Appendix F

Pilot Study of the VOC Eater Technology

ABS – VOCEATER™

PILOT STUDY REPORT

Prepared by Nic Korte

Nic Korte Consulting, Grand Junction, CO

For

Honeywell FM&T LLC

Kansas City, Missouri

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1. INTRODUCTION

The United States Department of Energy Kansas City Plant is evaluated the ABS VOCEater™ as a component of a replacement groundwater treatment system to be procured in the future. To that end, a pilot unit was brought to the site and a series of tests were performed.

The unit was shipped to the site by the vendor and installed by KCP personnel. The pilot test commenced on October 11, 2011. Because of problems encountered during the test, the planned four-week trial period was terminated on October 18.

2. SITE BACKGROUND

Groundwater at the KCP is being treated for chlorinated organic compounds. The vendor had been informed that nominal concentration of the contaminants was expected to be approximately 0.68 µg/L PCBs, 1,670 µg/L DCE (1,2-dichloroethene), 1,820 µg/L TCE (trichloroethene), and 98 µg/L vinyl chloride. Somewhat lower concentrations were encountered during the test with 1,2-DCE being on the order of 825 µg/L, TCE 27 µg/L, and vinyl chloride 53 µg/L. Based on recent results during regular system operation, PCBs were not expected in the influent.

Contaminated groundwater at the KCP presents a difficult treatment problem for three principal reasons:

1. The groundwater is reducing (anoxic) -- in contrast to water-supply aquifers which are oxidizing. Reducing groundwater may contain significant dissolved iron and manganese which precipitate on contact with air. At the KCP, certain locations in the shallow aquifer contain tens of ppm of dissolved iron and manganese. The KCP aquifer also contains naturally-occurring, dissolved arsenic in quantities exceeding the drinking water standard set by the US Environmental Protection Agency (EPA).
2. Groundwater such as the KCP shallow aquifer supports growth of a variety of bacteria, particularly as air is supplied. Hence, clogging with precipitates and bacterial growth are problematic and may cause more difficulty than removal of the principal contaminants.
3. The aquifer is in a clayey formation as opposed to water-supply aquifers which are typically sandy. Thus, there are generally more dissolved salts, including chloride, which

can cause corrosion as well as higher concentrations of suspended solids (clays) that also can cause clogging.

An additional issue for the KCP treatment system is the sporadic presence of a small amount of oil from one pumping well (273) and a small amount of poly-chlorinated biphenyls (PCBs) from another (276). Small amounts of oil can affect many treatment approaches by coating lamps or electrodes and requiring unanticipated maintenance.

3. NATURE OF TECHNOLOGY

The unique feature of the ABS Materials' catalytic chlorinated solvent scrubbing system is metallic particles of palladium entrapped within a glass matrix called Osorb™. Osorb is a newly discovered glass that has the unique property of swelling over 8 times its volume when contacting organic solutes, but does not swell in water.

The Osorb swelling process is reversible and delivers high capture affinity for chlorinated organics such as TCE, 1,2-DCE and vinyl chloride. Other organics, such as benzene, are also absorbed but are not degraded. Encapsulating palladium with an Osorb matrix is advantageous for the following reasons:

1. The glass matrix extracts and concentrates organic solvents causing them to have close contact with the palladium catalyst.
2. Salts and other inorganic species are excluded from the Osorb matrix. This serves to protect the palladium from being poisoned by dissolved ions or minerals.
3. The glass is inert and water resistant preventing palladium from entering the water stream.

The ABS Materials system requires the addition of a hydrogen source (hydrogen gas) at the inlet of a column filled with Osorb-Pd. Within the column, the Osorb rapidly absorbs the dissolved chlorinated organic (e.g. TCE) and hydrogen gas from solution. Inside the Osorb glass, the TCE and hydrogen rapidly react in a reduction reaction via palladium catalysis to yield ethane, ethene, and chloride. The mechanism is identical to that described in a 1997 publication, partially funded by the KCP. (Cheng, F., Q. Fernando, and N. Korte, 1997. Mechanism of reduction of 2-chlorophenol with palladized iron. *Environmental Science and Technology*.

31(4):1074-1078.) Palladium has a strong affinity for hydrogen and together palladium/hydrogen comprise a strong reducing agent capable of removing chloride from most organic compounds, even compounds considered recalcitrant such as PCBs. (Korte, N. O. West, L. Liang, B. Gu, J. Zutman, and Q. Fernando. 2002. The effect of solvent concentration on the use of palladized-iron for the step-wise dechlorination of polychlorinated biphenyls in soil extracts. *Waste Management.* 22:343-349.)

4. OPERATIONAL EVALUATION

Site Visit

A site visit was conducted by the author of this report on October 12-14. The unit was in full operation during a portion of this period. The flow rate was approximately 8 gpm. The flow rate was specified by the vendor based on the expected capacity of the pilot unit.

The unit consisted of two sections. The first portion employed two large columns and was called the OCC unit (Figure 1). Within this unit were 3 kg of Pd-Osorb at 35-60 mesh. This small mesh

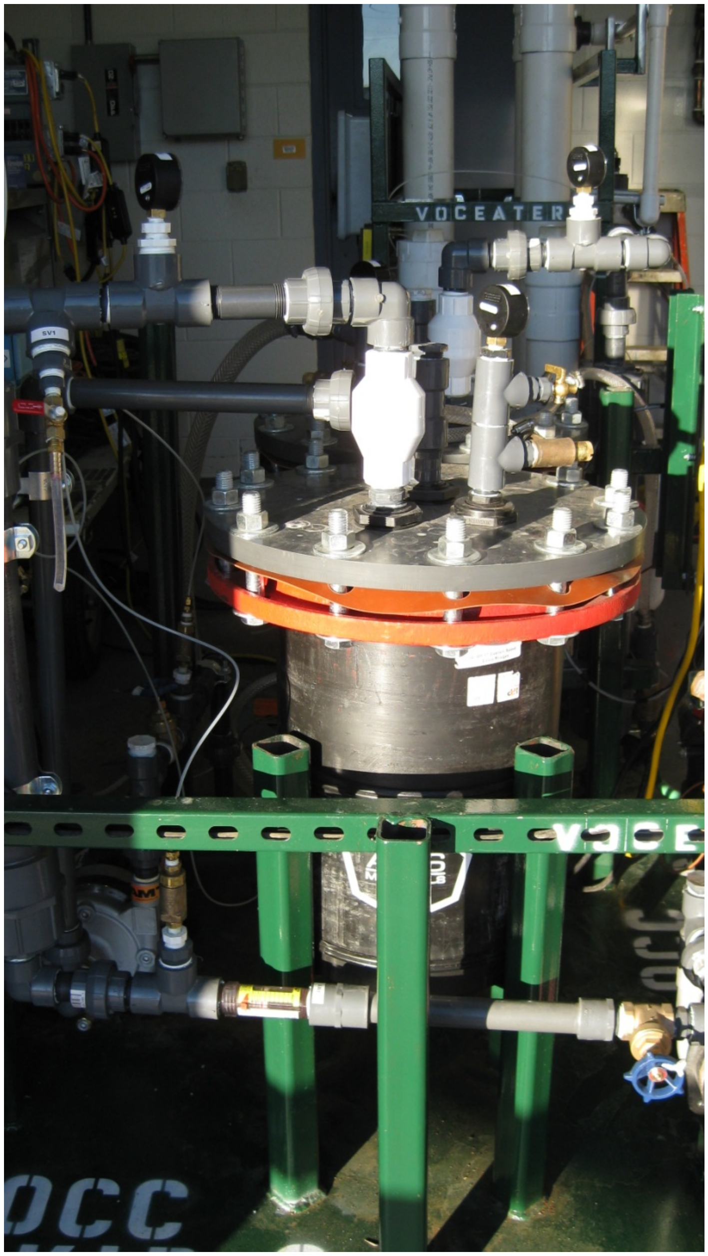

Figure 1. Initial, larger, educator-containing tanks employed for ~75% chlorinated contaminant removal.

(high surface area) material was retained within conical screen (100-mesh) filters. Within the tanks were two eductors used to circulate the solution. (Eductors use a Venturi design that enables small pumps to circulate large volumes of liquid in order to provide efficient agitation

/mixing. Eductors are typically capable of circulating four to five gallons of solution for each gallon pumped.) In this application, the eductors mix Osorb with the incoming water. These two larger tanks which comprise the OCC were expected to remove 75-80% of the contaminants.

The second part of the pilot unit, known as the VOCEater™, was expected to remove the remainder of the chlorinated contaminants. The VOCEater™ consisted of four packed columns containing 18kg of 5-20 mesh Osorb (Figure 2). It was noted that the media within

Figure 2. Fixed bed columns of 5-20 mesh Osorb.

these tanks could be stirred with a rod held with two fingers. Hence, the media is apparently more slurry-like than like a packed column.

The OCC and VOCEater™ components were hooked in series as shown in Figure 3.

Figure 3. OCC unit on far right, VOCEater™ in center, hooked in series, comprised the Pilot Unit tested at the KCP.

5. RESULTS

<u>Acidified Water</u>

The treatment system currently operating at the KCP includes acidification to pH ~2.5 in order to prevent iron and manganese from precipitating. Initially, treatment of this acidified water with the ABS pilot system was complete based on results from an on-site test kit used by the ABS technician and on data obtained from VOC analyses by Pace Inc., Lenexa, KS. Treatment efficiency was 98% with only ~13 µg/L of chlorinated VOCs remaining (Figure 4). (All analytical data from the pilot test are presented in Appendix A.)

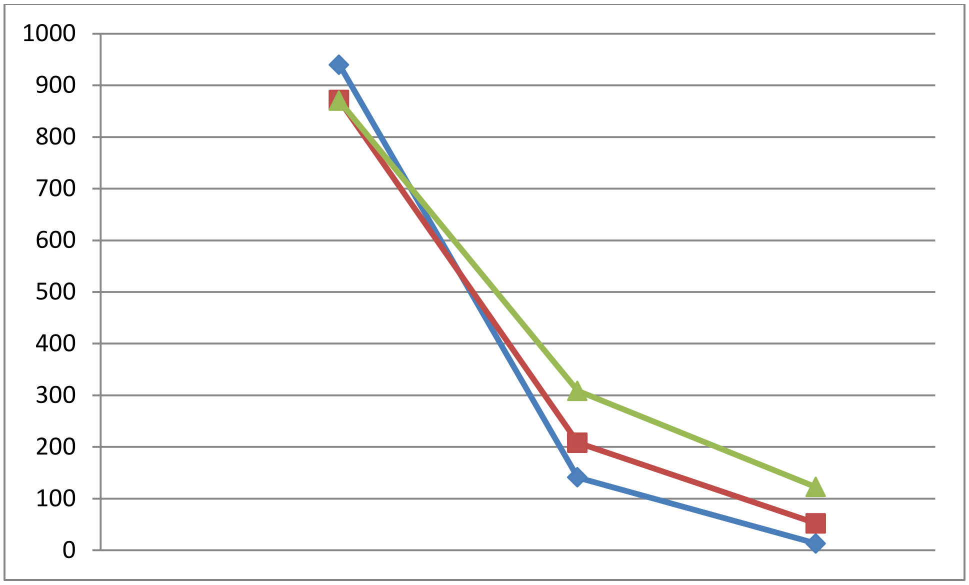

Figure 4. Treatment efficiency for the first three samples collected during the pilot study. (Water was acidified. Y-axis shows µg/L of chlorinated solvents. Each line shows concentration in the influent [first point], post-OCC (middle point) and post-treatment [last point]. Blue line shows sample at 1 hour, red line at three hours and green line at 6.25 hours.)

It was noted, however, that a large amount of bubbles were in the effluent line (Figure 5). The

Figure 5. There were a large amount of bubbles in the effluent line.

ABS technician on-site was unable to explain the origin of the bubbles. The hydrogen was shut off briefly to determine whether the amount of de-gassing varied but over the few minutes of this test; there was little evident change.

Unfortunately, treatment efficiency began to decrease. The second sample had 94% treatment (~52 µg/L remaining) which reduced further to 86% (122 µg/L remaining) by the end of the day on Oct 12 (Figure 4). No samples were sent to the laboratory on Oct 13 as the unit was inspected and re-tightened for leaks.

Ulitmately, the vendor's explanation for the decreasing treatment efficiency was that acidification was preventing the hydrogen from dispersing in the water. (ABS Lab tests indicate that the low pH hinders diffusion of HCl – a product of the dechlorination reaction- out of the glass material leading to slow kinetics of reaction.) In other words, the vendor believes that the Osorb had been highly charged with hydrogen before being shipped thereby accounting for the initial successful treatment. Treatment efficiency decreased as hydrogen within the palladium was consumed and not replaced.

To this point, acidified water had been used for treatment. As noted previously, groundwater at the KCP is near neutral in pH but is acidified to pH 2.5 to keep iron and manganese in solution in order to protect the presently-used treatment system. An acidification component is not a desirable requirement for a treatment unit because it increases cost and complexity. Thus, it was decided to attempt treatment of unacidified water.

<u>Unacidified Water</u>

Acidification is not necessary for the ABS VOCEater™, but was not expected to interfere either. Initially, the acidification step had been retained for simplicity in keeping the peroxidation systems treatment unit operating because the VOCEater™ was only treating a portion of the influent flow.

Because of the unexplained bubbles and the decrease in treatment efficiency, unacidified water was supplied on October 14. A single sample was collected. Although there were no longer bubbles in the treatment lines, overall treatment efficiency was only 69% (~264 µg/L remaining) (Figure 6).

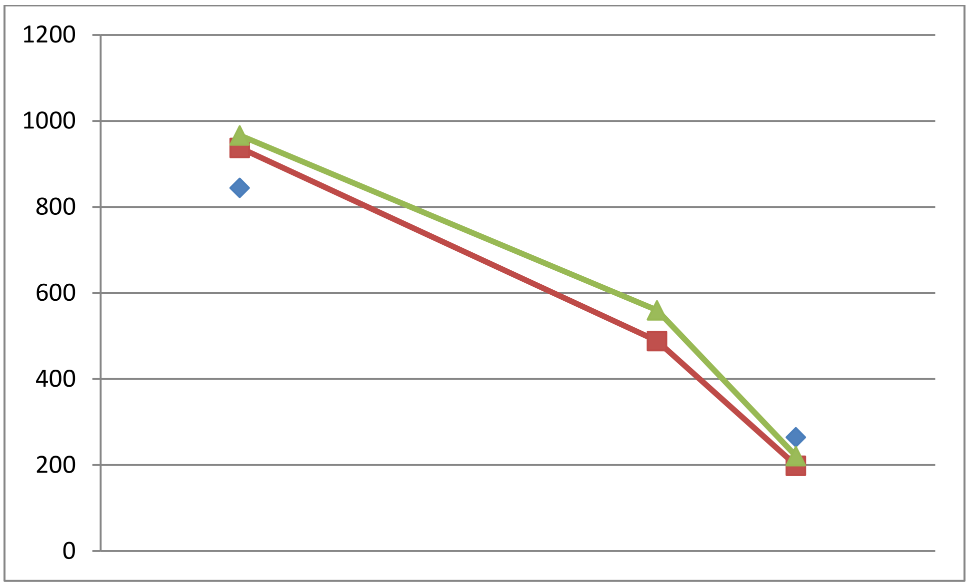

Figure 6. Treatment efficiency with unacidified water. (Y-axis shows µg/L of chlorinated solvents. Blue points show samples (no post-OCC sample was collected) from October 14, red line from October 17 and green line from October 18.)

Unfortunately, treatment efficiency did not improve and remained <80% (198 and 200 µg/L remaining) for two subsequent samples. It was at this time that the vendor informed KCP personnel that iron in the influent was now responsible for the decreased treatment. The vendor did not specify whether the iron poisoned the palladium catalyst or physically hindered treatment by precipitating within the columns. (In follow up conversations, the vendor noted that "the Pd-Osorb that had been affected by the process water was returned and rinsed with deionized water. Rinsing led to a return in catalytic performance in the laboratory as measured in a bench-top reactor vessel. It is likely adsorbed iron blinded the glass. Currently, an effort is being made to determine what form of iron leads to this blinding effect.")

Observations Concerning Iron

Even when the water was acidified, oxidized iron was evident in the influent line (Figure 7). Although not visually striking in Figure 7, it is apparent that there is a slight brown tinge in

Figure 7. Comparison of color of influent line (bottom) and effluent line (top), showing greater clarity in the effluent.

the bottom tubing (influent), whereas the top (effluent) is crystal clear. Based on knowledge of the water at the KCP, it is believed that the brown stain in the influent signifies the presence of minute particles or complexes of oxidized (ferric or Fe^{+3}) iron. Data collected indicates that iron was not retained within the ABS pilot unit when the water was acidified. Two samples of influent collected during this portion of the test contained 21,000 and 21,300 µg/L of iron respectively. The associated effluent samples contained 26,000 and 22,000 µg/L. Sampling and laboratory variability probably accounts for the differences in the influent/effluent measurements rather than any changes within the ABS unit. The clear effluent shown in Figure 7 indicates that the low pH in conjunction with the extreme reducing conditions in the VOCEater™ reduced all of the iron to the ferrous (Fe^{+2}) state which readily dissolves in water.

In contrast, when treating unacidified water, iron was retained within the pilot system. Two samples of influent collected during this portion of the test contained 9,290 and 13,400 µg/L of iron. The associated effluent samples contained 4,720 and 5450 µg/L of iron respectively. Hence, approximately half or more of the iron in the influent was being retained.

Cleaning and Shipment of Materials Following the Pilot Test

Prior to commencement of the pilot test, there was extensive discussion with personnel from the Missouri Division of Natural Resources (MDNR) regarding assurance that hazardous waste would not be generated. Approval for the test was granted by MDNR following submittal of a letter addressing a variety of questions regarding the technology (ABS Materials, Extended Responses and Complete Experimental for State of Missouri Hazardous Waste Program, Enforcement Section, June 9, 2011.) Accordingly, ABS was required to demonstrate the absence of contaminants in materials used at the KCP once the test was terminated. ABS performed the rinsing and analyses according to the agreement. Their certification of the results of that testing is provided in Appendix B.

6. DISCUSSIONS WITH SITE PERSONNEL

Initial comments from site personnel were mostly related to the large number of valves, gauges and pipe connections on the unit (Figures 8 and 9). The site water plant staff all expressed

Figure 8. Control Panel for the ABS Pilot System.

skepticism that the unit could operate automatically for extended time periods without developing leaks and suffering from periodic clogging. Concern was expressed because there were four pumps and numerous mechanical valves and pressure switches. Indeed, there were a few minor leaks during the test. Another comment was that a unit made of schedule 40 PVC "would never last."

Another potential issue was that discomfort was expressed because of the safety issues posed by use of hydrogen. The staff seemed more accepting when they were informed that a hydrogen generator and not a tank of compressed gas would be used in actual practice.

Finally, concern was expressed regarding whether the media would be stolen, saying the plant was in a neighborhood where catalytic converters were stolen from cars. Once the KCP manufacturing operations have moved; security will not be as tight as it is currently.

Figure 9. View showing many of the valves, meters and connections on the pilot system.

It is noted, however, that subsequent discussion with ABS personnel indicate that the unit at the KCP was only for pilot testing purposes. Full-scale units would employ different materials and be PLC controlled—presumably eliminating many of the concerns regarding ease-of-use and reliability. The vendor has stated that "full scale units will be PLC driven. We have one pilot unit deployed that is PLC driven and allows for remote retrieval of conductivity data via a telephone line. The water flow is intermittent at this site and features to turn the system 'on and off' according a preset water level in a surge is in place."

7. SYSTEMS AUDIT

Training for KCP personnel (CH_2MHill-OMI) was provided by the ABS technician. This training was observed throughout the time the technician was onsite. The OMI technician with primary responsibility for subsequent operation was queried and he regarded the training as sufficient.

The ABS technician used an AQR Colortech kit to evaluate VOC content on site. The performance of this test was observed on two occasions and the tests were performed according to the manufacturer's specifications. A check on these tests was provided by reviewing samples submitted to Pace Inc for VOC analysis. A sample was collected when the AQR Kit indicated complete treatment. The Pace result for a sample collected at this time showed 98% treatment. Subsequent samples with the AQR kit did not show complete treatment and this was also verified by samples from Pace.

Samples for the laboratory were collected both by KCP personnel and personnel from Pace Laboratory. Sampling was performed according to established protocols. Samplers were aware of the high concentration of bubbles in the water and the potential effect on VOC analyses. It was observed that samples were carefully obtained in order to eliminate any headspace.

8. POWER CONSUMPTION/REPLACEMENT MATERIALS

The KCP's portable power meter was not connected to the ABS Pilot unit both because of the short duration of the test and the simultaneous occurrence of a plant-wide strike. ABS has not yet constructed and sold a full-scale unit. Thus, costs are based on information provided by the vendor and are not based on operating experience. According to the vendor "the utility rates are 0.0553cents/kwhr (industrial) and 0.0749cents/kwhr (commercial) for Missouri. The pilot VOCEater™ unit runs off of 5 hp (uses approximately 4.63kwhr, which totals $148/month (industrial) and $201/month." Costs for a full-scale unit would have to be scaled up depending on the final design and size of pumps.

As with power consumption, there is insufficient operating history to evaluate the cost of replacement Osorb. As noted in the Report: Evaluation of Groundwater Treatment Technologies for the DOE Kansas City Plant, provided June 2010, "based on ABS's studies of their industrial separations; the glass slowly loses microscopic chips that escape the system. Their rule of thumb is a loss of approximately 1% mass per month of constant operations. Thus, the KCP would need $15,000 per year of replacement glass." Without a full-scale system in-place, these costs cannot be verified.

9. UNRESOLVED ISSUES

This section lists a number of issues or considerations which, while not precluding use of the ABS VOCEater™, should be considered in future decision-making.

1. Absorption of other hydrocarbons. If the Pd-Osorb encounters benzene in the influent, it will be captured and retained in the Osorb. In this instance, if the Osorb were ever taken off-site, it would need to be rinsed with acetone or a similar solvent to remove any trace benzene. Benzene is not typically observed in the groundwater treatment system influent, but is listed in the Permit as a site contaminant and, therefore, might create an issue with regulators because, unlike chlorinated hydrocarbons, it would be absorbed but not degraded. If the Osorb lasts indefinitely, as asserted by the vendor, this problem is minor because the materials would be cleaned or disposed of properly when the unit was retired.
2. Fluctuating DO (dissolved oxygen) as water flows change. The rate of hydrogen consumption is affected by the amount of dissolved oxygen. If the KCP treatment system is required to treat fluctuating flows due to storm water or even changing groundwater elevations because of rainfall, DO will vary. The vendor was queried regarding this problem and responded as follows: "If DO increases, we may need to add an OCC on the front end of the system to supply the rest of the system with a reducing environment, allowing Palladium-Osorb to properly function." Hence, there are additional design and testing issues involved with scaling up the present pilot unit.
3. Flexibility for fluctuating flows. The vendor stated that their suggested approach for fluctuating flows would be to " build the system in triplicate." When the water flow exceeds18 gpm, the second system would be brought on-line and the influent split between the two. When the influent water flow reaches 36-39 gpm, then the third system is brought-on." Considering that the extra capacity would be idle for as much as several months at a time, keeping the Pd charged and ready-to-function automatically at a moment's notice may prove difficult.
4. Effects of iron from other pre-treatment approaches. The KCP is considering use of a Filtra-Systems STiR unit for pre-treatment. Such a unit would likely remove the iron that appears to be the primary cause of treatment failure with the ABS VOCEater™. Another pilot test would have to be performed to evaluate this possibility.
5. Oxidized water from pre-treatment. Use of a Filtra-Systems STiR unit will require handling of many gallons of backwash water. One of the methods suggested for handling

this water is to pump it into a geotextile membrane in a dumpster or tank so that the water could "weep" through the membrane, thereby removing any residual solids. When the textile is full, it would be taken to a landfill, but the water that had weeped through the membrane would be recycled to the treatment system. This water, because of the extensive air exposure, would be more oxidized than usual and could affect the VOCEater^{TM} as described in point #3. In any case, if the pre-treatment system is changed, additional pilot testing would be necessary to evaluate the effects on the VOCEater^{TM}.

6. Experience with full-scale units is lacking. The vendor stated that as of October 2011, they have "3 pilot scale units out in the field currently, no permanent units yet." Present plans for the KCP are for groundwater treatment to continue after manufacturing has been moved to a new location. For this reason, the lack of operating history with an automated unit is more of a drawback than if manufacturing was continuing in the present location and a full-scale workforce was always present. It is noted, however, that the vendor does have an automated pilot unit in the field (see section 6).
7. Potential Removal of PCBs. There are no PCBs in the routine influent to the treatment system, but PCBs have been detected within the pumped groundwater. PCBs in this groundwater are typically not measured in the influent to the treatment system as a whole because of a sock filter on the well, dilution or because they precipitate in tank 3B. It is believed that the ABS VOCEater^{TM} would sorb and eventually reduce PCBs –even though the vendor did not provide such data. While the previously-mentioned work (see section 3) with palladized iron, however, suggests that PCBs would be dechlorinated by the Pd-Osorb, definitive studies have not yet been performed.

APPENDIX A

ANALYTICAL DATA COLLECTED DURING THE TEST

	Date	Time	1,2 DCE	TCE	VC	1,2-DCA	1,1-DCA	toluene	MIBK	Fe (total)	VOCs	% removed
influent			847	26.3	66.2		0		0		939.5	
post OCC			139	2			2.1		427		141	84.99201703
effluent			13.1	0	0		1.2		755		13.1	98.6056413
influent			781	26	64.7		0		84	21200	871.7	
post OCC			191	3.5	13.7		2.2		313		208.2	76.11563611
effluent			48.6	0	3.5		1.5		629	26000	52.1	94.02317311
influent			779	24.2	66.6		0		87.7	21300	869.8	
post OCC			282	5	21.5		2.5		224		308.5	64.53207634
effluent			115	0	7.5		1.9		511	22000	122.5	85.9163026
influent			766	23.5	55.3	0	0	61	0		844.8	
effluent			243	3.1	18.4	0.84	2.2	0	181		264.5	68.69
										9290		
										4720		
influent			881	28.9	27.1	0	0	0	0		937	
post OCC			463	7.2	18	0	2.7	0	76.9		488.2	48
effluent			186	0	12.5	0	2.2	0	220		198.5	78.8
influent			897	32.8	36.4	0	0	0	0		966.2	
post OCC			533	7	19.6	0	0	0	66.1		559.6	42
effluent			209	0	11.4	0	0	0	188		220.4	77
influent										13400		
effluent										5450		

MIBK(methyl-isobutyl ketone), toluene and 1,2-DCA (dichloroethane) are not contaminants in the KCP groundwater. These constituents are components of the glue used to construct the pilot unit.

APPENDIX B

CERTIFICATION FROM ABS THAT NO CONTAMINATED MATERIALS EXITED THE KANSAS CITY PLANT

ABSMaterials, Inc.
770 Spruce Street
Wooster, Ohio 44691

330.234.7999
www.absmaterials.com

December 1, 2011

Mr. Joe Baker
Honeywell FMT, LLC
Environmental Compliance Officer
Kansas City, MO 64141

Dear Mr. Baker,

The VOCEater System pilot unit was shut down and prepared for site removal by following the “Shut Down Flushing Procedure at Honeywell Location” (enclosed).

After flushing, the ABSMaterials field technicians conducted chlorinated material presence evaluatio on the effluent using the color changing tube technology marketed by Colortech and the result was “n color” (no chlorinated material present).

Additionally, the field technicians collected a sample of the effluent after final flushing for laborator analysis. The ABSMaterials laboratory conducted analysis for TCE, cis-DCE and VC compounds using a GC with a FID detector. The analysis shows “no detect” for all three with concentrations belc the resolution of the detector (<0.8 ug/L TCE, <0.6 ug/L 1,2-DCE, <0.1 ug/L Vinyl chloride).

The Pd-Osorb material contained within the VOCEater System after flushing was free of chlorinated species and therefore not a hazardous material.

If you have any questions, please feel free to contact me.

Kind regards,

Glenn Johnson
Chief Operating Officer
ABSMaterials, Inc.