SUMMARY: INVESTIGATION OF ENERGIZED OPTIONS FOR LEACHATE MANAGEMENT

Daniel E. Meeroff (PI), C. T. Tsai (Co-PI)

Because of widely varying practices in solid waste management across the State of Florida, an understanding of emerging issues and an inclusive solution to long-term management of landfill leachate is currently not available. Leachate is typically too strong to be discharged to classical wastewater treatment systems, and deep well injection systems are becoming increasingly more difficult to implement in certain portions of the State of Florida. This research will address a major technological need for sustainable, economical options for routine leachate treatment and safe discharge to the environment by investigating energized processes, such as photochemical oxidation, which include the futuristic photochemical iron-mediated aeration (PIMA) and TiO_2-magnetite photocatalytic technologies.

This research will build upon the FCSHWM-funded project entitled, "*Investigation of options for management of leachate and wastewater*," directed by Dr. J.D. Englehardt and Dr. D.E. Meeroff, who were the first to successfully demonstrate the iron-mediated aeration (IMA) process for in-situ remediation of organic and metallic contaminants in soil and groundwater at former nuclear weapons facilities managed by the U.S. Department of Energy, in laboratory tests. The IMA process was shown to remove 99.996 percent of arsenic and 99 percent of organic contamination from a high strength organic wastewater, with costs projected at one order of magnitude lower than competing processes. Dr. Meeroff designed the first photochemically-assisted iron-mediated aeration (PIMA) reactor and performed the first experiments to demonstrate its effectiveness using ethylenediamine tetraacetic acid (EDTA) and cadmium metal as the model contaminants. Results showed that PIMA accelerated reaction kinetics by a factor of 6 compared to non-energized controls without pH adjustment or chemical addition, indicating the potential that PIMA can be more rapid, and perhaps more thorough, than natural biodegradation and some forms of passive treatment (e.g. non-energized iron mediated aeration). Regarding photocatalytic nanoparticles, Dr. C.T. Tsai is a pioneer in this field and has recently developed a TiO_2-magnetite nanopowder through a collaboration between Florida Atlantic University and Dr. Xudong Sun (visiting research professor at FAU from Northeastern University, China) using a novel microemulsion method to coat a magnetic substrate for military applications. However, these nanoparticles have characteristics suitable for water treatment applications and are an excellent candidate for long-term leachate management. Dr. Tsai (Department of Mechanical Engineering) and Dr. Meeroff (Director of the Laboratories for Engineered Environmental Solutions) have teamed up to establish the Florida Atlantic University Nanoparticle Applications Laboratory to investigate other engineering uses of nanocatalysts.

The objectives of the research are to:

1. To examine the literature on energized alternatives for detoxification and treatment of leachate; collect leachate quality data; identify issues/trends associated with long-term leachate management; and prepare a list of energized alternatives ranked according to environmental sustainability, efficiency, risk, and economic factors.
2. To design and test laboratory reactors for leachate treatment using energized options such as the photochemical iron-mediated aeration technology (PIMA) and TiO_2-magnetite photocatalytic processes.
3. To prepare preliminary cost analyses and risk assessments on selected technologies to provide a Florida-specific matrix of engineering alternatives that are innovative, economical, and environmentally sound to aid solid waste management personnel in decision-making.

Before the grant was awarded in 2005, Eli Brossell (undergraduate) and Courtney Skinner (graduate) completed construction of the PIMA process reactor. It is functional, and the aeration system has been calibrated. Courtney Skinner, Tammy Martin (Lanny Hickman Internship Program) and François Gasnier have begun work towards their masters thesis on this project. Ms. Skinner and Mr. Gasnier conducted validation testing and method development of the equipment required to evaluate the concentrations of the six target pollutants (Pb, conductivity, TDS, ammonia, COD and BOD_5) to be monitored during performance testing of the photochemical oxidation technologies. The aim is to determine the conditions necessary to allow for safe discharge of treated leachate to the sanitary sewer or reuse on site. Using existing data on currently available technologies in conjunction with performance data generated from laboratory tests to develop unit treatment costs for scale-up, a matrix of Florida-specific engineering alternatives that are innovative, economical, and environmentally sound will be developed to aid solid waste management personnel in decision-making. This tool will help to address current barriers to the use of futuristic technologies for reducing toxic loads in water, wastewater, and soils in addition to leachate.

PROGRESS REPORT
(July 2007)

Project Title: Investigation of energized options for leachate management
Principal Investigators: Daniel E. Meeroff, C. T. Tsai
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Project website: http://slab.civil.fau.edu/~daniel/labees/html/leachate.html

Work accomplished:

- A literature review is ongoing concerning the photochemically-assisted iron-mediated aeration (PIMA) process and the TiO_2-magnetite photocatalysis process. A visiting researcher from the Indian Institute of Technology in Bombay, Mr. Swapnil Jain, conducted an exhaustive search of the photocatalytic literature [1990 and beyond] with the aid of the FAU S.E. Wimberley Library Information Services Department and prepared an annotated bibliography. The main focus of this targeted literature review topics was to identify precedents using TiO_2-magnetite for water treatment applications. Specific questions were addressed: 1) advanced oxidation process efficacy for various pollutants, 2) appropriate UV intensity range, 3) appropriate reactor conditions (i.e. pH, temperature, etc.), 4) appropriate range of catalyst dose (in grams or m^2), 5) appropriate hydraulic retention times or reaction/exposure times, 6) catalyst reconditioning, 7) reasons for catalyst poisoning, and 7) appropriate mixing regime. In addition, any factors that could impact the efficiency of the process such as catalyst poisoning, pH/temperature effects, etc. were identified.

- The second goal is to produce a matrix of different technologies, ranked according to:
    - Efficiency of Treatment, regarding pollutant removal performance
    - Other Parameters, included in this category are environmental impacts, odor generation, dependency on climate conditions, etc.
    - Preliminary Costs
    - Residuals, regarding solids or liquids generated during treatment
    - Footprint

  This work is underway and ongoing. Table 1 presents some preliminary results concerning this part of the literature review. They clearly demonstrate the benefits of using AOPs over traditional on-site techniques. Equally, the addition of UV energy improves the performance of the AOPs.

Table 1: Ranking of leachate treatment techniques

	Technology	Type	Total
Conventional Treatment Techniques	Deep well injection	On-site	14
	Hauling off-site	Off-site	15
	Evaporation	On-site	27
	Municipal sewer discharge without pre-treatment	Off-site	39
	Aerobic and Anaerobic biological process	On-site	24
	Air stripping	On-site	29
	Coagulation, precipitation, flocculation, and sedimentation	On-site	34
	Ion exchange	On-site	36
	Filtration	On-site	38
	Carbon adsorption	On-site	39
Innovative Treatment Techniques	Bioreactor: leachate recirculation	On-site	43
	Ozone and hydrogen peroxide	AOP	25
	Ozone	AOP	26
	Hydrogen Peroxide	AOP	35
	Fenton	AOP	36
	Iron-Mediated Aeration	AOP	41
	Ultraviolet light	EP	29
	UV and ozone	EP	31
	Photo-Fenton	EP	36
	UV and hydrogen peroxide	EP	36
	Ultraviolet light, ozone and hydrogen peroxide	EP	36
	Photocatalytic oxidation	EP	47

- Design and construction of the PIMA pilot scale reactor (Figure 1) is complete, and pilot scoping tests with simulated leachate and mixtures have been completed.
- A second reactor was developed for use with TiO_2-magnetite experiments (Figure 2). It is a free-standing, bench scale reactor. Additional experiments are planned with another micro scale reactor obtained through a partnership with the FAU Honors College to generate performance data for TiO_2-magnetite experiments.
- Dr. Chen has synthesized the first TiO_2-magnetite nanoparticles at FAU. He has begun the process of manufacturing sufficient particles to begin scoping tests with Mr. Jain. He has also synthesized some additional particles for follow-up testing.
- The first experimental phase with PIMA (individual simulated leachate tests) is finished: individual scoping tests on the six components have been completed. Figure 3 shows François Gasnier analyzing an ammonia sample. Figure 5 to Figure 10 below are graphs showing the results obtained during these scoping tests. Table 3 summarizes the maximum removal percentages obtained after 16 hours of treatment (unless stated otherwise in the remarks) and the initial values.
- The second experimental phase with PIMA (simulated leachate mixtures) is complete. Mixtures containing low, middle and high levels of the parameters of interest have been tested. Table 4 summarizes the maximum removal percentages obtained after 16 hours of treatment.
- The third experimental phase with PIMA (real leachate tests) is achieved. PIMA process was applied to real Class I landfill leachate from the Solid Waste Authority of Palm Beach County.

- Preliminary initial screening experiments to determine the magnitude of residual generation and removal kinetics using bench scale demonstration units for TiO_2-magnetite photocatalysis were performed.

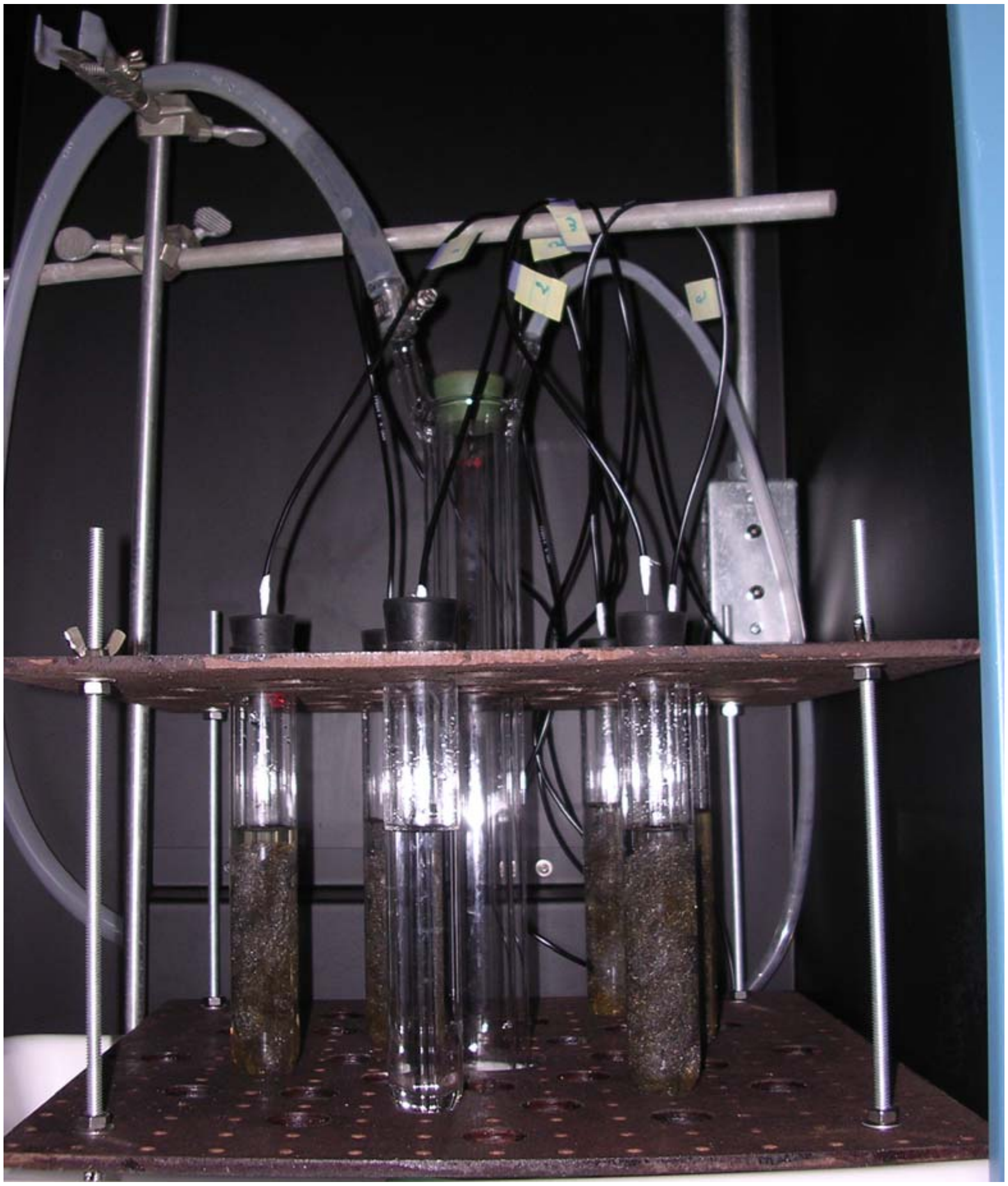

Figure 1: PIMA process reactor

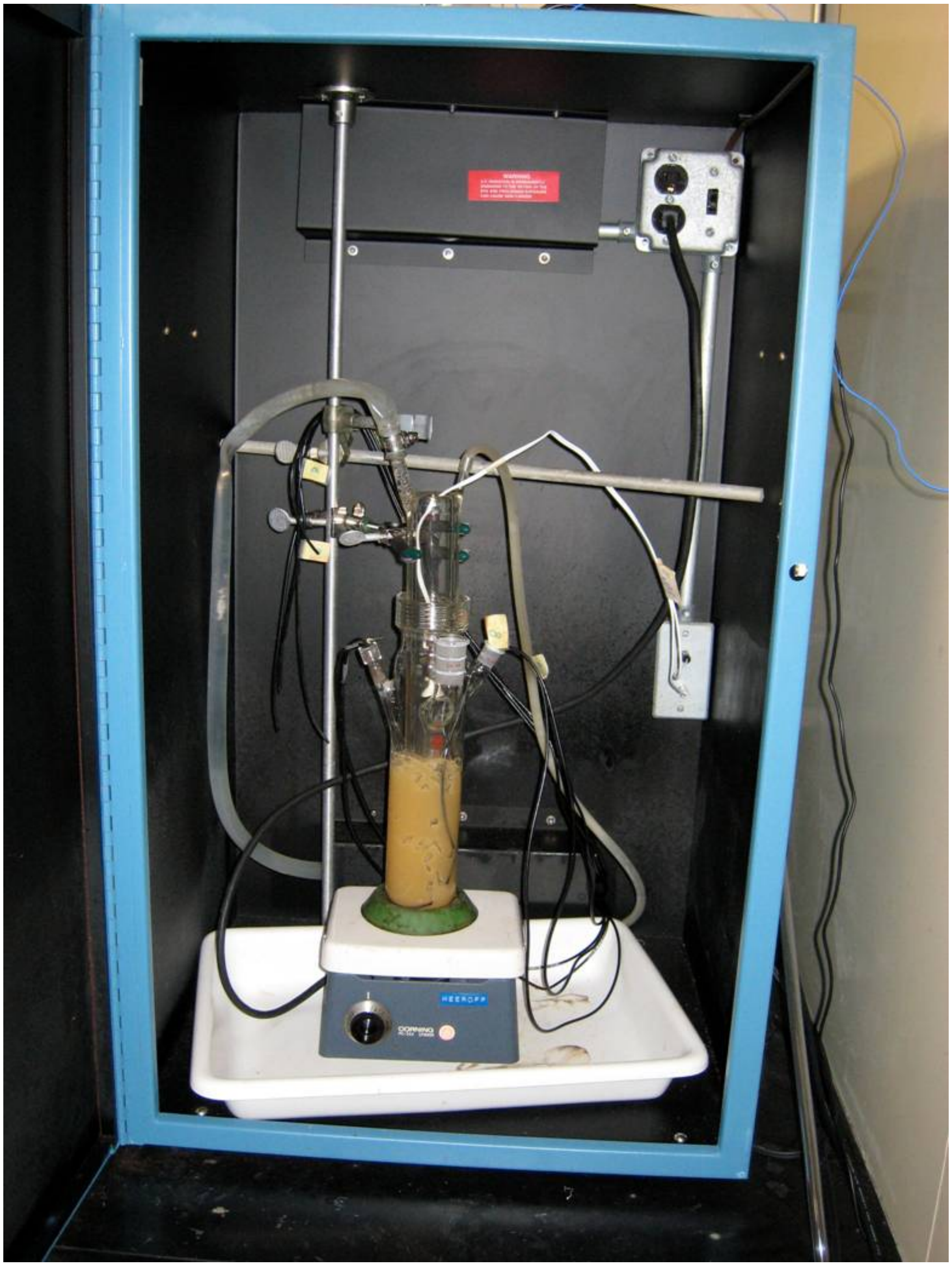

Figure 2: TiO_2-magnetite process reactor

Figure 3: Experiments to validate the ammonia meter.

Significant results:

- The aeration delivery system has been upgraded, and the air flow rate is checked with a digital flowmeter, prior to each experiment. Figure 17 is a picture of the system, Figure 18 shows the air flow measuring device, and Table 2 summarizes the recorded air flow measurements.

Table 2: Air flow measurements

Flow path	Date of measurement			
	05/03/06	05/04/06	02/19/07	06/12/07
1, IMA control process	0.138	0.130	0.084	0.105
2, UV control process	0.101	0.110	0.064	0.068
3, PIMA process	0.093	0.109	0.175	0.185
4, PIMA process	0.054	0.067	0.090	0.100
5, PIMA process	0.152	0.196	0.045	0.368
6, PIMA process	0.202	0.338	0.490	0.668
7, PIMA process	0.206	0.435	0.500	0.630
8, PIMA process	0.080	0.089	0.155	0.190

- During every experiment, each of the following parameters is evaluated: temperature, pH, dose of iron, and residence time.
- In terms of PIMA process performance measured during the individual simulated leachate scoping tests, the following were found:
  - COD: After 24 hours, the highest removal efficiency recorded was 40 percent with an initial concentration of approximately 10,000 mg/L (high level). However, after 16 hours, the highest removal efficiency recorded

was 50 percent with an initial concentration of approximately 3,000 mg/L (medium level).

  - Conductivity and TDS: After 2 hours, initial removal efficiency was low and concentrations started to increase due to the dissolution of iron and the reduction in volume due to evaporation.
  - Ammonia: No to low removal was observed. After additional research and experiments, the acidic pH of the simulated leachate is likely responsible for these results. Ionized aqueous ammonia exists in equilibrium with gaseous ammonia as shown in the following equation:

$$NH_4^+ \longleftrightarrow NH_{3(\uparrow)} + H^+$$

    The pK_a of the NH_4^+/NH_3 couple is 9.2. Since the unadjusted pH was recorded to be below 7.0 during each experiment, ammonia did not strip out of the simulated leachate. An additional experiment where the pH was adjusted to a higher value than this pK_a verified this conclusion. Reactor design was also demonstrated as a cause for this absence of removal: the ammonia gas has a higher density than air and can not escape from the test tube.
  - BOD_5: After 16 hours of treatment, an average of 44 percent removal was observed on the high concentration level. The addition of UV greatly increased the action of IMA process for the decrease of BOD_5 modeled by glucose and glutamic acid. Indeed, in the same amount of time, the IMA process removed only 28 percent of the initial BOD_5.
  - Lead: After 16 hours of treatment, a removal greater than 99.97 percent was achieved with the PIMA process. As noticed during the literature review, the IMA process also achieved a removal greater than 99.96 percent for metals such as arsenic. On the other hand, the UV control process, achieved only a removal of 54 percent.
- In terms of PIMA process performance measured during the simulated leachate mixtures scoping tests, the following were found:
  - Results obtained on COD during the mixture scoping tests followed the same trends as those obtained during the individual tests. Of the three processes, the one using only UV gave the lowest COD degradation performance. The IMA process is enhanced by UV radiation.
  - Results obtained for conductivity and TDS during the mixture scoping tests confirmed those obtained during the individual tests. None of the processes had a measurable impact on the NaCl concentration.
  - Results obtained on BOD_5 during the mixture scoping tests also confirmed those obtained during the individual tests. The UV control process presented the best biochemical degradation capacity. This justifies why the PIMA process achieves a better purification than the IMA process.
  - Results obtained on ammonia during the mixture scoping tests followed the same pattern as the results encountered during the individual ammonia tests. None of the three processes tested had an impact on the ammonia concentration. This is explained by the pH, which was not adjusted to the levels necessary to bring about enhanced ammonia removal.

- Results obtained on lead during the mixture scoping tests confirmed those obtained during the individual tests. The UV control process presents the lowest removal, and the PIMA process achieved the highest removal (33 percent).
- Results also demonstrated the interactions between the multiple pollutants, especially concerning COD and BOD_5.

- In terms of PIMA process performance measured during the real Class I leachate tests, the following were found: (graphs are presented in Figure 11 to Figure 16)
  - The PIMA process did not keep its promising results observed during the simulated leachate experiments. No removal was achieved: COD concentration remained stable around its initial value.
  - Conductivity and TDS remained unchanged over the course of the reaction (16 hr). No removal was observed.
  - Similar to COD, the PIMA process did not appreciably lower the BOD_5 content of the real leachate.
  - Concerning ammonia, the performance of the PIMA process confirms the conclusion drawn during the simulated leachate phase. No actual removal is achieved without pH adjustment.
  - Lead is the only component for which the PIMA demonstrated significant removal.
  - Concerning odor, no beneficial effect of treatment was noticed during the experiment. An odor was present at all sampling times.
  - Concerning color, PIMA was effective at eliminating the dark brown color of the raw leachate. This color was found to persist even after filtration, but the PIMA process can achieve, after filtration, an effluent of very high color quality. Figure 4 shows the extent of the color removal.

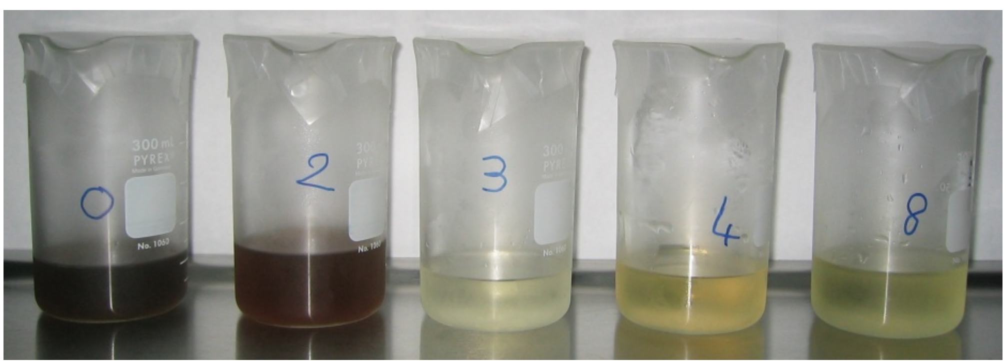

Figure 4: Comparative of the color removal between raw leachate and treated leachate

Note: Sample 0 is raw leachate, sample 2 is UV treated leachate, and samples 3, 4, and 8 are PIMA treated leachate.

- The experiment phase of the project showed the limitations of the laboratory scale reactor and of the PIMA process as applied on real leachate. Some recommendations have been formulated in order to achieve equivalent removal with real Class I leachate than during scoping tests: re-engineering of the reactor to improve aeration and mixing, evaluation of the pH influence, evaluation of a two step process (first at high pH and then at low pH), using an alternate source of iron and COD simulant (i.e. humic acids or phenol).

- In terms of TiO_2-magnetite process performance tests, the following were found:
    - The TiO_2-magnetite process used a different reactor compared to the PIMA testing. The main difference is that the UV lamp was suspended directly in the simulated leachate using a reactor designed specifically for this purpose. The aeration tubes were replaced by four pipes that bubbled air into the solution. It has the function of suspending the catalyst particles in the solution for the reaction to occur. For this we also used a magnetic stirring egg, which was placed in the reactor tube. The whole system was then placed over a magnetic stirrer. When it was switched on, the egg inside the reactor rotated and lifted the catalytic particles into suspension. The air supply helped mix it properly in the solution
    - The first experiment was conducted with ammonia. No removal was achieved: Ammonia concentration remained stable around its initial value, except for the 3 hr sample point, which was likely a measurement error.
    - The second experiment was conducted with COD. The best removal was 49%, which occurred after 3 hours. The solution color darkened with time (Figure 19), and the particles appeared permanently darkened after reconditioning and washing.
    - Subsequent experiments with reconditioned particles did not show any removal for COD and ammonia.
    - Tests were then conducted with TiO_2 particles (Degussa P25). These tests (Figure 20 and Figure 21) also showed no removal, and after the reconditioning and washing, the particles changed from white to black and changed from powder to very sticky agglomerates.
    - The reconditioned particles were incinerated in a blast furnace to remove any adsorbed organics, and then the experiment was repeated. However, no removal was observed for COD or ammonia (Figure 22).
    - The initial particles that showed COD removal and the reconditioned particles (Figure 23) were sent for X-ray diffraction analysis to determine if any surface chemistry has been altered.
- Dr. Hala Sfeir from Brown and Caldwell was contacted to share results on a statewide survey of leachate management options.
- Mr. Gasnier successfully defended his thesis in July 2007.
- Mr. Gasnier is preparing a scholarly publication for submittal to the Journal of Hazardous Waste Management.
- Two abstracts were presented for upcoming conferences (Florida A&WMA conference and the Global Waste Management Symposium)

Next step:

- Pursue further investigations according to the recommendations.
- Complete the cost analysis of candidate alternatives.

- A visiting researcher from Japan will be joining the research team in September. Her task will be to continue the work started by Swapnil Jain and act on the recommendations of Mr. Jain and Mr. Gasnier.

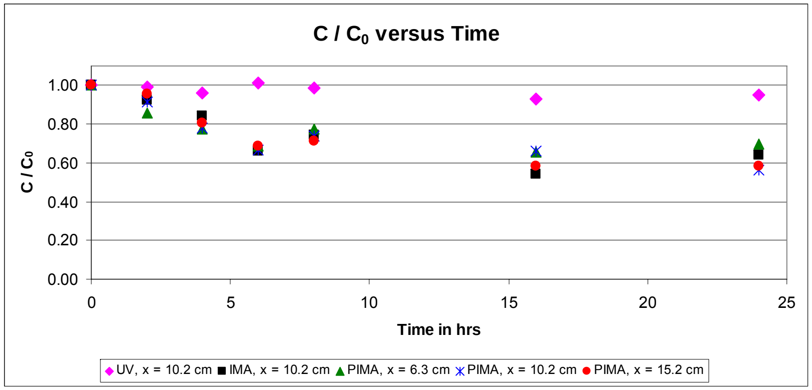

Figure 5: COD scoping tests results

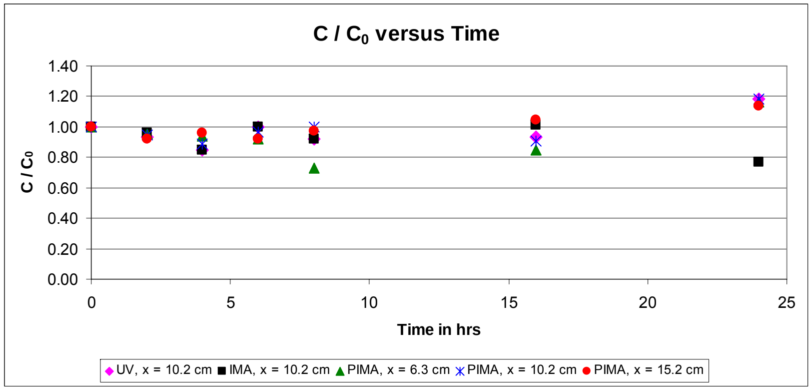

Figure 7: TDS scoping tests results

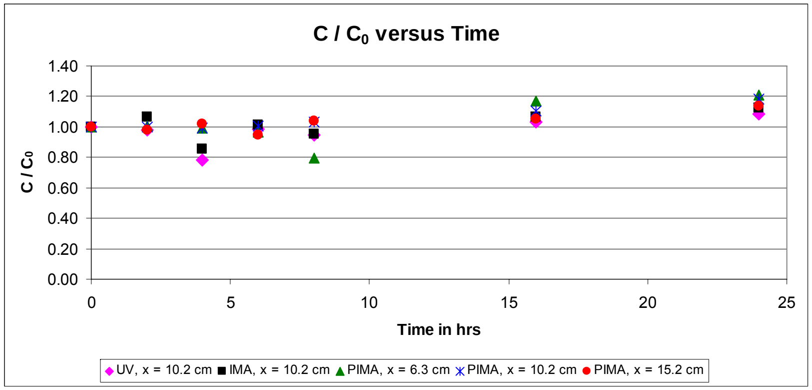

Figure 6: Conductivity scoping tests results

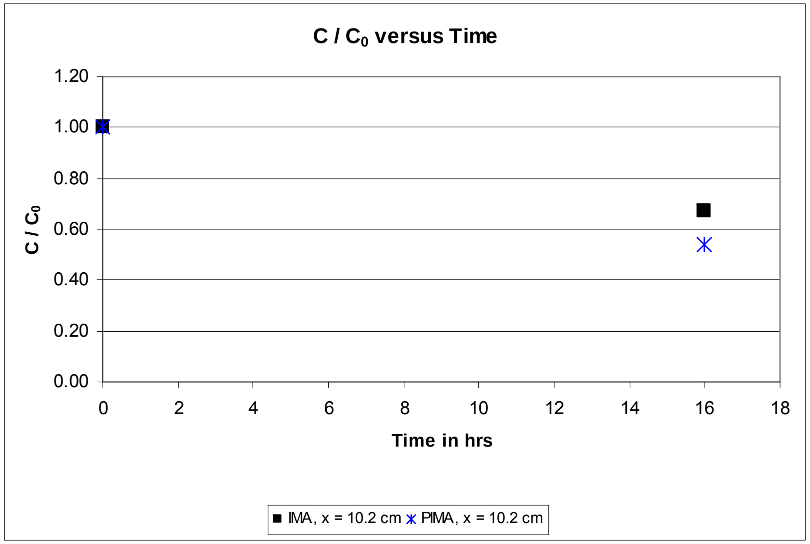

Figure 8: BOD_5 scoping tests results

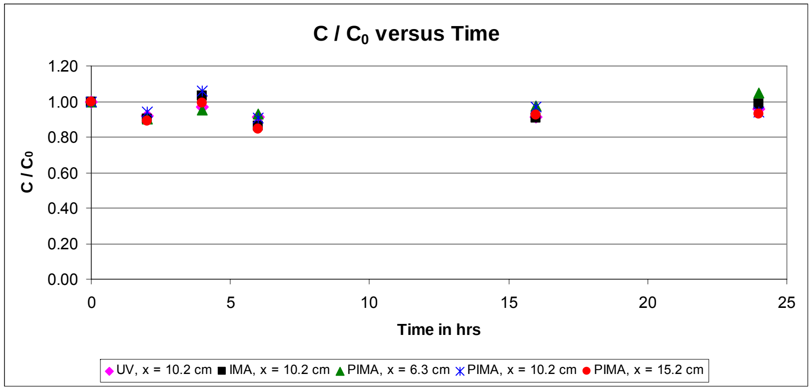

Figure 9: Ammonia scoping tests results

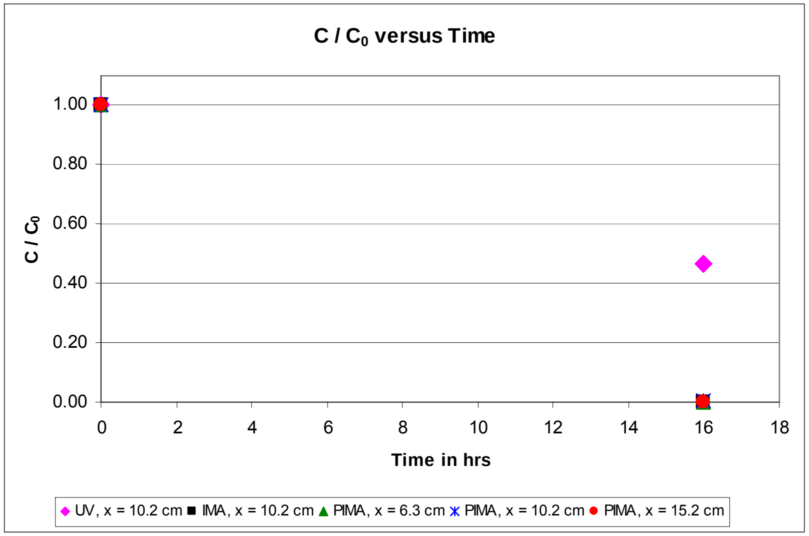

Figure 10: Lead scoping tests results

Table 3: Best removal percentage observed during individual scoping tests.

		COD			Conductivity			TDS		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
Starting concentration or value		1.05	3.30	10.90	2,750	16,250	81,625	0.83	8.12	40.00
Process	IMA, x = 10.2 cm	21	53	39	-3	-14	-2	-	-3	0
	UV, x = 10.2 cm	-	11	3	3	-19	2	-	8	6
	PIMA, x = 6.3 cm	54	42	35	-26	-16	-9	-	38	-8
	PIMA, x = 10.2 cm	51	49	29	-12	-14	0	-	13	3
	PIMA, x = 15.2 cm	44	52	32	6	-12	-3	-	-8	-1
Remarks		concentrations in g/L as O_2; values after 24 hrs			values in µS/cm			concentrations in g/L; Sensitivity issue		

		BOD$_5$			Ammonia			Lead
		Low	Medium	High	Low	Medium	High	Medium
Starting concentration or value		55	120	425	110	540	930	0.30
Process	IMA, x = 10.2 cm	38	-	28	-5	24	-8	99.96
	UV, x = 10.2 cm	-	100	-	-2	20	-12	53.33
	PIMA, x = 6.3 cm	-	-	-	-16	21	-4	99.97
	PIMA, x = 10.2 cm	39	55	44	-13	19	-3	99.97
	PIMA, x = 15.2 cm	-	-	-	-5	22	13	99.97
Remarks		concentrations in mg/L as O_2			concentrations in mg/L as NH_3-N		values after 24 hrs	concentration in mg/L

Table 4: Best removal percentage observed during mixture scoping tests.

		COD			Conductivity			TDS		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
Starting concentration or value		0.74	3.83	11.60	3,915	28,250	78,750	0.17	13.34	43.75
Process	IMA, x = 10.2 cm	28	36	20	2	2	14	0	0	23
	UV, x = 10.2 cm	40	3	14	2	2	19	0	0	20
	PIMA, x = 10.2 cm	38	28	33	5	0	10	0	-2	19
Remarks		concentrations in g/L as O_2			values in µS/cm			concentrations in g/L		
								Sensitivity issue	Sensitivity issue	

		BOD_5			Ammonia			Lead		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
Starting concentration or value		> 417	-	> 1,650	52.5	470	-	0.07	0.3	0.3
Process	IMA, x = 10.2 cm	> 37	-	-	-13	10	-	-	95	> 99.97
	UV, x = 10.2 cm	> 65	-	-	-25	12	-	-	3	79
	PIMA, x = 10.2 cm	> 48	-	*	-15	7	-	77	98	> 99.95
Remarks		concentrations in mg/L as O_2			concentrations in mg/L as NH_3-N			concentration in mg/L		
			No results				No results			

- No results obtained (experiment not completed)

* Can not conclude due to the inequality

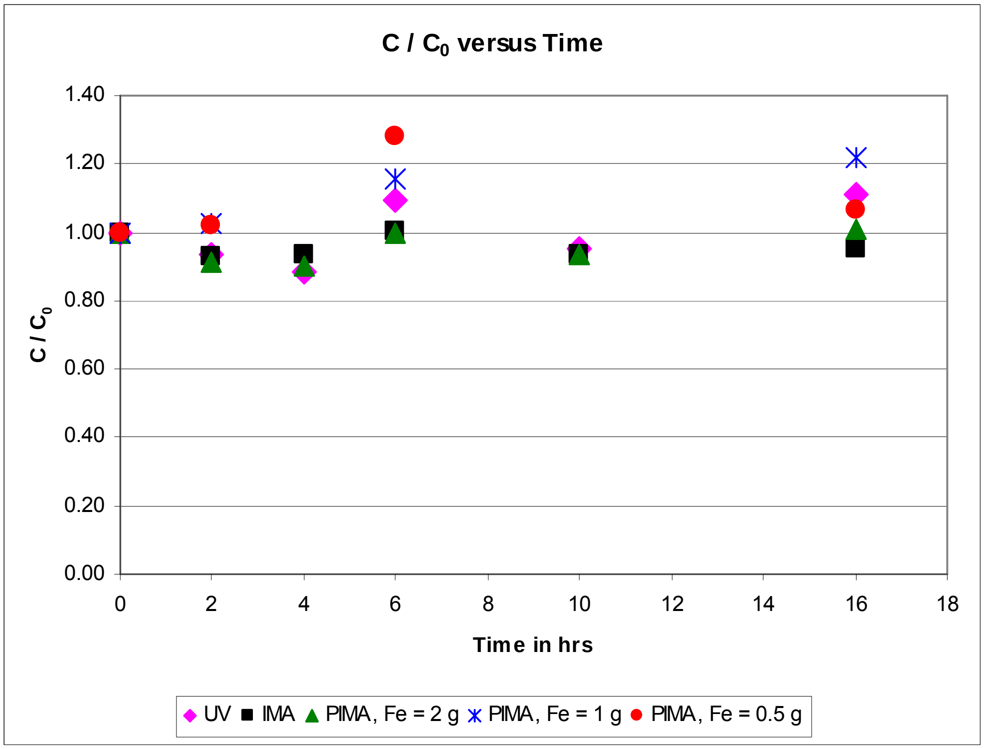

Figure 11: Global summary of real leachate experiments concerning COD

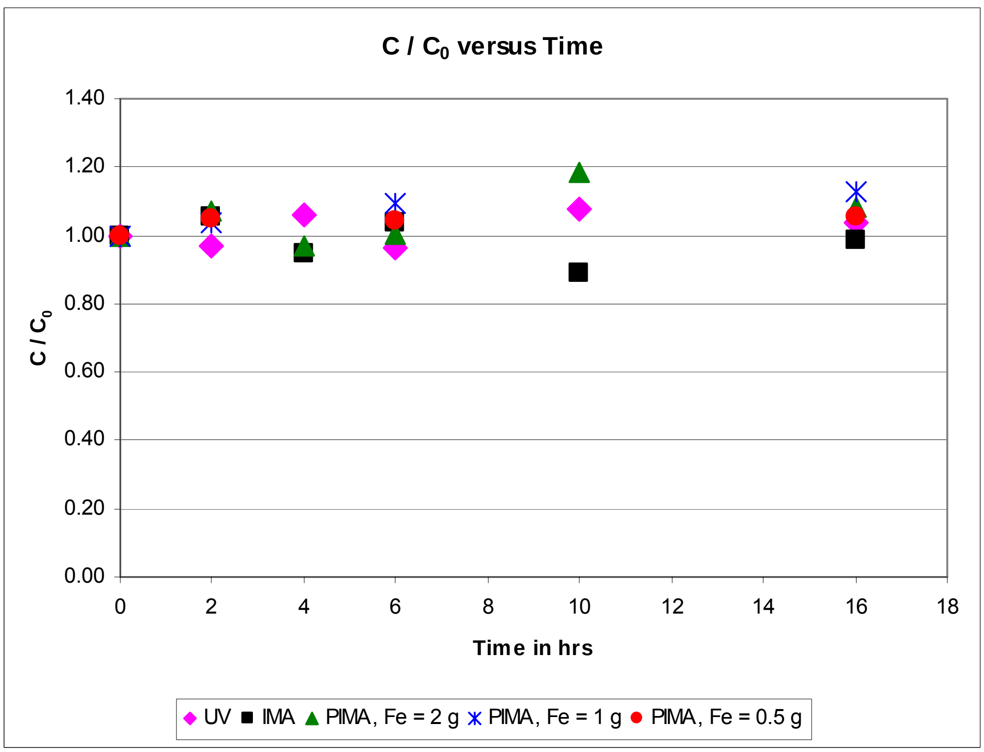

Figure 12: Global summary of real leachate experiments concerning conductivity

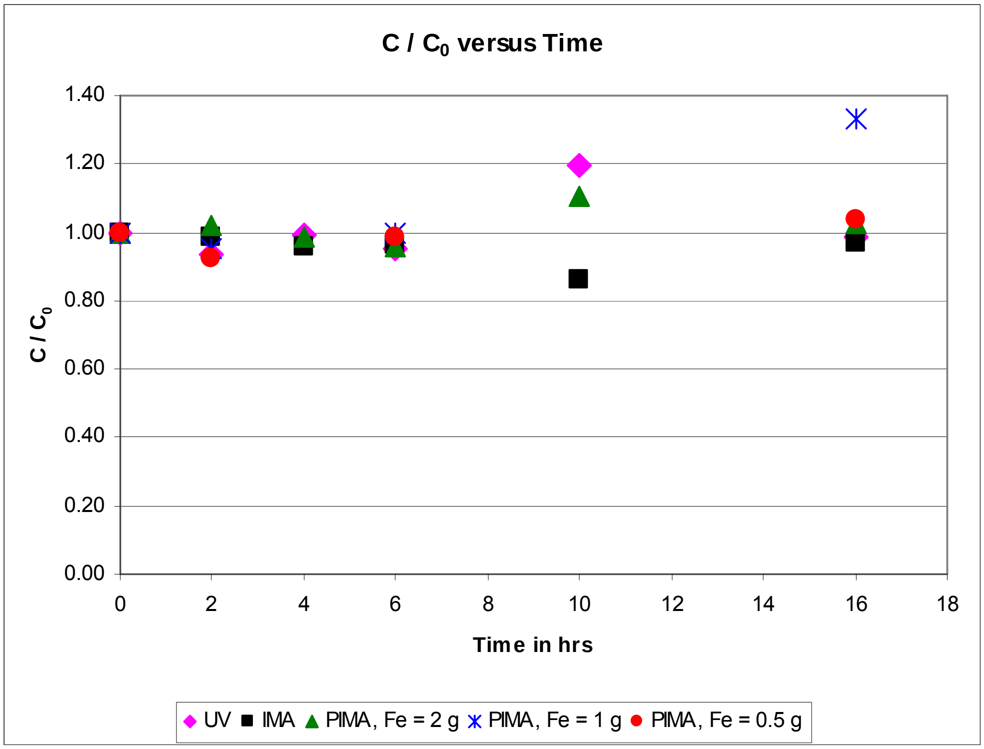

Figure 13: Global summary of real leachate experiments concerning TDS

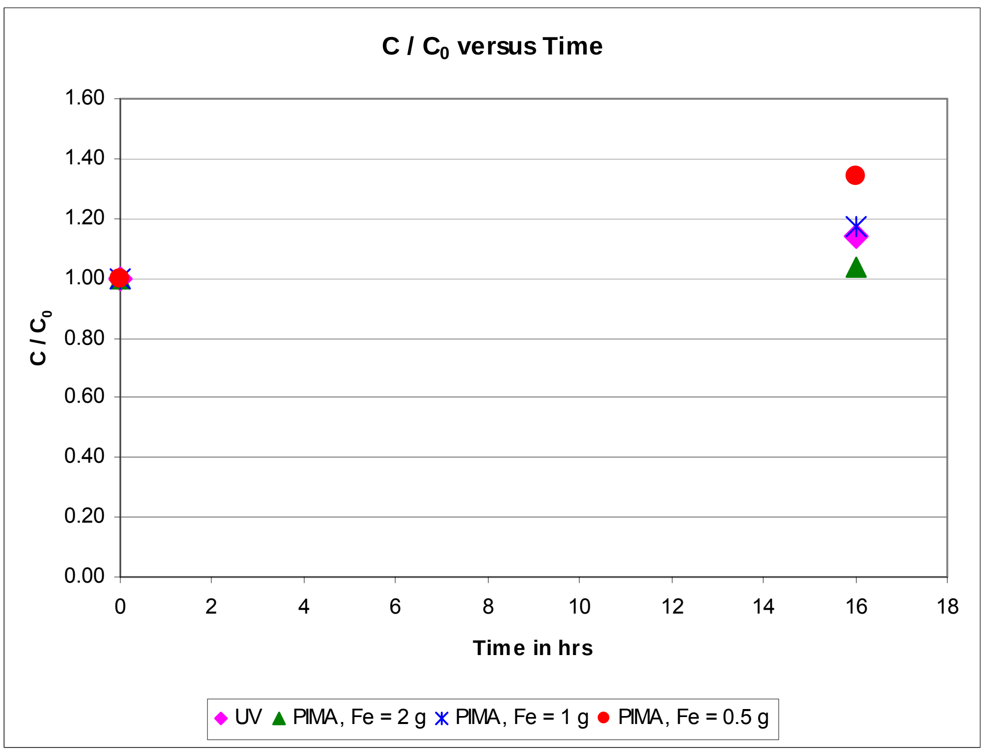

Figure 14: Global summary of real leachate experiments concerning BOD_5

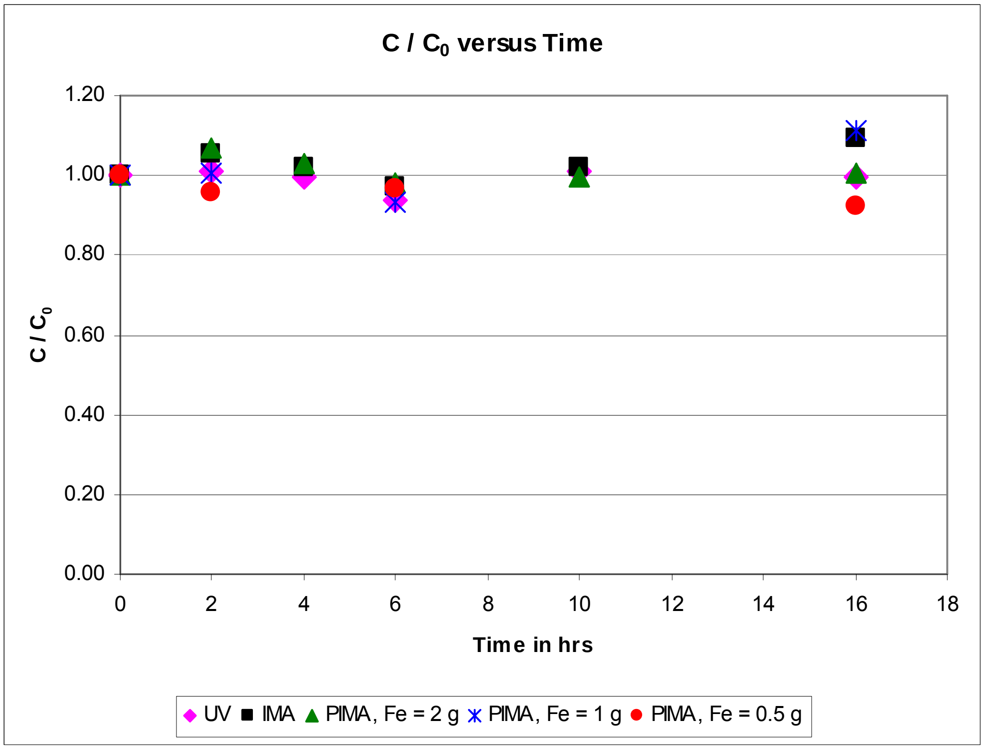

Figure 15: Global summary of real leachate experiments concerning ammonia

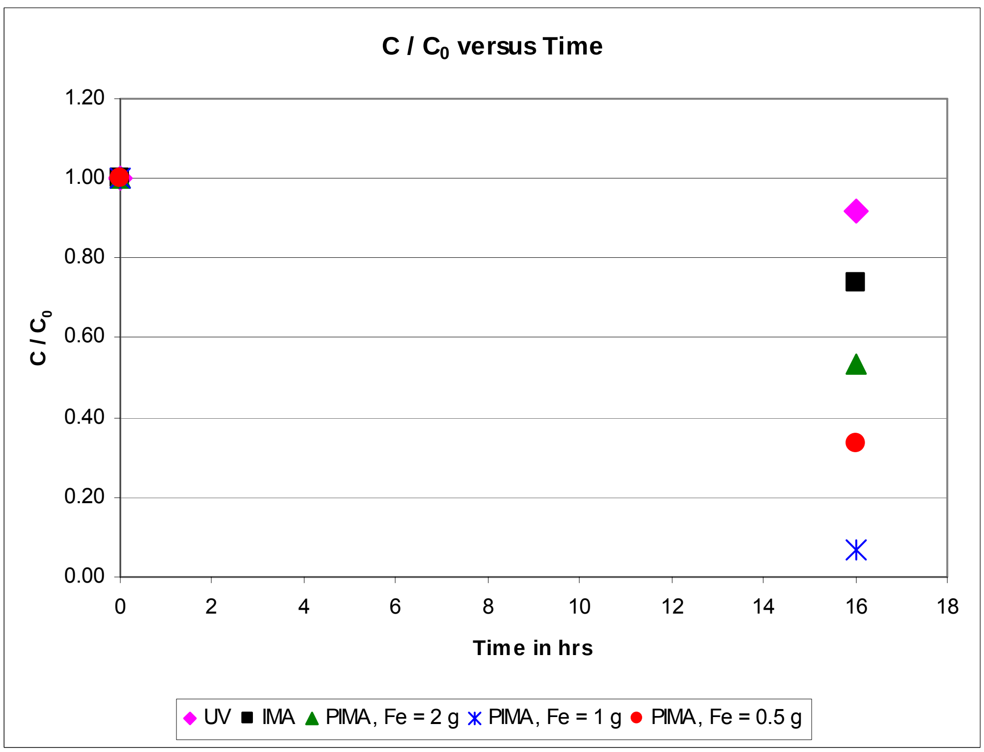

Figure 16: Global summary of real leachate experiments concerning lead

Here are some more pictures of the student working on the project.

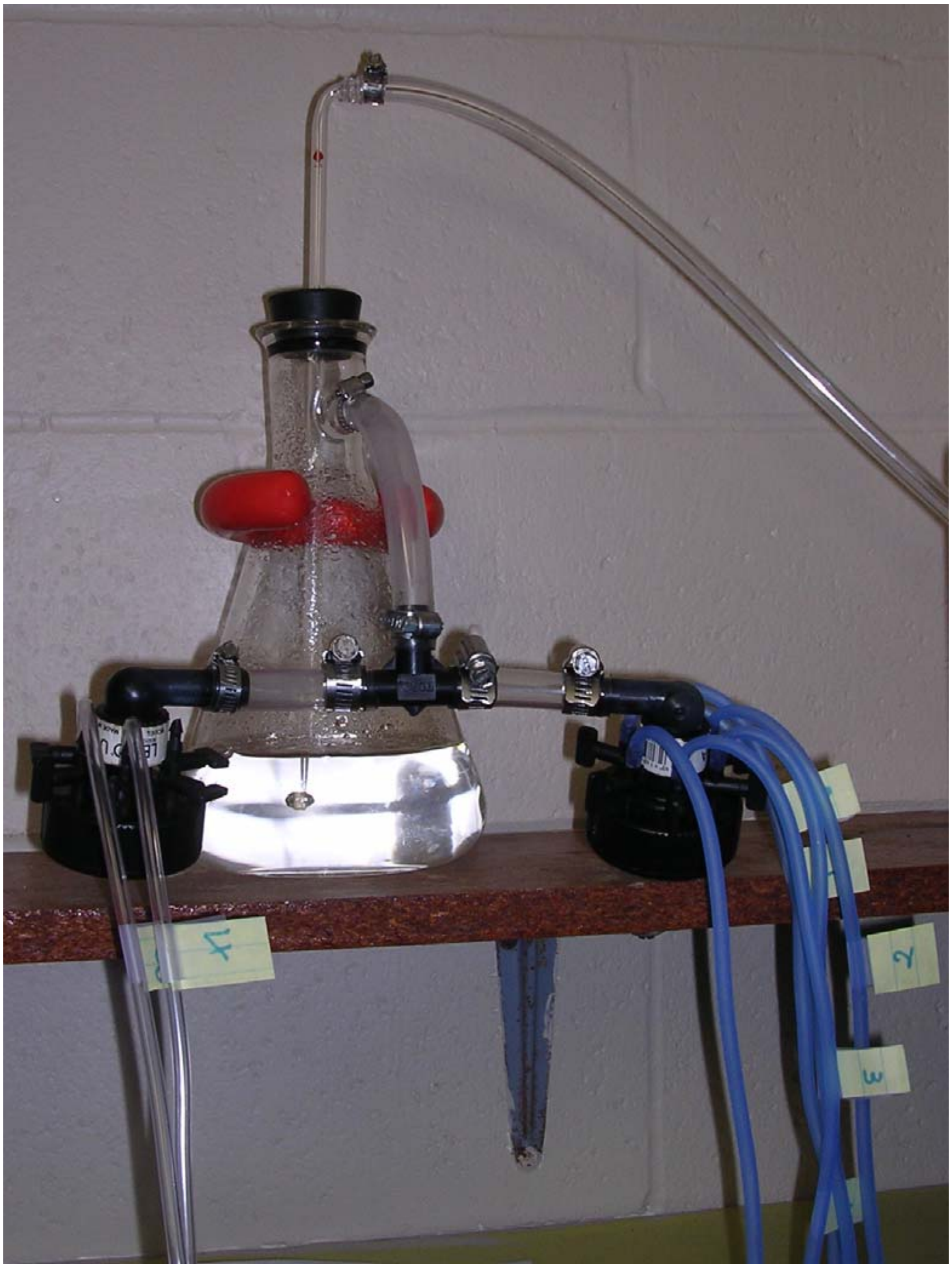

Figure 17: Upgraded aeration system.

Figure 18: Measurement of the air flow rate.

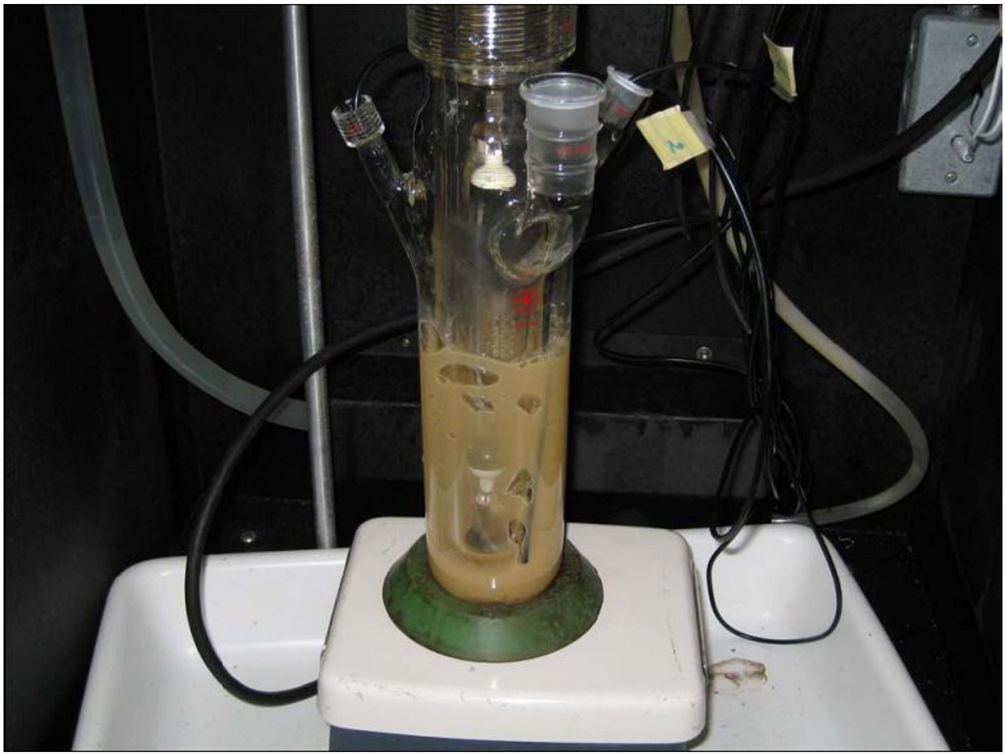

Figure 19: Experiment #2 using an ammonia leachate with TiO_2-mangetite particles

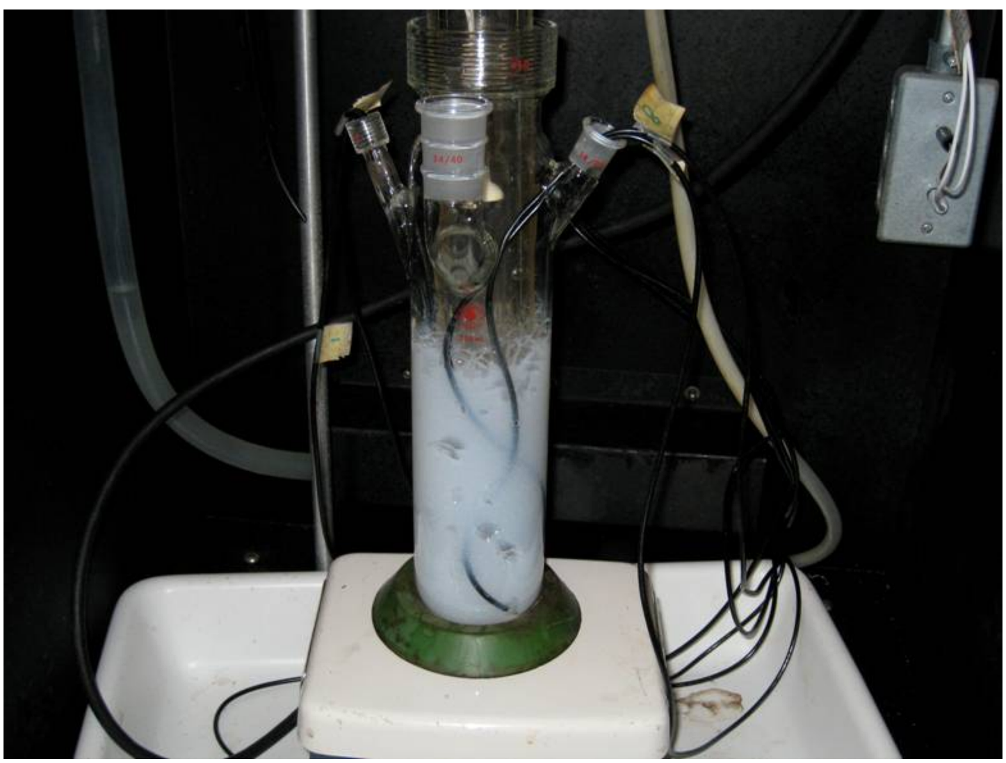

Figure 20: Experiment #5 using a COD (KHP) synthetic leachate with TiO_2 particles (Degussa P25) at time, t = 0 hours

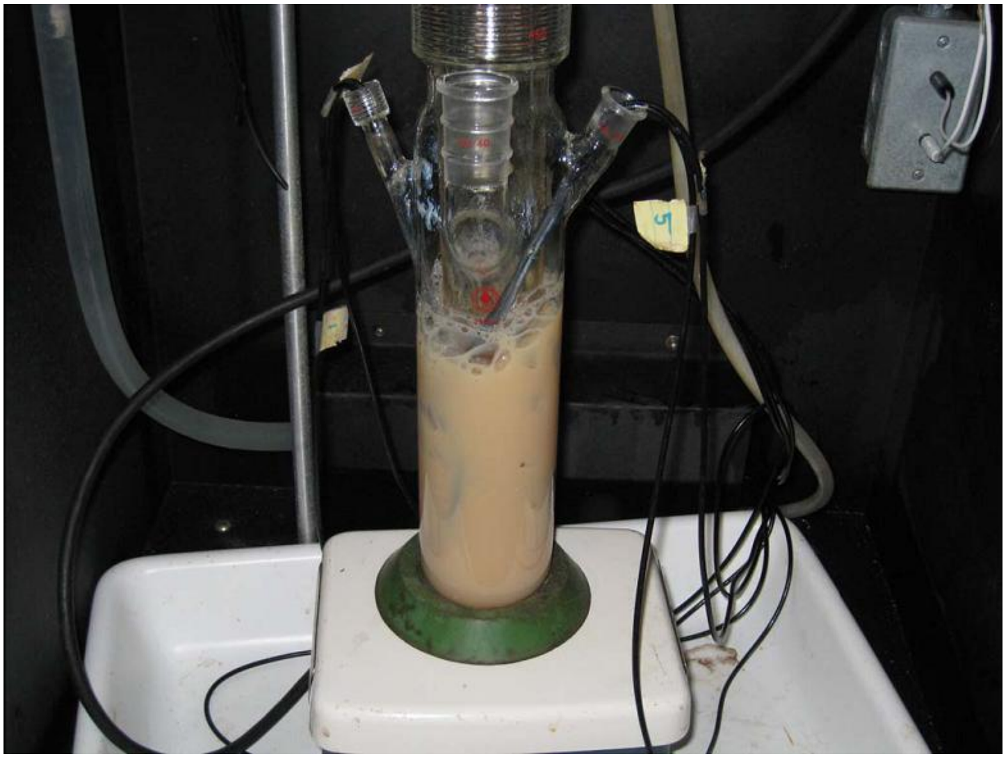

Figure 21: Experiment #5 using a COD (KHP) synthetic leachate with TiO_2 particles (Degussa P25) at time, t = 1.0 hour

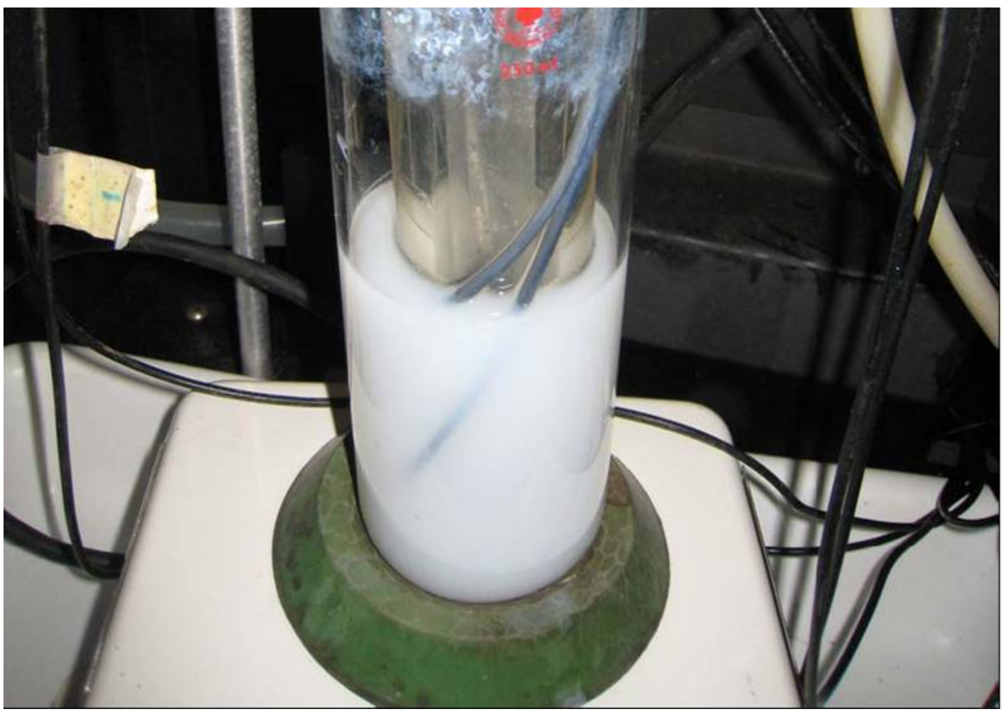

Figure 22: Experiment #6 using an ammonia synthetic leachate with TiO_2 particles (Degussa P25) at time, t = 5.0 hours. Note no color change.

Figure 23: Experiment #5: Reconditioning (drying at 105°C for 24 hours) of left over TiO_2 particles after treatment of synthetic leachate containing COD