## SUMMARY: SAFE DISCHARGE OF LANDFILL LEACHATE TO THE ENVIRONMENT Daniel E. Meeroff (PI)<sup>1</sup>

Some closed or partially closed landfills still produce important quantities of leachate, but instead of blending this material with active Class I leachate for disposal, there may be better alternatives. If a relatively inexpensive way to pretreat the leachate and safely dispose of it onsite can be developed, a giant step toward the potential for zero liquid discharge can be achieved. FAU has pioneered the advancement of landfill leachate treatment systems using photochemical iron-mediated aeration and TiO<sub>2</sub> photocatalysis at laboratory scale in previous research funded by the Hinkley Center, which has led to the development of reactor prototypes for pilot scale testing. The objective of the proposed research is to test a prototype photooxidative reactor at pilot scale to determine the feasibility of safely discharging or reusing this leachate as a resource on-site.

In previous work funded by the HCSHWM, 23 different engineering alternatives for long-term leachate management were evaluated (Meeroff and Teegavarapu 2010). For on-site treatment to work, some form of aerobic treatment would be expected to reduce leachate strength prior to discharge. However, biological systems are not well-suited for the removal of bio-toxics from water and are inefficient in dealing with wastes of varying quality, such as leachate. Thus post-treatment, using constructed wetlands, combined physicochemical treatment, or evaporation systems, would then be required. Unfortunately, technologies such as activated carbon and certain advanced treatment processes, such as ozone, do not adequately address inorganics, and membrane systems or air stripping merely transfer organics to another phase or create a side stream, like concentrate brine, that cannot be discharged readily. Furthermore, multiple barrier systems are complicated to operate, costly, and generally inefficient. For on-site treatment options, the most effective strategies involve technologies that can destroy different classes of harmful contaminants all at once, without producing adverse byproducts and residuals.

Fortunately, FAU has been working to address this need for sustainable, economical options for routine leachate treatment and safe discharge to the environment by investigating energized processes, such as photocatalytic oxidation. In our previous studies involving the use of photocatalytic oxidation technologies for treatment of landfill leachate, we were able to demonstrate destruction of 1400 - 2500 mg/L of COD in just 24 hours. But these leachates had initial COD concentrations on the order of 6,000-10,000 mg/L, so if we start with a less concentrated material (e.g. partially closed landfill leachate), it should be possible to completely destroy the COD with the added potential of meeting the requirements of F.A.C. 62-302 for metals and 62-777 for surface water target levels or even meeting the less stringent industrial water quality guidelines for onsite beneficial reuse of this material.

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#### **PROGRESS REPORT**

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Project Title: Safe Discharge of Landfill Leachate to the Environment
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The research is focused on using a falling film reactor on a field scale pilot test to remove COD/BOD, ammonia, heavy metals, color, and pathogens from leachate. It is anticipated that guidelines will be developed for acceptable reaction times needed to treat the weak leachate from Dyer Park. The proper catalyst dose will be found. Additional research will determine the appropriate UV intensity along with the effect of pH, and temperature on the reaction. Once an optimal process is determined, the cost of treatment in dollars per gallon will be determined.

A falling film reactor is being used in two configurations for testing. First, as a falling film reactor where 10 liters of leachate is loaded into a reservoir, and second, as a flow through reactor. In the falling film configuration, the leachate is pumped from the reservoir to the top of the weir. From the weir, the leachate is dispensed in a thin film along the outer lens of the reactor, where it falls to the bottom between the inner lens and outer lens. The falling time in the reactor is 0.41 seconds, and each liter is recirculated making 32-34 passes through the reactor an hour. In the flow through reactor configuration (backpressure falling film reactor), leachate is loaded in the reservoir and pumped to the weir in the top of the reactor. From the weir, the water flows down the outer lens until it reaches the back pressure between the inner and outer lens. The retention time of the flow through reactor is 1.8 minutes (4 times as much as the falling film reactor). Each liter of leachate passes through the reactor 24 times per hour in this configuration.

The introduction of the flow through reactor created the need to clean the inner lens of scale between tests. This requires the full dismantling of the reactor, exposing delicate parts to handling. Because of this, two critical parts were damaged. First was the inner reactor lens which was cracked at the bottom due to the moment applied by being unsupported at the top during reassembly (Figure 1). This lens has been temporally repaired, and a new lens has been ordered.



**Figure 1: Broken Inner Lens** 

Second was the 150-W lamp, which was also broken during cleaning because of torque applied to it when the reactor lid was stuck on a guide pins. A new lamp was ordered and arrived on 08/19/2014. After these two issues a new dismantling procedure has been implemented. The order is as follows: 1) unplug lamp, 2) remove lamp from reactor and wrap lamp in protective foam, 3) remove metal plug holding inner lens, 4) remove reactor lid, 5) remove inner lens for cleaning, and 6) reassemble in reverse order, making sure to apply silicone lubricate to all gaskets.

After reviewing literature on  $TiO_2$  advanced oxidation it was discovered that there is a close relationship between photocatalyitc efficiency and the concentration of dissolved oxygen in the reaction medium (Altomare et al. 2012). To provide more oxygen directly into the flow through reactor modifications to the reactor were made. To preserve the function of the falling film reactor, a new top was fabricated from HDPE plastic (Figure 2). To accommodate aeration, holes were drilled into the top, which will also allow cleaning of the reactor's inner lens without disassembly.



Figure 2: New reactor top, aeration entering top, aeration in flow through reactor

### UV light power

Calculations for energy that the titanium dioxide was exposed to per liter were made for both the falling film and the flow through reactor. The energy available for titanium dioxide to absorb in conjunction with exposure time should be directly related to efficiency. Results are shown in Table 1 and Table 2. These results show that the flow through reactor imparts more than 200 times the light energy per liter in an eight hour test when compared to the falling film reactor. The improvement is not seen in COD removal with essentially no removal with the 150-W and only a 9 percent decrease in the 450-W. The results were the same for ammonia removal with a 10 percent increase in 150-W and 24 percent increase for the 450-W.

# Table 1: Flow Through Reactor Energy

Light	Arch Length (cm)	Circumference (cm)	Area (cm2)	Measured UV (mW/cm2)	Total Power (W)	test size (L)	Retension Time ( hr)	Percent Expsoure per Retentions Time	Times recirculated per hour per liter (1/hr)	Expsoure per Liter (1/L)	Watts per Liter (W/L)	Test (hr)	Total Watt Hours/ Liter (Whr/L)
450W UV A&B	27.94	15.70	438.66	56.00	24.56	8.60	0.03	0.34	24.42	0.27	6.63	8.00	53.08
450W UV C	27.94	15.70	438.66	0.06	0.03	8.60	0.03	0.34	24.42	0.27	0.01	8.00	0.06
150W UV A&B	79.30	15.70	1245.01	0.50	0.62	9.10	0.03	0.96	23.08	0.72	0.45	8.00	3.61
150W UV C	79.30	15.70	1245.01	7.21	8.98	9.10	0.03	0.96	23.08	0.72	6.50	8.00	52.02

# Table 2: Falling Film Reactor Energy

Light	Arch Length (cm)	Circumference (cm)	Area (cm2)	Measured UV (mW/cm2)	Total Power (W)	Test Size (L)	Falling time (Seconds)	Expsoure time (Seconds)	Recirculated Rate (L/hr)	Number of Pass per liter per hour	Expsoure Time per hour (Seconds)	Energry per Hour per liter (W/L)	Length of test (hours)	Total Watt Hours/Liter (Whr/L)
450W UV A&B	27.94	15.70	438.66	56.00	24.56	9.30	0.41	0.14	320.00	34.41	4.75	0.03	8.00	0.26
450W UV C	27.94	15.70	438.66	0.06	0.03	9.30	0.41	0.14	320.00	34.41	4.75	0.00	8.00	0.00
150W UV A&B	79.30	15.70	1245.01	0.50	0.62	10.00	0.41	0.39	320.00	32.00	12.54	0.00	8.00	0.02
150W UV C	79.30	15.70	1245.01	7.21	8.98	10.00	0.41	0.39	320.00	32.00	12.54	0.03	8.00	0.25

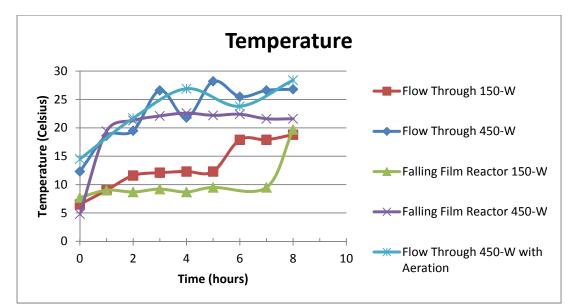
# Testing

A flow through experiment using the 450-W lamp with the addition of 10 g/l of titanium dioxide was performed. The new aeration system was also used during this test, putting the aeration directly into the reactor. 60-ml samples were taken at 2-hour intervals from the reactor discharge pipe. Each sample taken was tested for COD, ammonia, pH, dissolved oxygen, temperature and alkalinity. Results are shown in Table 3.

Sample	Temperature °C	COD mg/l	COD C/C <sub>o</sub>	NH <sub>3</sub> mg/l	NH <sub>3</sub> C/Co	pН	DO mg/l	Alkalinity mg/l as CaCO3	Alkalinity C/Co
0	14.5	240	1	100	1	8.55	9.34	700	1
2	21.7	220	0.916667	94.5	0.945	8.62	8.57	700	1
4	26.9	217	0.904167	84.5	0.845	8.67	8.13	490	0.7
6	23.8	210	0.875	77	0.77	8.69	8.53	430	0.614286
8	28.4	189	0.7875	75	0.75	8.76	7.85	700	1

Table 3: Result of 450-W Flow	Through Test with	10mg/l TiO, and agration
Table 5: Result of 450-W Flow	Infough rest with	10  mg/r $1102  and a eration$

Graphs comparing all five tests conducted to date, starting with temperature (Figure 3) were created. Temperature should not affect the  $TiO_2$  reaction (Kaneco et al. 2006) but has a major impact on reaction kinetics and could play a role in the removal of alkalinity. Alkalinity and calcium may interact to form scaling on the inner lens due to the heat generated from the UV lamp. The pH helps to identify optimum levels for removal (Figure 4). COD is best removed with a pH below 7, while ammonia is best removed with pH above 7 (Rocha et al. 2011). COD was sampled to see the efficiency of treatment (Figure 5). The COD removal was less than 20 percent for each test, this could be linked to the pH being above 7 but also the reaction times and catalyst dose were low. Ammonia removal rates were the highest, ranging from 5 percent to 46 percent (Figure 6). The pH was above 7 during all tests and can be linked to higher ammonia removal. Alkalinity removal is important because hard water would cause many problems. The alkalinity removal is shown in Figure 7. The high alkalinity of the leachate could reduce the effectiveness of the TiO<sub>2</sub> treatment. High concentrations of Cl, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, and Na have been shown to reduce the photocatalytic activity on TiO<sub>2</sub> surface (Rocha et al. 2011).



**Figure 3: Temperature of reactor** 

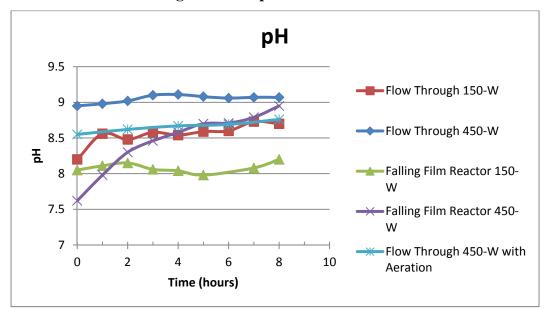
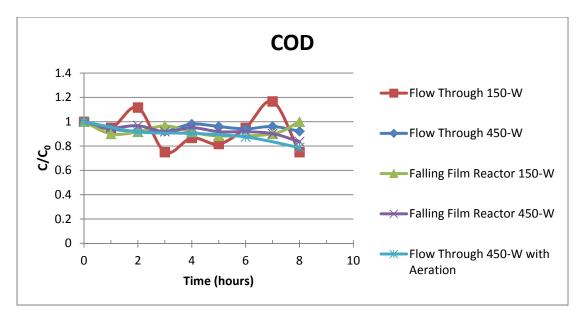


Figure 4: pH of samples



**Figure 5: Chemical Oxygen Demand Removal** 

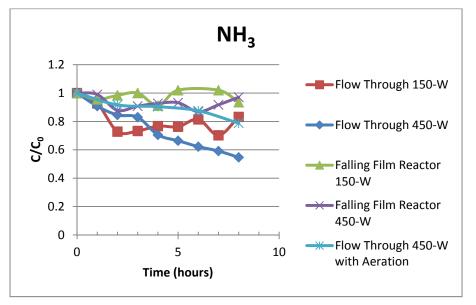
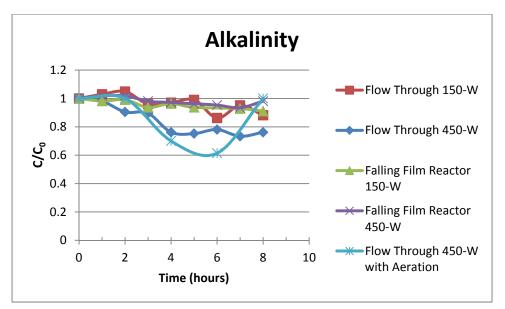


Figure 6: Ammonia Removal



**Figure 7: Alkalinity Removal** 

The tests have been run in series that results for total removal for the 450-W lamp over 24 hours and the 150-W lamp for 16 hours. The initial values and final values are listed in Table 4. The pH over the 24 hour period can be seen in Figure 8. The COD removal can be seen in Figure 9. The Ammonia removal can be seen in Figure 10. The alkalinity removal can be seen in Figure 11.

Paramter	C <sub>0</sub>	C of 150-W lamp at 16 hours	C of 450-W lamp at 24 hours
COD mg/l	341	225	189
NH <sub>3</sub> mg/l	313	193	75
pН	7.35	8.7	8.76
Alkalinity mg/l as			
CaCO <sub>3</sub>	1550	900	700

Table 4: Initial and final Value of Removal

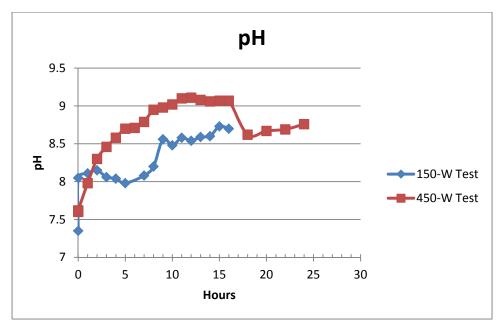


Figure 8: pH of 24 hours of testing

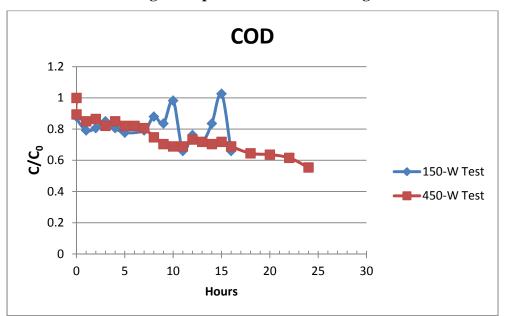


Figure 9: COD removal of 24 hours of testing

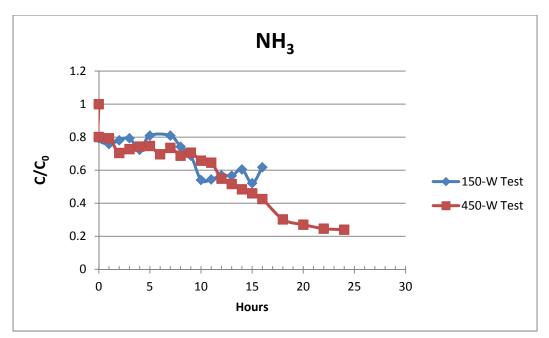


Figure 10: Ammonia removal of 24 hours of testing

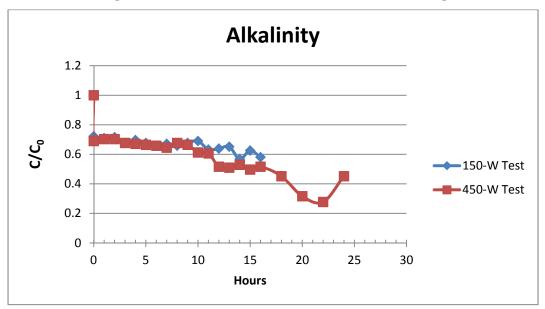


Figure 11: Alkalinity removal of 24 hours of testing

# **Titanium Dioxide Recovery**

After treating the leachate with  $TiO_2$ , the  $TiO_2$  must be recovered for the water to be used for any purpose. Different methods of recovering the  $TiO_2$  from the treated leachate were researched and tested.  $TiO_2$  has a molecular size of 21 nm. The small particle size makes it difficult to remove with straining or conventional filtration. To remove  $TiO_2$  in the samples, a centrifuge is used at 6000 rpm for 5 minutes, which removes all visual appearance of  $TiO_2$  in the sample. This

method would not be effective in a plant size application. Two different methods were tested: filtering and settling. Filtering was tested using three filters with 20 mm mesh, 10 mm mesh, and 0.45 $\mu$ m glass filter. The 20 and 10 mm mesh were placed into a plastic funnel; this funnel was then placed at the discharge of the reactor. It was observed that most of the partials passed through the filter of both the 10mm and 20mm size (Figure 12). Future tests for filtering will be conducted using a 1-mm mesh filter.

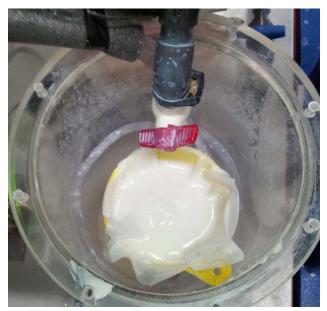


Figure 12: 10mm mesh filter

15-g of TiO<sub>2</sub> was recovered from the 90-g in the solution. This is a recovery rate of only 17%, too low to be effective. The final filter was the 0.45- $\mu$ m glass filter, which to the naked eye appears to remove all of the TiO<sub>2</sub>, but because of the fineness of the material, the filter clogs quickly. Further tests are needed on this filter with a larger surface area to determine if the 0.45- $\mu$ m glass microfiber filter can be used further.

Settling the  $TiO_2$  out of solution is another option. From storing the solution it was observed that the particles do settle out. A settling test was used to determine the settling rte. A 100-ml sample was placed in a beaker and allowed to settle. An image was captured every minute until the settle was observed to stop. This process can be seen in Figure 13. The settling test functioned well with at total settling time of 9 minutes, with a settling rate of 2.5 mm per minute. Settling tanks with lamella tubes are being considered for testing.



Figure 13: Settling Test Time-lapse

## Conclusion

With all testing to date, COD or ammonia have not reached levels acceptable to discharge to the environment. However, there is some evidence to suggest that once alkalinity is removed the  $TiO_2$  reaction increases. The COD removal rate for the 450-W flow through reactor with aeration and  $TiO_2$  concentration increased 12 percent when compared to the 450-W flow through reactor. This increase in COD removal could be related to the drop in pH. Ammonia removals levels increase by 5 percent when compared to the same tests. When looking at the full 24 hour test of the 450-W lamp, the removal rates were improving. COD dropped from 341 mg/l to 189 mg/l (45 percent decrease). Ammonia dropped from 313 mg/l to 75 mg/l (76 percent decrease). Alkalinity dropped from 1550 mg/l to 700 mg/l (55 percent decrease). COD removal may be effected by the amount of BOD contained in the leachate; tests will be conducted on BOD to track these levels. Since acceptable levels have not been reached to this point, more testing will be done using higher doses of  $TiO_2$  to find a more effective range. The link between alkalinity and then dosing with TiO<sub>2</sub>.

# **Research planned for the upcoming months:**

- Complete the update to the literature review.
- Meet with FDEP to discuss treatment targets for beneficial uses.
- Refinements need to be made for the removal of all TiO<sub>2</sub> in the piping network. There is some evidence that this could impact the results of COD testing. The alkalinity test needs to be completed on all the samples, and the total hardness needs to be measured for all the samples. A method of cleaning the inner light during testing need to be devised so that the light is not blocked from reaching the water for treatment.