

Western Research Institute

2008 Publication

Fallgren, P.H. and S. Jin, 2008, "Biodegradation of Petroleum Compounds in Soil by a Solid-Phase Circulating Bioreactor with Poultry Manure Amendments," *Journal of Environmental Science and Health Part A*, 43: 125-131.

Abstract: Petroleum compounds account for the vast majority of contaminants in soils. Bioremediation is a widely accepted strategy in degrading these contaminants. This study demonstrates the effectiveness of nitrogenous nutrient (nitrogen) amendments in enhancing biodegradation of petroleum contaminants in soil by using a solid-phase circulating bioreactor (SCB). In a bench-scale SCB, total petroleum hydrocarbon (TPH) concentration ($\sim 5000 \text{ mg kg}^{-1}$) in soil decreased 92% within 15 days. In a scaled-up SCB system containing $\sim 120 \text{ kg}$ petroleum-contaminated soil (TPH at $\sim 125,000 \text{ mg kg}^{-1}$), a degradation rate of $635 \text{ mg kg}^{-1}\text{d}^{-1}$ was obtained from the poultry manure-amended treatment during a 200-day period of operation. Treatments with the same amount of nitrogen (as ammonium nitrate) attained a TPH degradation rate of $469 \text{ mg kg}^{-1}\text{d}^{-1}$ during same period. Control SCB unit, which was maintained under the same aerobic conditions but not amended with nitrogen, had a TPH degradation rate of $273 \text{ mg kg}^{-1}\text{d}^{-1}$. Results from this study indicate that SCB can achieve significantly higher degradative rates than conventional land farming (reported rates $< 150 \text{ mg kg}^{-1}\text{d}^{-1}$) and poultry manure appears to be a preferred nitrogen amendment that can further enhance the biodegradation of petroleum contaminants in soils.

Goual, L., J.F. Schabron, T.F. Turner, B.F. Towler, 2008, "On-column Separation of Wax and Asphaltenes in Petroleum Fluids," *Energy and Fuels*, in press.

Abstract: The utility of a novel method based on the new on-column precipitation and re-dissolution technique is explored. This method, called Waxphaltene Determinator (WAD), is strictly solubility-based and allows the detection of waxes and asphaltenes in minutes. The principle of the method is to first precipitate waxes and asphaltenes together on a ground polytetrafluoroethylene (PTFE)-packed column using methyl ethyl ketone at $-20 \text{ }^\circ\text{C}$ then re-dissolve the precipitate with solvents of increasing polarity at different temperatures. Waxes precipitated under these conditions are composed mainly of n-alkanes with carbon numbers greater than C_{20} and heptane-soluble alkanes that are slightly-to-moderately branched. The method is first verified with model compounds including n-alkanes and commercial waxes then applied to waxy crude oils and deposits. The method is compared to differential scanning calorimetry (DSC) and a linear correlation is found between the wax content by WAD and DSC. Asphaltene amounts by WAD also compare well with the gravimetric data.

Huang, S-C. and A. T. Pauli, 2008, "Particle Size Effect of Crumb Rubber on Rheology and Morphology of Asphalt Binders with Long-term Aging." *Road Materials and Pavement Design*, 9: 73-95.

Abstract: Two different particle sizes of crumb rubber at three different concentrations were mixed with two asphalts to investigate the effect of rubber particles on the fundamental internal microstructure of asphalt binders with respect to their long-term aging performance. The rheological, morphological, and chemical properties of unaged and aged unmodified and rubber modified asphalt binders were studied as a function of long-term oxidative aging. Based on the limited study, the results indicate that the amounts of rubber particles added into asphalt binder are asphalt dependent. For highly incompatible asphalt, rubber concentration has substantial effect on the long-term flow properties of asphalt binders. For compatible asphalt, addition of rubber increased the elasticity of asphalts and also reduced viscosity buildup with aging. In addition, particle size of rubber does not show significant differences in terms of its effect on the long-term aging characteristics of asphalt binder. Furthermore, results from atomic force microscopy (AFM) showed that some fractions of the rubber particles may be dissolved in the asphalt due to devulcanization of the rubber, and hence, could explain the appearance of "new" material in the AFM image of the recovered asphalt samples.

Jin, S., P.H. Fallgren, J.M. Morris, and J.S. Cooper, 2008, "Source Treatment of Acid Mine Drainage at a Backfilled Coal Mine Using Remote Sensing and Biogeochemistry," *Water, Air, and Soil Pollution*, 188:205–212

Abstract: A biological source treatment (BST) technique using remote sensing and biogeochemistry has been developed to address acid mine drainage (AMD) at its source. The BST technique utilizes down-hole injections of microbial inoculum and substrate amendments to establish a biofilm on the surface of metal sulfides (AMD source material). The treatment results in an elevated groundwater pH (from acidic to circum-neutral levels) and prevents further oxidation of AMD source material. The first 2 years of an ongoing field study of the BST technique at a reclaimed coal mine in central Tennessee (USA) has produced successful results. For instance, the water chemistry in a monitoring well down-gradient from injection wells has improved substantially as follows: the pH increased 1.3 units from 5.7 to 7.3, the dissolved (0.45 μm -filtered) iron concentration decreased by 84% from 93 to 15 mg/L, the conductivity decreased by 379 $\mu\text{S}/\text{cm}$, and sulfate decreased by 78 mg/L. Electromagnetic induction surveys were conducted to identify AMD source material and monitor BST performance by measuring changes in subsurface resistivity throughout the site. These surveys revealed a treatment zone created between injection wells where the resistance of contaminated groundwater from up-gradient AMD sources increased as it flowed past injection wells, thus, suggesting this technique could be used to treat AMD sources directly or to intercept and neutralize sub-surface AMD.

Jin, S., P.H. Fallgren, J.M. Morris, and R.B. Gossard, 2008, "Biological Source Treatment of Acid Mine Drainage Using Microbial and Substrate Amendments: Microcosm Studies," *Mine Water and the Environment*, 27:20-30.

Abstract: Microcosm studies in the laboratory demonstrate that sufficient dosages of wastewater effluent (microbial inoculum) and returned milk (substrate) can effectively raise the pH of pyrite-amended acid mine drainage water to circumneutral levels under aerobic conditions in as little as 7 d, and the pH remains at these levels for > 19 months. Microbial analysis indicates that a complex biofilm (>70 species) forms over the pyrite. The biofilm dominantly consists of facultative anaerobes, which potentially interact with obligate anaerobes, such as sulfate-reducing *Desulfosporosinus* sp., to maintain an oxygen-free micro-environment surrounding the pyrite, even though the overlying water remains aerobic. The biofilm became established in water samples with an initial pH as low as 2, and subsequently caused the water pH to increase to circumneutral levels. Concurrently, concentrations of Al, As, Cu, Fe, Pb, Ni, and Zn all decreased substantially compared to baseline concentrations in the control microcosms.

Jin, S., P.H. Fallgren, J.M. Morris, E.S. Edgar, 2008, "Degradation of Trichloroethene in Water by Electron Supplementation," *Chemical Engineering Journal* 140:642–645.

Abstract: Trichloroethene (TCE) is a common and recalcitrant contaminant in groundwater. Microbially catalyzed reductive dechlorination is a dominant pathway for TCE degradation, in which substrates and electron donors are essential. In this study, extraneous electron supplementation was attempted to enhance reductive dechlorination of TCE and its derivatives. Reactors were established with groundwater containing TCE, and a 6-V battery was used to supply an average current of 29 μ A of dc power to feed electrons to the microcosms. We measured 80–90% depletion of TCE within 70 d in reactors (both sterile and non-sterile) containing 300–400 μ g TCE/l and from 97 to 98% depletion in microcosms containing 10 mg TCE/l. No intermediate products such as dichloroethylene or vinyl chloride were detected during this study. Results demonstrate that electron-supplemented degradation of TCE appears to be an abiotic process that is unassociated with microbial populations or indigenous redox conditions. No apparent accumulation of TCE daughter products were observed and overall efficiency of this electroremediation process was calculated to be 6.9 g TCE degraded/kW h. This efficiency would make electron supplementation an attractive alternative to the substrate-amended biological reductive dechlorination of TCE.

Jin, S., P.H. Fallgren, J.S.Cooper, J.M. Morris and M.A. Urynowicz, 2008, "Assessment of Diesel Contamination in Groundwater using Electromagnetic Induction Geophysical Techniques," *Journal of Environmental Science and Health Part A*, 43:584-588.

Abstract: Determining hydrocarbon plumes in groundwater is typically accomplished through the installation of extensive monitoring wells. Issues of scale and site heterogeneities tend to introduce errors in delineating the extent of

contamination and environmental impact. In this study, electromagnetic induction survey was investigated as an alternative technique for mapping petroleum contaminants in the subsurface. The surveys were conducted at a coal mining site near Gillette, Wyoming, using the EM34-XL ground conductivity meter. Data from this survey were validated with known concentrations of diesel compounds detected in groundwater from the study site. Groundwater data correlated well with the electromagnetic survey data, which was used to generate a site model to identify subsurface diesel plumes. To our knowledge, this is one of the first studies to use electromagnetic survey techniques for mapping hydrocarbon contamination in groundwater. Results from this study indicate that this geophysical technique can be an effective tool for assessing subsurface petroleum hydrocarbon sources and plumes at contaminated sites.

Miknis, F. P. and K. P. Thomas, 2008, "NMR Analysis of Polyphosphoric Acid-modified Bitumens." *Road Materials and Pavement Design*, 9: 59-72.

Abstract: Phosphorous-31 NMR spectroscopy has been used to study the behavior of polyphosphoric acid (PPA) in bitumen. Phosphorous NMR spectra were acquired on a PPA-modified bitumen immediately after blending, and on samples that were stored at 135°C for different periods of time. The initial NMR spectra showed resonances characteristic of phosphorous atoms in orthophosphoric acid, and in middle and end groups of phosphate chains. However, over time the number of phosphorous atoms in the middle and end groups decreased, indicating a preference of polyphosphoric acid to revert back to the orthophosphoric acid in the presence of bitumen. The NMR data did not suggest the formation of organic phosphate esters as a result of PPA modification. Phosphorous NMR spectra were also acquired on bitumen samples modified with Elvaloy® in which polyphosphoric acid was used as a catalyst. The data showed that over time only one type of phosphorous atom remained in the bitumen. The NMR data suggest that the PPA did not react with Elvaloy® to form esters.

Morris, J.M., S. Jin, K. Cu, 2008, "Removal of Endocrine Active Compounds Using Layered Double Hydroxide Material," *Chemical Engineering Journal*, in press.

Abstract: A granular form of a layered double hydroxide (LDH) material was used as an anionic adsorbent in packed column and slurry experiments to remove endocrine active compounds (EACs) from river water downstream from wastewater treatment plants and from laboratory water spiked with 17 β -estradiol (E2). The estrogenic activity of the samples was estimated using the biological yeast estrogen screen (YES) assay and the E2 concentrations were analyzed using radioimmunoassay techniques. The LDH in a packed column significantly ($p < 0.05$) decreased the estrogenic activity of the river water from 519 to 387 ng E2 equiv./L after one pass through the column. The LDH packed column reduced the E2 concentration in a different river water sample from 12 ng/L to below detection limit (1.8 ng/L) with minimal retention time. Finally, LDH in a slurry treatment reduced the E2 concentration in water from 317 ng/L to below detection limit. The results of these experiments suggests that LDH may be used to treat waste or drinking water for estrogenic endocrine disrupting components (EDCs)

such as E2 and possibly other anionic compounds that affect the endocrine system.

Morris, J.M., S. Jin, B. Crimi, and A. Pruden, 2008, "Microbial Fuel Cell for Enhancing Anaerobic Biodegradation of Diesel," *Chemical Engineering Journal*, in press.

Abstract: Microbial fuel cell (MFC) technology can potentially be applied to enhance subsurface bioremediation of contaminants such as petroleum hydrocarbons by providing an inexhaustible source of terminal electron acceptors to a groundwater environment that is likely depleted in thermodynamically favorable electron acceptors such as oxygen and nitrate. Results indicate that anaerobic biodegradation of diesel range organics (compounds eluting with n-alkane markers ranging in size from C-8 to C-25) was significantly enhanced ($P=0.007$) in an MFC (82% removal) as compared to an anaerobically-incubated control cell (31% removal) over 21 days at 30°C, meanwhile, as much as 31 mW/m² cathode of power was generated during diesel degradation (as measured during a polarization curve experiment). The microbial consortium on the anode of a diesel-degrading MFC was characterized by cloning and sequencing 16S rRNA genes. The majority of the clone sequences showed > 98% similarity to bacteria capable of denitrification, such as *Citrobacter* sp., *Pseudomonas* sp., and *Stenotrophomonas* sp. The remaining clone sequences showed high similarity with organisms capable of using a wide range of electron acceptors, including sulfate, arsenate, and chlorinated inorganics. In particular, *Shewanella* sp. and *Alishewanella* sp. were found, which are typically capable of using multiple electron acceptors. This study suggests that MFC technology may be used for enhancing biodegradation of petroleum contaminants in anoxic environments, thus, eliminating the need to amend terminal electron acceptors such as oxygen.

Morris, J.M. and S. Jin. 2008, "Feasibility of Using Microbial Fuel Cell Technology for Bioremediation of Hydrocarbons in Groundwater." *Journal of Environmental Science and Health-Part A* 43: 18-23.

Abstract. A single-cell microbial fuel cell (MFC) design was used to study anaerobic microbes that utilize petroleum contaminants as a sole substrate to produce power during remediation. Additionally, we tested various proton bridge designs to physically separate the anode and cathode chambers of a two-cell MFC by ~9 m (~30 ft.). This separation enables the potential use of MFC technology for in-situ bioremediation of petroleum hydrocarbons in the groundwater, in which oxygen is usually depleted and oxygen availability only exists at or near the surface. Sustained power generation (as high as 120 mW/m² cathode) was recorded for ~6 d in a single-cell MFC utilizing a mixture of refinery waste (containing various concentrations of hydrocarbon contaminants) and cell growth media. MFC cell potential (1KΩ external resistance) decreased by ~55% over the length of 9-m proton bridge with a 6.9% decrease in potential per m of bridge.

Netzel, D. A., and T. F. Turner, 2008, "NMR Characterization of Size Exclusion Chromatographic Fractions from Asphalt." *Petroleum Science and Technology*, 26(12): 1369-1380.

Abstract: Size exclusion chromatography was used to separate an asphalt into nine fractions and these fractions were then investigated by ^1H and ^{13}C NMR. From the integration of the spectra, various molecular structural parameters were calculated. The aromatic carbon to nitrogen and the aromatic carbon to sulfur ratios were determined for six of the fractions. The catenation (linear and circular) of the aromatic ring structure was determined for six fractions. It appears that circular catenation is more probable for the high molecular weight fraction. For the lower molecular weight fraction, both linear and circular catenation are equally probable.

Schabron, J.F. and Rovani, J.F., "On-Column Precipitation and Re-Dissolution of Asphaltenes in Petroleum Residua," *Fuel*, 87(2), 2008, 165-176.

Abstract: A new automated separation technique was developed for measuring the distribution profiles of the most polar, or asphaltenic components of an oil, using a continuous flow system to precipitate and re-dissolve asphaltenes. Methods of analysis based on this new technique were explored. One method based on the new technique involves precipitation of a portion of residua sample in heptane on a polytetrafluoroethylene-packed (PTFE) column. The precipitated material is re-dissolved in three steps using solvents of increasing polarity; cyclohexane, toluene, and methylene chloride. The amount of asphaltenes that dissolves in cyclohexane is a useful diagnostic of the thermal history of an oil and its proximity to coke formation. For example, about 40% (w/w) of the heptane asphaltenes from unpyrolyzed residua dissolves in cyclohexane. As pyrolysis progresses, this number decreases to below 15% as coke and toluene-insoluble pre-coke materials appear. Currently, the procedure for the isolation of heptane asphaltenes and the determination of the amount of asphaltenes soluble in cyclohexane spans three days. The automated procedure takes one hour. Another method uses a single solvent, methylene chloride, to re-dissolve the material that precipitates in heptane on the PTFE-packed column. The area of this second peak can be used to calculate a value which correlates with gravimetric asphaltene content. Currently, the gravimetric procedure to determine asphaltenes takes about 24 h. The automated procedure takes 30 min. Results for four series of original and pyrolyzed residua were compared with data from the gravimetric methods. Methods based on the new on-column precipitation and re-dissolution technique provide significantly more detail about the polar constituent's oils than the gravimetric determination of asphaltenes.

Thomas, K. P., and T. F. Turner, 2008, Polyphosphoric-acid modification of asphalt binders: Impact on rheological and thermal properties. *Road Materials and Pavement Design*, 9(2): 181-205.

Abstract: Three compositionally different binders were modified (1.5 wt %) by the addition of polyphosphoric acid (105%). The rheological and thermodynamic properties of the unmodified and acid-modified binders are compared. These

same properties for the unaged and aged binders are also compared in the report. Acid modification increases the complex modulus at 58°C and the increase is persistent in the aged, modified binders. The impact of acid modification on the thermodynamic properties of the binders is variable, with binder AAM-1, which contains microcrystalline wax and has a substantially higher average molecular weight, being the exception. In all cases, the glass transition temperature is reduced and, in general, the height of the transition is reduced, while the width is increased. These thermodynamic results indicate that the changes for binders ABD and AAD-1 are consistent with the conversion of some of the maltenes to asphaltenes and for AAM-1 the results are consistent with a conversion of some asphaltenes to maltenes.