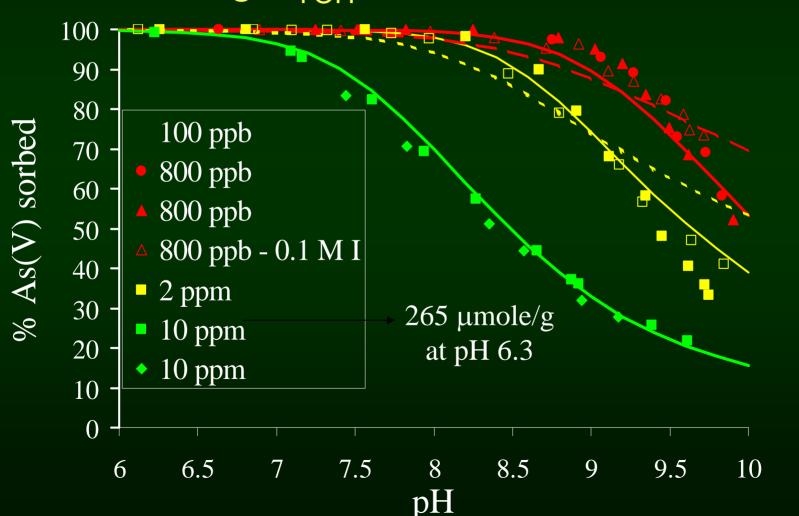
- inorganic forms in the +3 and +5 oxidation states
- pK<sub>a</sub>s for H<sub>3</sub>AsO<sub>4</sub> (As (V)) : 2.19, 6.94, 11.5
- pK<sub>a</sub>s for H<sub>3</sub>AsO<sub>3</sub> (As (III)) : 9.23, 12.13, 13.4



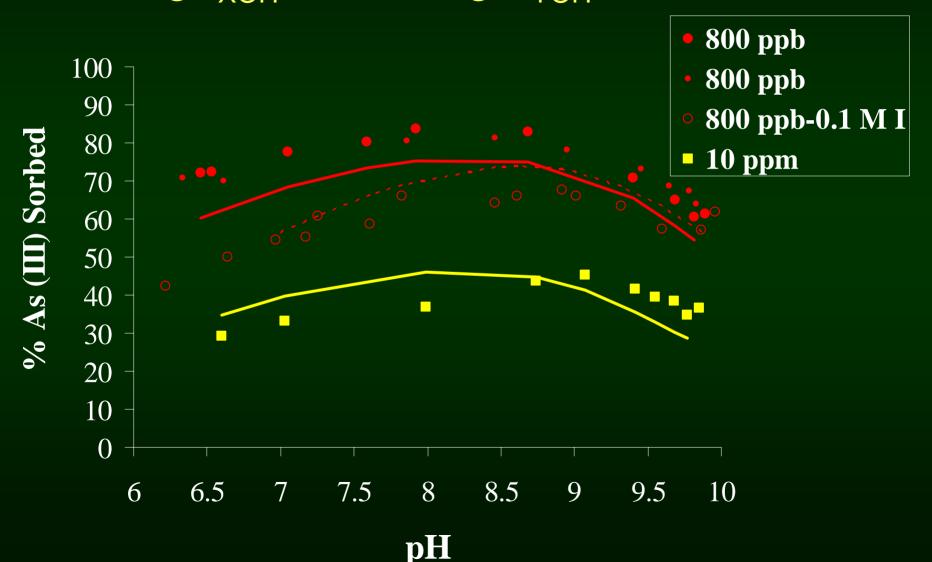
# As(V) Sorption: 0.5 g/L DD660 0.01 M NaNO<sub>3</sub>, no $CO_2$



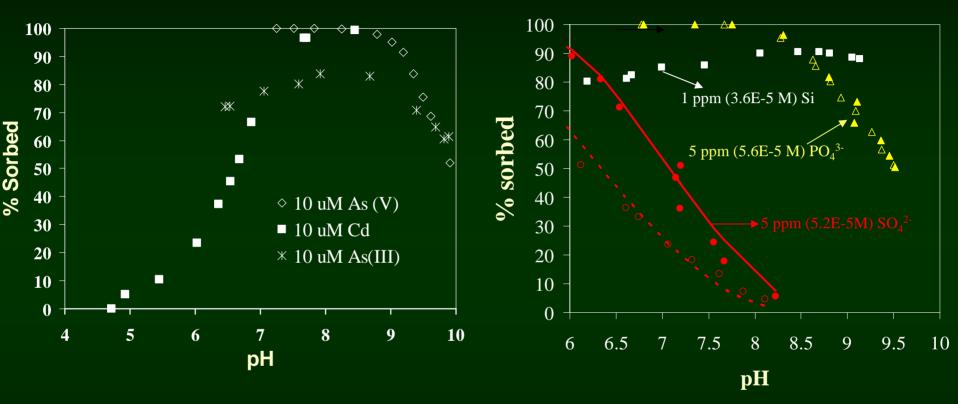
As(V) Sorption: lines are TLM fits 0.5% YOH:  $SOAsO_3H^-$  &  $SOH_2^+...HAsO_4^{2-}$  log  $K_{XOH} = 25.0$ ; 25.1 log  $K_{YOH} = 25.5$ ; 25.3



As(III) Sorption: lines are TLM fits 0.5% YOH:  $SOH_2^{+0.5}...H_2AsO_3^{-0.5}$   $logK_{XOH} = 37.5$ ;  $logK_{YOH} = 40.5$ 



## Sorption of ions to DD660 Alumina



0.5 g/L, 0.01 or 0.1 N NaNO<sub>3</sub> background electrolyte. No CO<sub>2</sub>. Binary systems.

## Project Objectives

Objective 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.

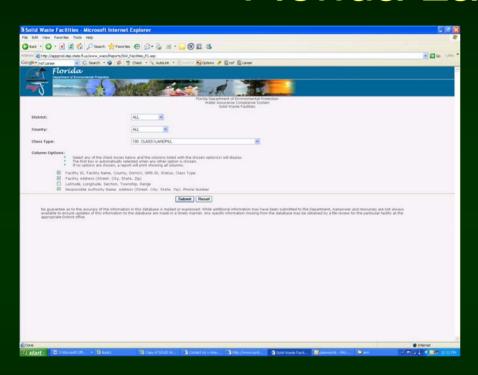
Objective 2: To determine the influence of geochemical conditions (pH, temperature, ionic strength, competing ions) on the removal of arsenic from landfill leachate solutions using mineral oxide surfaces

Objective 3: To establish an equilibrium modeling dataset that can be used to predict the feasibility of arsenic removal under a range of geochemical conditions.

# Objectives/Tasks/Timeline

October 2005	January 2006	April 2006	July 2006	October 2006
		Î	·	
Task 1 (a): Identificat	tion and ranking of F	lorida landfills with A	rsenic in leachate	
Task 1 (b):	Compilation of leach	ate data for landfills	identified in Task 1 (a	)
Task 1 (c): Literature	review of treatment	options for landfill lea	chate with arsenic	
	1st quarterly	report		
	Task 2: Characteriza	tion of sorbents and l	andfill leachates	
		2nd quarter 1st TAG me	ly report eting	
	Task 3: Batch	sorption experiment	s using clean systems	and landfill leachate
		Task 4: Modelin	g of batch sorption ex	perim ents
			3rd quarter	ly report
				4th quartrely report
				Final report

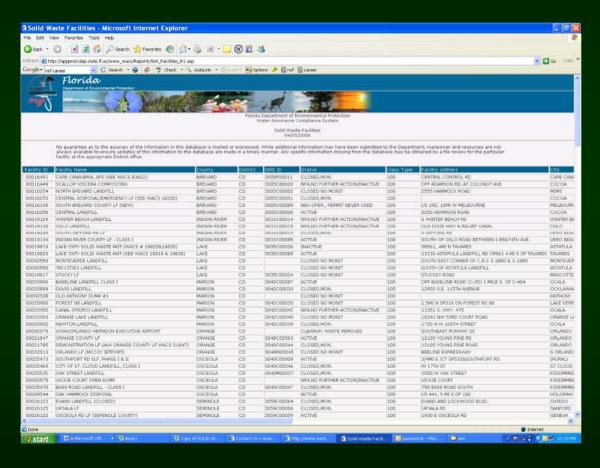
# Identification and Ranking of Florida Landfills



An excel spreadsheet of solid waste facilities was also provided by Lee Martin of the FDEP. This list also included non Class 1 landfills. We attempted to contact all 68 people on that list:

- 1. email
- 2. phone

# Identification and Ranking of Florida Landfills



230 Class 1 Landfills
52 are ACTIVE
1 ACT NOT PERMITED
1 CLEANUP, WASTE REMOVED
19 CLOSED NO MONIT
127 CLOSED, MONITORING
21 INACTIVE
4 NEV.OPER., PERMIT NEVER USED
5 NFA.NO FURTHER ACTION/INACTIVE

# Landfills in Florida with arsenic leachate concerns

- Alachua County Public Works. phone: (352) 374-5213, contact: David Wood; Average Arsenic concentration 130 ppb, cost of transporting to facility \$70-73/1000 gallons.
- Lake County, Solid Waste Mgmt Services. phone: (352) 343-6030, contact Gary Debo. Leachate disposal is accomplished by trucking to Jacksonville (approx. 130 miles one way) at a cost of \$0.13/gallon for transportation & disposal. \$130.00/1,000 gallons. Arsenic Levels 10/2/04 11ug/L, 10/26/04 -18ug/L, 05/10/05 19ug/L.
- Marion County Solid Waste Dept, Ocala, FL. phone: (352) 245-4584, contact: Mike Sims. current Arsenic concentrations 78 ppb, method of disposal is a Pipeline to the City of Ocala Waste Water Treatment Plant #2. Cost of disposal \$9.00 / 1000 gallons. Arsenic surcharge in effect.
- Martin County Solid Waste Management Department. phone (772) 221-1386, Stuart, FL, contact: Patrick N. Yancey. Arsenic concentration level 280 ppb. Martin County hauls all leachate and it is deep well injected at a local Utility (a permitted disposal site). Hauling and disposal costs are \$23.23/1000 gallons.

# Landfills in Florida with arsenic leachate concerns cont'd

- Orange County Resource Rec Dept. phone (407) 836-7251, contact: Ryan. Arsenic concentration is 280 ppb. The leachate is disposed of through a pipe network to the nearby Orange County wastewater treatment plant. Cost of treatment is \$3.17/1,000 gallons. Though they are surcharge for high concentration of heavy metals and for BOD that is over 300 mg/l and TSS that is over 300 mg/l. For July the flow was 3,584,000 gallons (\$11,361.28) and the surcharge bill was \$43,737.53.
- Polk County Solid Waste Division. (863) 284-4319, Interim solid waste director, Brooks Stayer. Maintain North Central Polk county, NE Landfill (Hanes City), SE Landfill (whales); also contact Allan Choate Sample date 4/14/05, 0.131 mg/l at Phase I Leachate Pumping Station; 0.072 mg/l at Phase II Leachate Pumping Station. Haul by truck to an industrial wastewater treatment facility. The County has an annual contract for the service. The contractor is Aqua Clean Environmental Co., Inc. in Lakeland. Hauling at \$10.00 +Treatment/Disposal at \$100.00 = \$110.00/1,000 gallons.

## Leachate Characteristics

#### Marion County

	City of Ocala Limits	Marion County Leachate				
	mg/L					
		10/2/2002	3/26/2003	3/4/2004	3/8/2005	3/10/2006
Arsenic	0.06	0.04	0.033	0.066	0.1	0.1
Cadmium	0.53	0.005	<.001	0.00024	0.00013	0.00051
Chromium	14.44	0.038	0.013	0.039	0.1	0.072
Copper	2.95	0.05	0.013	0.0052	0.015	0.011
Lead	2.42	0.01	<.005	<.00189	0.097	0.0056
Mercury	0.6	0.0005	<.0001	0.000056	0.00018	0.000073
Nickel	4.38	0.11	<.0052	0.15	0.17	0.11
Selenium	0.54	0.01	<.01	<0.004	0.0021	0.0065
Silver	1.43	0.01	<.005	0.0042	0.0022	0.003
Zinc	5.51	0.1	0.022	0.05	0.19	0.066

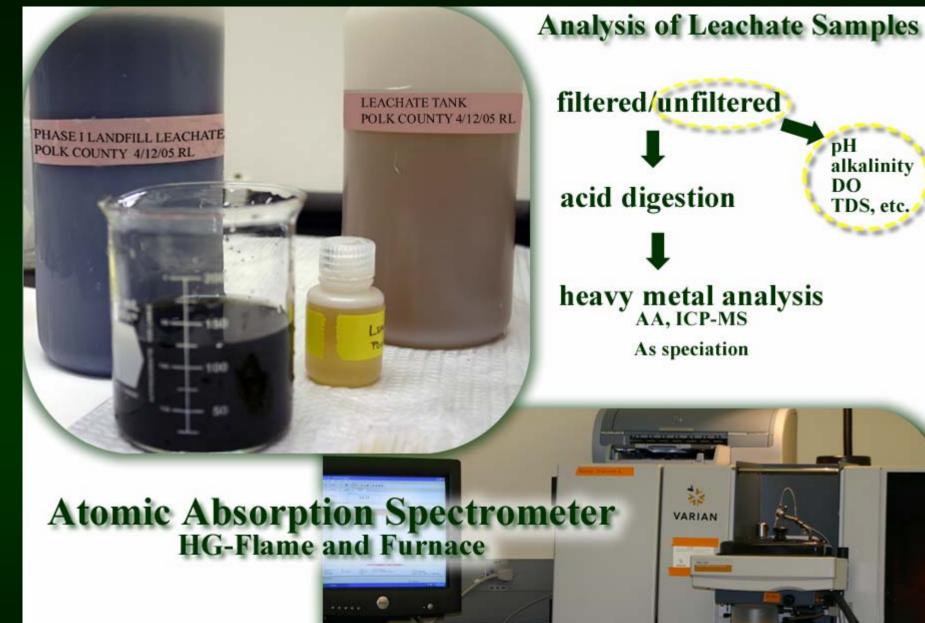
Obtained from the Mike Sims of the Marion County Board of County Commissioners, Marion County Solid Waste Department.

## Leachate Characteristics

#### Polk County

	Polk County Leachate (mg/L)			
	3/6/2003-	9/10/200 3-	9/10/200 3-	3/8/2004-
	7/16/2003	1/15/200 4	1/15/200 4	7/15/2004
	Leachate Tank	Leachate 1	Leachate 2	Leachate Tank
Arsenic	0.043	0.083	0.07	0.0712
Cadmium	0.011	0.0183	0.0081	0.002
Chromium	<0.001	0.0251	0.0214	0.0198
Copper	<0.005	<0.005	<0.005	0.0147
Lead	0.0335	0.0282	0.0256	0.0329
Mercury	<0.0001	0.0003	0.0001	<0.0001
Nickel	<0.0722	0.219	0.161	0.148
Selenium	<0.005	<0.005	<0.005	<0.005
Silver	0.0143	0.0063	0.0093	0.0074
Iron	27.16	3.746	21.278	6.3
Zinc	0.0129	0.0346	0.121	0.0343

	Polk County Leachate			
	3/6/2003-	9/10/20 03-	9/10/20 03-	3/8/2004-
	7/16/2003	1/15/20 04	1/15/20 04	7/15/2004
	Leachate Tank	Leachat e 1	Leachat e 2	Leachate Tank
рН	7.21	7.12	7.12	7.51
DO (mg/L)	6.21	1.89	2.04	4.82
Bicarbonate (mg/L)	1873	2611	3424	2913
Chlorides (mg/L)	592	1266	867	1463
TDS (mg/L)	2480	3820	3820	4300
xylenes (ug/L)	44.2	88.5	34.47	51.6
benzene (ug/L)	<10	2.21	5.71	3.99



# Leachate Treatment: Green Applications

- Phragmites australis, or common weed was used in constructed wetlands in a leacahte treatment study.
- Leachate was pumped through constructed wetland beds, where metals that could act as nutrients to the plant were adsorbed though the roots.
- Because of the natural environment of the plant, its roots are suited to grow in low oxygen environments, rich in iron and manganese.
- These conditions can lead to the development of anaerobic micro-zones and coating of Fe and Mg on the plant roots.
- The Fe and Mg plaque acts as a filter and adsorptive surface for metal content, removing amounts of copper, phosphorus, and Zn, etc.

### **Basic Treatments**

- Membrane Processes
  - Membrane processes are becoming increasingly popular in leachate treatment
  - Some examples include: nanofiltration, ultrafiltration, or reverse osmosis
- Adsorption Processes
  - Pollutants are adsorbed to different solid materials such as activated carbon
- Oxidation Processes
  - This is the only type of treatment where contaminants are chemically transformed into biodegradable substrates or harmless materials
- Coagulation-Flocculation
  - A substance (usually Ferric Chloride or Fentons reagent (Fe(III) + H<sub>2</sub>O<sub>2</sub>) is used to precipitate contaminants out at lower pH values

## Some highlighted treatments

- Wet OXONE oxidation + coagulation-flocculation + adsorption to activated carbon
  - This process achieved 90% COD removal from stabilized older leachate. The only treatment required after this would be a final biological polishing stage
- Electrochemical oxidation
  - After 240 minutes of electrolysis with a oxide coated titanium anode, 92% of COD in leachate was removed.
  - However, when compared to energy costs, it proves to be inefficient, because of the high ammonia content that had to be broken down.
  - So if nitrogen removal treatment could be applied before hand, not only would effeciency increase, but total COD removal would increase as well.

## Sorbent Characterization

### **Materials:**

The adsorbents studied are:

- Kemiron from Kemiron, U.S.A (iron oxide)
- Lanxess Bayoxide E33 from Severn Trent Services, USA (iron oxide)
- ADSORBSIA GTO (titanium dioxide) from DOW Chemical Company, USA
- ALCOA DD660 (aluminum oxide)

## Sorbents cont'd







### Sorbent Characterization Methods

#### Media grinding and sieving:

The dry media was ground in a mortar and pestle made of porcelain. The ground material was sieved in Tyler sieves (Fisher scientific, USA) to produce size range of particles.

#### **Size fractions for analysis:**

425  $\mu$ m  $\leq$ size fraction  $\geq$ 500  $\mu$ m used for surface area analysis, porosity, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Less than 38  $\mu$ m was used for X-ray diffractometry

**Surface Area:** BET Multi point N<sub>2</sub> sorption isotherm with NOVA 2200 Surface Analyzer at 77 Kelvin. The Bayoxide and Kemiron were dried and degassed at 80°C for 18 hours and 3 hours respectively prior to the surface area analysis while Adsorbsia GTO was degassed at 250°C for three hours. Analysis done by Dr. Sunol's lab group.

**Porosity:** Mercury Intrusion Porosimetry by Micromeritics

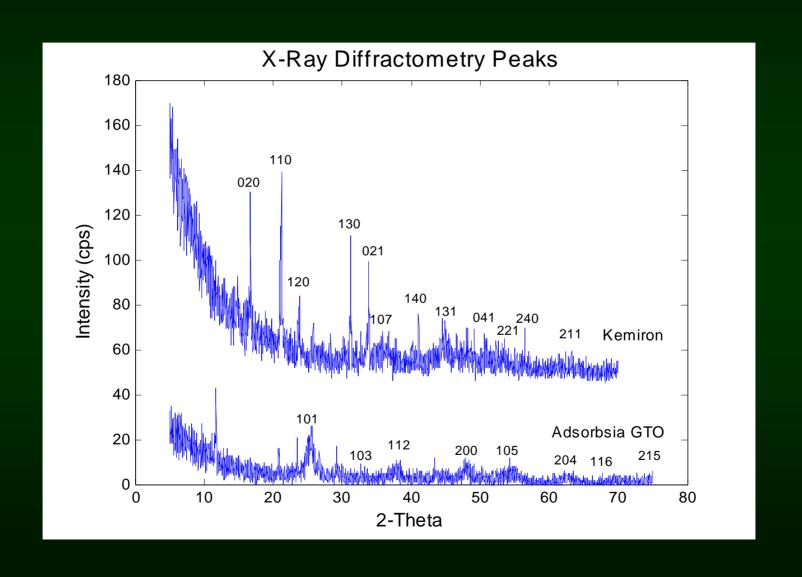
Philips MRD PW3060/20 X-Ray Diffractometer for lattice structure and d-spacing

Hitachi S-800 Scanning Electron Microscope.

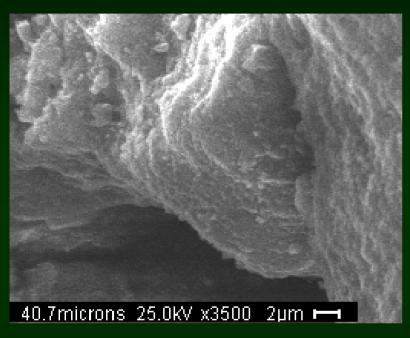
## Sorbent Characterization

Property	Bayoxide E33	GTO Absorbsia	Kimiron
Total Pore Volume (ml/g)	1.5	0.90	0.25
Bulk Density @ 55 psia (g/ml)	0.571	0.74	1.32
Porosity (%)	85.36	67.35	55.19
Max Pore Diameter (μm)	328.456	327.6878	327.6878
Min Pore Diameter (μm)	0.003016	0.003016	0.003016
Median Pore Diameter (μm)	0.002	0.0057	0.0073
Mean Pore Diameter (μm)	0.0395	0.0348	0.0756
Total Surface Area (m²/g)	94.98	207.45	89.52
XRD			goethite

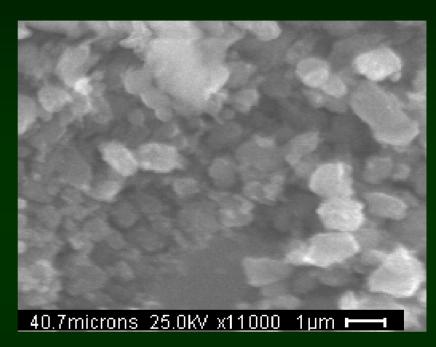
## Sorbent Characterization



## Sorbent Characterization: SEM

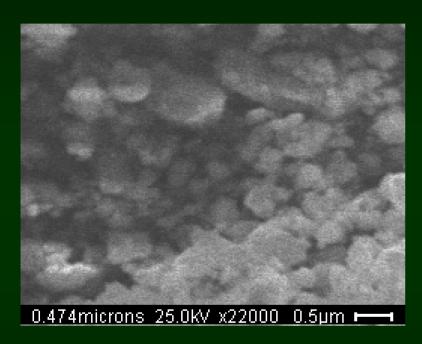


**BAYOXIDE E33** 

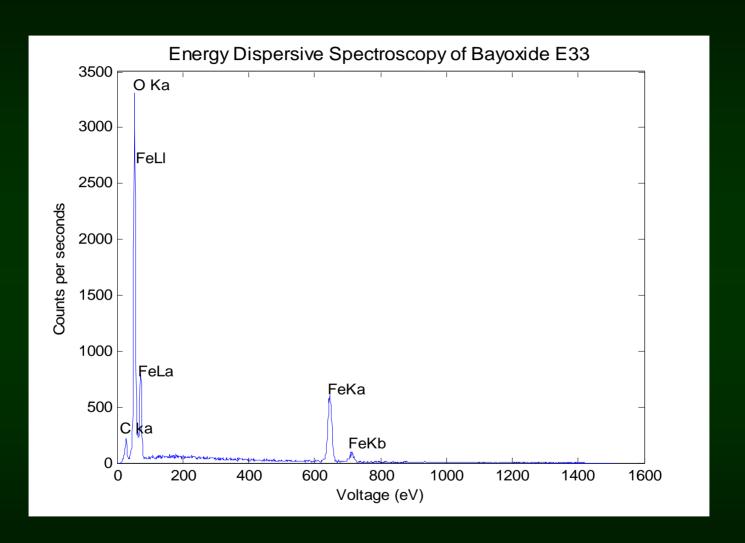


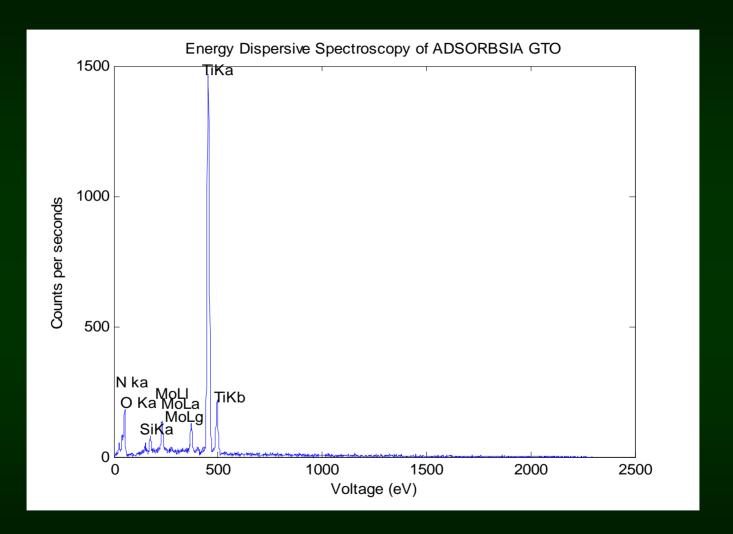
**ADSORBSIA GTO** 

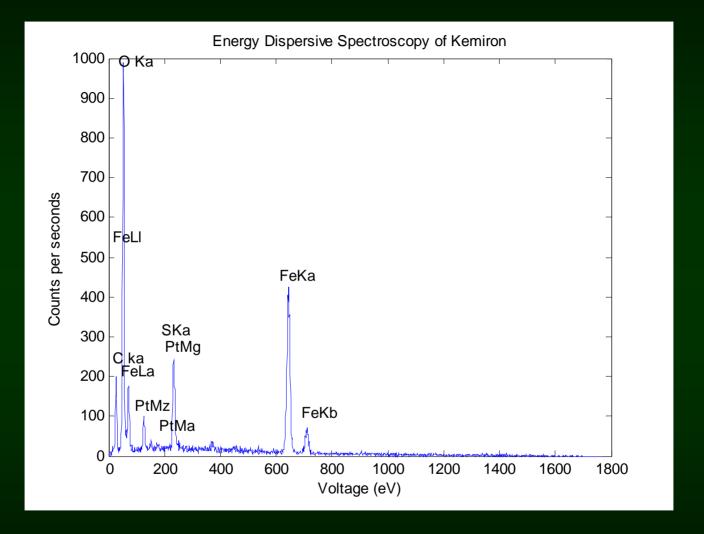
## Sorbent Characterization: SEM



Kimiron





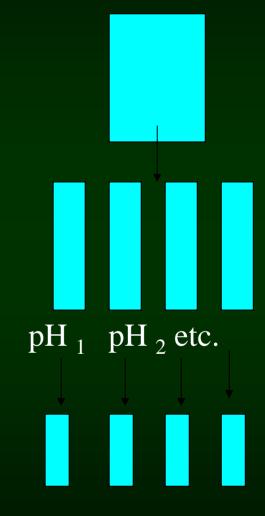


# Batch Experiments: Equilibrium Sorption

1. Pre-equilibrate fines (<38  $\mu m$  ) Overnight. Increase pH to  $\sim$ 10, add As soln.

2. Drop pH & sample into 10 ml PC tubes. Equilibrate for 24 hrs on end over end shaker. Measure pH.

3. Pass through 0.2 µm PES filter, acidify & analyze for As (GFAA)



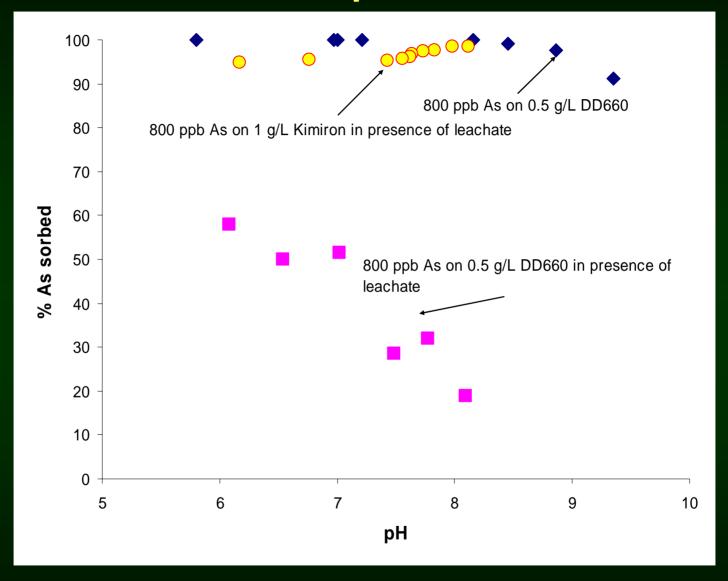
# Batch Adsorption Tests

	Alumina DD660	Kimiron
Solids Conc. (mg/L)	0.5	1
m²/L	200	180
[As] <sub>tot</sub> spiked	800, 800	100, 100, 800
With phase 1 leachate?	Yes, Yes	No, Yes, Yes
[NaNO <sub>3</sub> ]	0.1	0.1

	Total As (u		
	phase1	phase 2	phase 1&2
filtered	29.64	75.57	98.40
filtered & digested	91.28	60.94	126.42

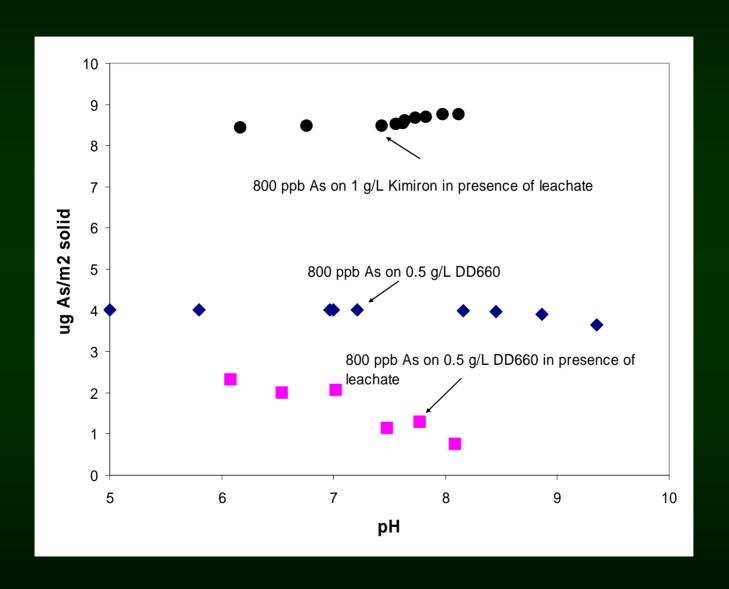
→ North Central Polk County Sampled: 4/21/06

## Batch Adsorption Tests



100 ppb As tests on Kimiron gave undetectable aqueous arsenic.

## **Batch Adsorption Tests**



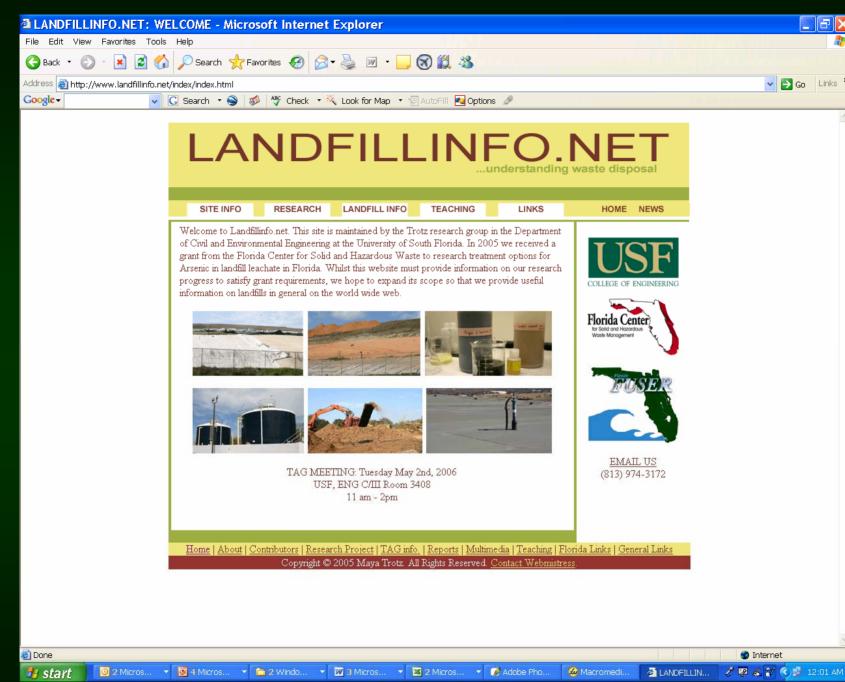
## Students Involved



Ryan Locicero (graduating senior) and Austin Roe (first year honor's student) taking a sample of phase II leachate at the North Central Landfill in Polk County



Douglas Oti, Ph.D. student analyzing Samples on the AA. Now trained on SEM and XRD.



✓ → Go Links »

## The next 6 months

- Complete compilation of landfill leachate information for the 7 identified landfills
- Develop protocol for arsenic speciation.
- Complete batch adsorption experiments using: Kimiron, Bayoxide and GTO Adsorbsia.
- Complete equilibrium modeling experiments.

### Acknowledgements

- Mr. Allan Choate, P.E. (Polk County Landfill)
- Mr. William "Lee" Martin, P.E. (FDEP)
- Mr. Ryan Locicero, REU student at USF
- TAG committee members for attending
- Mr. Douglas Oti, PhD. student at USF
- Mr. Austin Roe, Undergraduate researcher at USF

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