

REPORT TITLE: Treatment of Produced Waters Using a Surfactant Modified Zeolite/Vapor Phase Bioreactor System

REPORT TYPE: Semi-Annual Technical Report

REPORT PERIOD: 1 March 2003 – 31 September 2003

PRINCIPAL AUTHORS: Lynn E. Katz, Kerry A. Kinney, R.S. Bowman, E.J. Sullivan

REPORT ISSUE DATE: October 2003

DOE AWARD NUMBER: DE-FC26-02NT15461

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Lynn E. Katz
Project Manager

Abstract

Co-produced water from the oil and gas industry is by some estimates the largest single waste stream in the country, aside from nonhazardous industrial wastes. Characteristics of produced water include high total dissolved solids content, dissolved organic constituents such as benzene and toluene, an oil and grease component, and chemicals added during the oil-production process. While most of the produced water is disposed via reinjection, some of them must be treated to remove organic constituents before the water is discharged. An efficient, cost-effective treatment technology is needed to remove these constituents. Surfactant-modified zeolite (SMZ) has been used successfully to treat contaminated ground water for organic and inorganic constituents. In addition, the low cost of natural zeolites makes their use attractive in water-treatment applications. Our previous DOE research work (DE-AC26-99BC15221) demonstrated that SMZ could successfully remove BTEX compounds from the produced water. In addition, SMZ could be regenerated through a simple air sparging process. The primary goal of this project is to develop a robust SMZ/VPB treatment system to efficiently remove the organic constituents from produced water in a cost-effective manner.

This report summarizes work of this project from March 2003 through September 2003. We have continued our investigation of SMZ regeneration from our previous DOE project. Ten saturation/stripping cycles have been completed for SMZ columns saturated with BTEX compounds. The results suggest that BTEX sorption capacity is not lost after ten saturation/regeneration cycles. The composition of produced water from a site operated by Crystal Solutions Ltd. in Wyoming has been characterized and was used to identify key semi-volatile components. Isotherms with selected semi-volatile components have been initiated and preliminary results have been obtained. The experimental vapor phase bioreactors for this project have been designed and assembled to treat the off-gas from the SMZ regeneration process. These columns will be used both in the laboratory and in the proposed field testing to be conducted next year. Inocula for the columns that degrade all of the BTEX compounds have been developed.

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1. Introduction

Co-produced water from the oil and gas industry accounts for a significant waste stream in the United States. For each barrel (bbl) of oil produced, an average of 10 bbl of water is produced for an annual total of about 3 billion tons (API, 1987). This is by some estimates the largest single waste stream in the country, aside from nonhazardous industrial wastes (Allen and Rosselot, 1994). Although as much as 95% of this produced water is disposed via reinjection, the remaining amounts that are discharged on the surface are significant. Environmental and cost considerations make surface discharge of this water a more practical means of disposal in many instances. In addition, reinjection is not always a feasible option because of geographic, economic, or regulatory considerations. In these situations, it may be desirable, and often necessary from a regulatory viewpoint, to treat produced water before discharge. It may also be feasible to treat waters that slightly exceed regulatory limits for re-use in arid or drought-prone areas, rather than losing them to re-injection.

Characteristics of produced water include high total dissolved solids content (TDS), dissolved organic constituents such as benzene and toluene, an oil and grease component (which may be a dissolved product, an emulsion, or a separate phase) and chemicals added during the oil-production process. Current solutions to oil and grease restrictions and dissolved toxics (mostly from dissolved organic constituents) include ultrafiltration, advanced oil-water separation, hydrocyclones, chemical clarification, and gas flotation. Although many of these treatment options are successful at reducing the organic content of produced waters, they cannot always meet the levels of the current or proposed regulations (EPA NPDES, Federal Register V. 66, No. 14, pp.6607-6610). A need therefore exists to develop a cost-efficient treatment technology for the organic content in produced water. Such a technology is estimated to potentially maintain several thousand bbl of domestic production in a single impacted county. This can be multiplied by a factor of 10 to 20 for other counties that may be potentially impacted within the state of Texas alone. Therefore, the impact of regulation and the need for inexpensive treatment processes is considerable.

Surfactant-modified zeolite (SMZ) is an innovative filtration/sorption medium that can meet these needs. This adsorbent can be cost-effectively produced using naturally occurring zeolites and commercially available surfactant. Zeolites are hydrated aluminum tectosilicates characterized by cage like structures having high internal and external surface areas, and high-cation exchange capacities. The low cost of natural zeolites (\$45 to \$60/ton) makes their use attractive in water-treatment applications. In contrast to clays, however, natural zeolites can occur as millimeter- or-greater-sized particles and are free of shrink-swell behavior. As a result, zeolites exhibit superior hydraulic characteristics and are suitable for use in filtration systems (Breck, 1974).

Treatment of natural zeolites using cationic surfactants dramatically alters their surface chemistry. The large organic cations exchange readily with the native counterions on the external surface of the zeolite. This exchange produces a high-organic-carbon-content external surface while preserving a significant portion of the internal-surface cation-exchange capacity. The surfactant used to coat the external surface of zeolites in our previous work was hexadecyltrimethylammonium bromide (HDTMA). In addition to increasing the organic content of the sorbent, the HDTMA cation also produces the unique property of oxyanion sorption under high loading levels. Thus, the adsorbent produced can remove cationic, anionic and organic constituents of produced water.

In our previous research project batch and laboratory column adsorption studies suggested that: 1) sorption of benzene, toluene, ethylbenzene and xylenes (BTEX) to SMZ follows linear isotherms in which sorption increases with increasing solute hydrophobicity; 2) the presence of high salt concentrations can substantially increase the capacity of the SMZ for BTEX; 3) competitive sorption among the BTEX compounds is negligible; and, 4) in tests conducted to date, a reduction in sorption capacity of benzene (the design-controlling solute) was not evident in the samples containing produced water. Our studies also indicate that due to benzene's relatively low sorption potential, the column design and regeneration requirements are controlled by benzene breakthrough from the SMZ columns.

A key feature required for successful application of SMZ to the treatment of produced water is regeneration of the SMZ. Although SMZ is not as efficient as activated carbon in removing highly soluble organics such as benzene, studies completed by the PIs indicate that SMZ can be readily regenerated for BTEX compounds simply by sparging ambient air through the SMZ column. This process generates a moist air stream contaminated with relatively low concentrations of volatile organic compounds (VOCs) including BTEX. Because these VOCs are biodegradable and present in dilute concentrations, a vapor phase bioreactor can be used to destroy the pollutants generated in the SMZ regeneration step. In vapor phase bioreactors (VPBs), microorganisms growing on a fixed packing media are used to biodegrade organic pollutants found in the waste gas stream being treated. Products of the biodegradation include carbon dioxide, water and new biomass. This technology has several advantages for this application including high destruction efficiencies for many VOCs including BTEX compounds, low operating costs and minimal generation of undesirable byproducts (van Groenestijn and Hesselink, 1993; Deshusses and Webster, 2000). For instance, removal efficiencies of greater than 90% can be achieved at BTEX loads below $96 \text{ g/m}^3_{\text{packing}}\text{hr}$, (Lu, et al., 2000). The hydrocarbon load produced from the SMZ regeneration step is far below this value and thus high removal efficiencies are expected. In fact, VPBs were originally developed to treat waste gas streams containing low concentrations of VOCs and this is considered the ideal application for the VPB technology (Leson and Winer, 1991; Leson and Smith, 1997; van Groenestijn and Hesselink, 1993.).

Several VPB configurations are possible for the SMZ application including a biofilter configuration with a stationary liquid film containing nutrients and biomass. Biofilters are often packed with a natural media such as peat or compost which is biologically active and can provide nutrients to the microorganisms growing on the packing material. Synthetic packing materials such as silicon oxide pellets have also been used successfully in biofilters (Song and Kinney, 2000; Woertz, *et. al*, 2001) and allow greater control over key operating parameters such as nutrient supply, biomass distribution and microbial composition of the biofilm. Biotrickling filters are an alternative VPB configuration in which a liquid nutrient phase is continuously recirculated throughout a synthetic packing material. Microorganisms living in the

biofilm attached to the packing material as well as suspended in the recirculating liquid phase are responsible for the degradation of the VOC pollutants. Both VPB configurations have been used successfully to treat waste gas streams containing BTEX and other volatile hydrocarbons and hybrid systems which contain both biofilter and biotrickling filter design elements are also currently under development for treating complex VOC mixtures (Song, *et. al*, 2002).

Although VPBs are an attractive treatment for the SMZ regeneration step, several issues will need to be investigated to ascertain the effectiveness of the SMZ/VPB combination. For instance, the presence of multiple VOCs in the inlet gas stream can lead to competitive inhibition between the VOC substrates (Deeb and Alvarez-Cohen, 1999; Deshusses et al., 1995). In addition to BTEX compounds, the air stream generated from the SMZ regeneration step will include other volatile hydrocarbons. Vapor phase bioreactors have the ability to treat complex hydrocarbon streams such as those generated from the remediation of gasoline-impacted sites (Jutras, et al., 1997) but interactions between the VOC components of the waste gas stream must be determined for a particular application. For instance, the PIs have observed in a biofilter packed with synthetic media that the presence of toluene can inhibit the degradation of xylene; however, once the toluene has been degraded in the front end of the bioreactor, the remaining aromatic constituents can be successfully degraded. The PI's research team has also recently observed that such VOC degradation interactions may be mediated by the nitrogen availability in the biofilm. In the presence of excess nitrogen, for instance, toluene, xylene and ethylbenzene can be degraded simultaneously but under nitrogen limitation, xylene degradation is reduced (Song et al., 2002). The effect of nitrogen on VPB performance has been studied by the PI and others and is an important operating parameter for the system (Kinney et al., 1999; Moe and Irvine, 2001).

Another issue to consider for the SMZ/VPB combined treatment system is that VPBs prefer a continuous feed stream and thus the operation of the SMZ/VPB system will need to be optimized to match SMZ regeneration and VPB feed cycles. For instance, in a recent study completed by the PIs, it was determined that a VPB supplied with a very small but continuous VOC feed achieved much higher removal efficiencies following restart of the bioreactor than did a system that was simply shut off and not provided any

VOCs during the shutdown period (Park and Kinney, 2001). Finally, it is important to note that although many of the organic constituents found in produced water are biodegradable, the high salinity of produced water prevents direct biological treatment of the produced water. Furthermore, direct air stripping of the produced water phase will not remove the less volatile organic contaminants. Thus, treatment of the water via SMZ followed by treatment of the regeneration gas via a VPB allows the removal of organic and inorganic constituents and ultimate destruction of the VOCs without the problems associated with high salinity and the presence of heavier organic species.

The overall goal of this project is to develop a robust SMZ/VPB treatment system to efficiently remove the organic constituents from produced water in a cost-effective manner. Although both SMZ and VPB technologies have been developed separately by the PIs, a series of laboratory and field scale experiments are required to optimize the SMZ/VPB combination specifically for produced water. Once the air sparging/VBP system has been developed for the primary regeneration of the volatile constituents, a secondary regeneration step will be required on an infrequent basis for the non-volatile hydrophobic constituents. Evaluation, selection and design of the secondary regeneration method for the non-volatile organic constituents will be a key component to the success of the project.

Thus, the four objectives of the proposed project are as follows:

- Objective 1:** Characterize and optimize the SMZ primary and secondary regeneration processes to enable long-term operation of the SMZ process for a wide range of produced water applications (Project Phase 1);
- Objective 2:** Develop a VPB that is optimized for treating the waste gas streams generated by SMZ regeneration for a variety of produced waters (Project Phase 2);
- Objective 3:** Optimize the coupled SMZ/VPB treatment technology both at the laboratory and field scale (Project Phases 3 and 4); and
- Objective 4:** In conjunction with industry and DOE, conduct a detailed cost and feasibility evaluation to compare the SMZ/VPB treatment technology to

existing techniques for treating produced water from a variety of processes across the country (Project Phase 5).

Research over the first year of the project has focused on Objectives 1 and 2 which corresponds to Phases I and II of the project. A description of the tasks for each of these phases is presented below.

1.1 Phase 1. Optimize SMZ Regeneration Process (Lab-Scale)

Task 1.0 Determine SMZ Sorption Characteristics for Volatile and Non-Volatile Components of Produced Waters

Our previous work on sorption of dissolved organics from produced water by SMZ has focused on the more volatile and toxic BTEX compounds. For this task we will evaluate, using laboratory batch and column experiments, the SMZ sorption capacity for the full range of produced water dissolved components. Produced waters from the projected field demonstration sites will be collected and used for this purpose.

Subtask 1.1 Determination of Produced Water Composition. In this subtask we will characterize the produced water composition in terms of individual compounds and dissolved organic weight fractions. Gas chromatographic methods will be optimized for accurate quantitation of the organic components/fractions

Subtask 1.2 Characterization of Organics Sorption in SMZ Batch Reactors. Batch sorption isotherms will be prepared to determine the affinity of SMZ for the various soluble organics in the produced waters. In these experiments, the produced water will be diluted to provide a range of solute concentrations that will be equilibrated with a fixed amount of SMZ. Sorption isotherms developed from these experiments will be used to determine the relative sorption of each component and to estimate the loading capacity in the column experiments under Subtask 1.3.

Subtask 1.3 Characterization of Organics Retention Capacity in SMZ Column Reactors. Based upon the sorption isotherms developed in Subtask 1.2, we will conduct column experiments to predict the loading and migration rates of produced water components through packed beds of SMZ. Initially, the columns will be leached with a synthetic water that matches the inorganic composition of the produced water, but is free of organics. Prior to introduction of the produced water into the column, a nonreactive tracer (tritiated water) will be introduced into the column to allow determination of the hydrodynamic properties (mean pore water velocity and dispersion coefficient) of each column. Using this hydrodynamic information along with the isotherms developed in Subtask 1.2, we will predict the breakthrough behavior of each organic component. Breakthrough curves for the produced water components will be compared to the predictions and used to determine the regeneration cycle times to be used in Task 2.

Task 2.0 Optimize Regeneration Schemes for All Produced Water Components

Subtask 2.1. Regeneration for Volatile Components. SMZ will have the lowest sorption capacity for the most volatile, lower molecular weight components of the produced water. Thus, the minimum regeneration time will be controlled by the loading capacity for these components. Columns based upon the design under Subtask 1.3, will be constructed, and leached with produced water until the least sorbed components appear in the effluent above regulatory levels. At this point the column will be drained and sparged with air to strip the volatile components. The composition of the stripping gas will be monitored to track the progress of the regeneration. Based upon results from our current DOE-sponsored project, which had focused on waters containing only BTEX, the air stripping will restore most of the SMZ sorption capacity. The loading/stripping procedure will be performed repeatedly to determine the longevity of the SMZ for removing the most volatile compounds. Two possibilities are envisioned:

1. The SMZ gradually loses sorption capacity due to buildup of lower-volatility components. This is the situation frequently encountered with activated carbon

sorbents. In this case, a more aggressive stripping procedure will be developed to remove this tightly bound material.

2. The sorption capacity of the SMZ for volatile components will gradually *increase*, as the bound heavier fractions provide additional bound organic carbon into which the volatiles can partition. In this case the inter-regeneration period will gradually lengthen. Eventually, however, the heavy components will build up to such an extent that column permeability will suffer, and a more aggressive regeneration procedure will be required, as described under Subtask 2.2.

Subtask 2.2. Regeneration for Non-volatile Components. Some of the produced water organics will be nonvolatile, or have such low volatility that air stripping times and volumes would be too large to be practical. At this point it may be most cost-effective to replace the SMZ column and incinerate or otherwise dispose of the spent SMZ. However, we will test several methods for removing the bound fractions to prolong the life of the SMZ packed bed. One method will be solvent extraction with an aqueous cosolvent such as methanol, which should remove much of the bound material. Another approach, ultimately less expensive, will be extraction with high pH (ca. 12) sodium carbonate solution. Earlier work on regeneration of bound inorganic anions such as chromate showed that sodium carbonate fully regenerated spent SMZ (Li and Bowman, 2001). SMZ effectively sorbs organic anions such as phenolics (Li et al., 2000), which we expect can also be removed by the carbonate procedure. The carbonate treatment should be able to strip sorbed organic acids present in the produced water. Along with solubilization, the high pH solution will hydrolyze the more labile organic species.

We will initially test the carbonate regeneration by removing spent SMZ from the columns and evaluating the extraction efficiency in batch tests. Once the parameters for carbonate regeneration have been defined, we will return to the column system for Subtask 2.3.

Subtask 2.3. Combined Regeneration for All Components. In this subtask we will rinse the columns with the optimized regeneration solution of Subtask 2.2 after the appropriate number of saturation/air-stripping cycles. The composition of the spent regeneration solution will be determined to the extent possible, although it is likely to be a complex mixture including breakdown products. The air-stripping/regeneration solution sequence will be repeated to determine the ultimate useful life of the SMZ. The regeneration solution will be a concentrated organic waste that will require offsite disposal or incineration. The volume of this solution will be miniscule, however, in comparison to the volume of produced water treated.

A technical report will provide a detailed summary of produced water analytical methods, results of the batch sorption and column loading experiments and recommendations for regeneration.

1.2 Phase 2. Optimize VPB for the Treatment of Waste Gases Expected from SMZ Regeneration (Lab-Scale)

(Lead PIs: Dr. Lynn Katz and Dr. Kinney at UT Austin)

In this project phase, the VPB system will be optimized to treat the waste gas stream expected from the SMZ regeneration process. Pollutant degradation efficiencies as a function of key operating parameters will be assessed in existing laboratory-scale (20L) bioreactors. Operating parameters that will be assessed for their effect on pollutant removal will include inoculation culture selection (Subtask 1.1), nutrient supply rate, pollutant loading rate, gas phase residence times as well as packing media selection. Pollutant removal profiles as well as carbon dioxide and biomass production rates across the VPB will be monitored to assess the performance and stability of the system.

Just as the composition of produced water varies greatly, the composition and concentration of the pollutants generated in the SMZ regeneration step are expected to vary widely. In Subtask 1.2, the effect that waste gas composition has on VPB performance will be evaluated. As noted earlier, microorganisms in VPBs may

preferentially degrade one pollutant over another or the presence of one pollutant may inhibit the degradation of another pollutant. To assess these effects, it is important to systematically vary the composition and relative concentration of the key pollutants expected in the mixture to determine the limits of the system and to ascertain what pollutant(s) control the overall removal in the VPB.

Subtask 1.1 Inoculation Culture Development. VPB performance is greatly enhanced by inoculating the VPB prior to startup with a mixed microbial culture that has been pre-acclimated to the pollutants of interest. For this reason, several hydrocarbon-degrading microbial cultures that have already been developed will be evaluated in a series of batch kinetic tests to determine which provides the most rapid (and complete) degradation of the volatile organic compounds expected in the SMZ regeneration step. In addition, microbial samples will be collected from our field site and used to supplement existing cultures as needed to enhance performance.

Subtask 1.2 Evaluate Effect of Hydrocarbon Mixtures on VPB Performance. The effect of hydrocarbon mixtures on VPB performance will be evaluated by examining the pollutant removals obtained during single VOC-feed experiments and comparing these results to those obtained when the complete mixture is present. These studies will be conducted first with a simple BTEX mixture and then with a more complex waste gas stream that better represents the full suite of the VOCs expected during the SMZ regeneration step. In this way, the pollutants that are the most difficult to remove in the VPB will be identified so that they can be considered in the final design.

Task 2.0 Periodic Operation Assessment

It is expected that some facilities will generate produced water in a discontinuous fashion. To address this possibility, a series of laboratory scale experiments will be conducted to optimize a slip feed system developed by Dr. Kinney to maintain VPB performance during periodic operation. Shutdown periods ranging from hours to days

will be evaluated and a the mass flow rate and composition of the slip feed stream needed to maintain biomass activity in the VPB will be determined.

2. Experimental

2.1 SMZ Column Reactors

2.1.1 SMZ Preparation

The zeolite used in this study was a natural clinoptilolite-rich tuff obtained from the St. Cloud mine near Winston, NM. The mineral composition was 74% clinoptilolite, 5% smectite, 10% quartz/cristobalite, 10% feldspar, and 1% illite. The zeolite had an external surface area of 15.7 m²/g. The internal cation exchange capacity was 800 meq/kg and the external cation exchange capacity was 90-110 meq/kg (Bowman et al. 2000). The zeolite was crushed and sieved to two different grain sizes: 1.4 to 0.4 mm (14-40 mesh) for the field test and 0.18 to 0.15 mm (80-100 mesh) for the laboratory batch and column experiments.

The SMZ used in the laboratory experiments was produced by treating 1000 g of zeolite with 3000 mL of a 0.10 M HDTMA-Cl (Aldrich, Milwaukee, WI) solution and shaking for 24 h. The HDTMA-zeolite was rinsed with two 180 mL aliquots of Type I water (purified with Milli-Q system, Millipore Corp., Bedford, MA) and air-dried. The final HDTMA loading was 157 mmol HDTMA/kg zeolite. The SMZ for the field test, bulk produced at the St. Cloud mine and described by Bowman et al. (2001), had an HDTMA loading of 180 mmol HDTMA/kg zeolite.

2.1.2 Produced Water

The site selected for the field test was a produced water treatment facility operated by Crystal Solutions, LLC. The facility is located near Wamsutter, Wyoming, where a large natural gas reservoir exists. Produced water from the region is delivered to the facility by tanker truck, where it is unloaded into an oil/water separation tank. Overflow from this tank is transferred into a second separation tank. From the second tank, oil is sent into an oil condensate tank for later processing, while water flows into a lined separation pond and is then pumped through a series of lined evaporation ponds.

Produced water for use in the laboratory studies was collected from the separation tanks at this site in December 2002 and stored in sealed 208 L drums. The composition of this water is shown in Table 1.

Table 1. Produced Water Composition

Organic Compound	Concentration (mg/L)
Benzene	20,000
Toluene	35,000
Ethylbenzene	25,000
o-Xylene	5000
m-Xylene	5000
p-Xylene	5000
phenol	1000
2-methylphenol	1000
4-methylphenol	1000
2,4-dimethylphenol	500
naphthalene	250
2-methylnaphthalene	500

2.1.3 BTEX Sorption/Regeneration in Laboratory Columns

Laboratory columns were scaled based upon a proposed field treatment design using the rapid small-scale column test method, developed for sorption of organic compounds onto granular activated carbon (Crittenden et al. 1986). The scaling method is based on the Dispersed Flow Pore and Surface Diffusion Model (DFPSDM) and incorporates advective flow, axial dispersion and diffusion, liquid phase mass transfer resistance, local adsorption equilibrium at the exterior surface of the adsorbent, surface diffusion, pore diffusion, and competitive equilibrium of solutes on the surface (Crittenden et al. 1986). For perfect similitude between small-scale and large-scale systems, dimensionless parameters contained in the DFPSDM must be equal in both systems, and the scaling law is defined as:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{SC}}{d_{LC}} \right]^2 \quad (1)$$

where: SC = small column

LC = large column

$EBCT$ = empty bed contact time (bed volume/volumetric flow rate)

d = particle diameter

Table 2 contains the parameters from the proposed field treatment design that were used in Eq. 1 to determine the volumetric flow rate in the laboratory column. The EBCT ratio is 0.0330 and the square of the particle diameter ratio is 0.0332. SMZ particle size in the laboratory column was chosen to be close to the minimum requirement of a 50-to-1 column diameter-to-particle size ratio to avoid channeling (Crittenden et al. 1991).

Table 2. Dimensions and operating parameters for field and laboratory columns.

	Field Column	Laboratory Column
Column radius (mm)	178	4.0
Column length (mm)	1220	100
Bed volume (L)	102	$5.03 * 10^{-3}$
Ave. SMZ particle size (mm)	0.90	0.164
Volumetric flow rate (L/min)	1.67	$2.92 * 10^{-3}$
EBCT (min)	52.3	1.74

Four glass columns (Ace Glass, Vineland, NJ) with a 4 mm radius and 100 mm length (Table 2) were packed with 80-100 mesh SMZ. Precision made PTFE end-fittings were designed for use with these columns and provided a leak-tight seal. Four-way valves (Cole-Parmer, Vernon Hills, IL) were connected to the end-fittings with Luer fittings. These valves served as sampling ports and could seal the columns shut between experiments. Once packed, the columns were purged with CO₂ for 24 hours to displace air in the columns. They were then saturated from the bottom with an organic-free synthetic brine (3110 mg/L HCO₃⁻, 4400 mg/L Cl⁻, 4020 mg/L Na⁺) which approximated the inorganic composition of the produced water (Table 1). The brine was injected with 10-mL gastight syringes (Hamilton, Reno, NV) loaded in a syringe pump (Harvard Apparatus, Holliston, MA) at an average flow rate of $2.3 * 10^{-3}$ L/min (approximately 70 mm/min). These flow conditions were maintained for the duration of the experiments.

The columns were assumed to be at steady state when no gas bubbles were visible and the water-filled column weights remained constant.

A 2 pore-volume (PV) slug of tritiated water tracer (tritium) was injected into each column to determine the flow velocity and column dispersion coefficient. Effluent samples were collected every 0.2 PV in 7 mL vials. One-half milliliter of effluent solution was combined with 4.5 mL of scintillation cocktail solution (ICN Biomedicals, Inc., Irvine, CA) for analysis with an LS6500 liquid scintillation counter (Beckman Coulter, Inc., Fullerton, CA).

Produced water for the column experiments was transferred to a collapsible 30 L Tedlar® Gas Sampling Bag (Alltech Associates, Inc., Deerfield, IL) with a barbed on/off valve for injection into the columns. The water in the bag was spiked with additional ethylbenzene and o-xylene (Aldrich, Milwaukee, WI) to yield concentrations of approximately 15 mg/L, similar to the benzene concentration. The produced water was continuously injected into the columns until an air-sparging cycle was begun (see below). To remove iron oxide precipitates from the influent water, 0.45 μm and 0.2 μm nylon syringe-tip filters (Supelco, Bellefonte, PA) were added in series to the influent tubing just upstream of the columns. Using the four-way valves, influent and effluent samples were collected in 10-mL gastight syringes and sealed in 10-mL glass headspace vials with Teflon-faced butyl septa (Supelco) for subsequent analysis via gas chromatography. The columns were sampled at 3 PV intervals for the first 20 PV of effluent, 15 PV intervals for the next 60 PV of effluent, and 50 PV intervals for the remaining effluent. Flow was terminated when the effluent BTEX concentrations were approximately equal to influent concentrations (after 450-500 PV).

The spent SMZ was regenerated by air-sparging. A compressed air tank and 65-mm single-float flow controller (Cole-Parmer) were attached to the effluent end of the columns, reversing the flow direction from the water injection stage. A soap-film flow meter (Hewlett-Packard, Palo Alto, CA) was attached to the exhaust end. No water was removed during gravity drainage prior to air-sparging, but most retained water was removed during the first minute of sparging. The compressed air tank regulator was set to 30 psi and the flow controller was used to control air flow rate through the columns. Flow rate was set at 20 mL/min (6 PV/min). Using a 1.0-mL gastight syringe, samples

were collected by withdrawing 0.2 mL from the effluent gas stream and analyzed immediately by direct injection into the gas chromatograph. Air-sparging continued until the concentration of each BTEX compound in the effluent gas stream was reduced to 2% or less of its initial concentration observed during regeneration (approximately 3500 PV of air).

The regenerated SMZ was again saturated with produced water under the same conditions as the original saturation, except the columns were not purged with CO₂ or leached with organic-free brine prior to produced water injection. This cycle of produced water injection/regeneration was repeated for a total of ten repetitions in two duplicate columns (columns 10A and 10B), while the injection/regeneration cycle was repeated for a total of five repetitions in two other duplicate columns (columns 5A and 5B). Columns 5A and 5B were operated simultaneously with columns 10A and 10B. Influent and effluent samples were not collected for columns 5A and 5B, which were used for batch sorption studies (see below).

2.1.4 Sorption Characteristics of Virgin and Regenerated SMZ

Sorption isotherms were prepared using virgin SMZ (no exposure to produced water), SMZ from columns 5A/5B (SMZ from both columns was combined), and SMZ from columns 10A/10B (combined). Batch experiments were performed using produced water. In order to achieve desired initial BTEX concentrations, the produced water was placed in uncovered beakers for several hours to allow BTEX volatilization, and then spiked with the desired levels of BTEX. Initial concentrations were 3, 6, 9, 12, and 15 mg/L for benzene, ethylbenzene, p-&m-xylene combined, and o-xylene. Initial concentrations of toluene were 6, 12, 18, 24, and 30 mg/L. These values were chosen so that the maximum concentration of each compound was similar to the influent concentration during the column experiments. Three milliliters of produced water and 0.75 g of SMZ were combined in 10-mL headspace vials (in duplicate) and shaken for 24 hours at 25°C, conditions which have been previously shown sufficient to attain sorption equilibrium (Neel and Bowman 1992). Each sample was centrifuged at 900 × g for 20 min, and 1 mL of the supernatant transferred to a 10-ml headspace vial containing 2 mL Type I water for gas chromatography analysis. To monitor volatilization losses, two sets

of duplicate blank samples containing produced water at each initial BTEX concentration but no SMZ were prepared, shaken, and centrifuged. One set of blank samples was analyzed without transferring the water to a separate vial, and the other set of blank samples was analyzed after transferring 1 mL of water to a separate vial containing 2 mL Type I water, following the same procedure as the samples containing SMZ. The two sets of blank samples allowed determination of volatilization losses during the shaking/centrifugation processes, and during the transfer of supernatant to a vial for analysis.

2.1.5 Field Test of a Prototype SMZ Treatment System

The field treatment system was conducted prior to the start of this project; however, results from this project will be compared to the field data. As a result, a description of the field test is described here. The treatment system consisted of a fiberglass column designed for use in ion exchange systems with SMZ substituted for the ion exchange resin. The column design dispersed the influent stream at the top of the SMZ and collected the effluent via a perforated plate and tube at the bottom. The column dimensions are given in Table 2. The system was filled to the top with 87.1 kg of 14-40 mesh SMZ.

The field column was connected to the second separation tank at the Crystal Solutions facility on a 102-mm diameter valve located about 610 mm from the bottom of the tank. Flow through the SMZ system was driven by approximately 4.5 m of produced water head in the tank. A flow meter was installed at the influent end of the column, and sampling valves were installed at the influent and effluent ends.

Influent and effluent water samples were collected using 10-mL gastight syringes and stored in 10-mL glass headspace vials sealed with Teflon-faced butyl septa for later analysis via gas chromatography. A portable photoionization detector (MiniRAE 2000 PID, RAE Systems, Sunnyvale, CA) was used to estimate total concentrations of volatiles in water and air during produced water treatment and SMZ regeneration. Air samples were collected during regeneration by affixing Tygon® tubing to the effluent end of the column and filling 10-mL glass headspace vials with the effluent gas stream until all the

original air in the vial had been displaced. Each vial was quickly closed and sealed with a Teflon-faced butyl septum.

Produced water was passed through the SMZ system for about 46 hours. The flow rate began at 85 L/hr (1.6 PV/hr), increased to 108 L/hr (2.1 PV/hr), then dropped to 66 L/hr (1.3 PV/hr) at the end of the run. This drop in flow rate was caused by clogging of the SMZ pores inside the column by particles in the unfiltered water.

Regeneration was performed in the field by attaching a portable air compressor to the influent port on the column. Air-sparging was performed for 8.5 hours at air flow rates between 85 and 100 L/min (1.6 to 1.9 PV/min). Following regeneration, another sorption cycle was performed by passing produced water through the system for an additional 47 hours. The flow rate ranged from 91 L/hr (1.7 PV/hr) at the beginning of the run to 62 L/hr (1.2 PV/hr) at the end.

2.1.6 Analytical Methods

Aqueous BTEX concentrations from the laboratory column and batch experiments were measured using a Hewlett-Packard (HP) Model 7694 headspace sampler attached to a HP Model 5890A gas chromatograph (GC) with a 10-m, 0.53-mm I.D. HP-5 capillary column and flame ionization detector. The carrier gas (He) had a flow rate of 35 mL/min and the split gas (He) flow rate was 28 mL/min. No makeup gas was utilized. The analyses were performed isothermally at 55°C, with an injector temperature of 210°C and detector temperature of 240°C. The GC was calibrated during each run with five BTEX standards of varying concentrations over a linear response range from 0.5 mg/L to 40 mg/L. *p*-xylene and *m*-xylene were not resolved by this method and were treated as a single compound. For headspace analysis, a 3-mL aqueous sample was sealed in a 10-mL headspace vial fitted with a Teflon-faced butyl septum. The headspace sampler run conditions were as follows: Oven temperature 70°C, loop temperature 75°C, transfer line temperature 75°C, equilibration time 1.0 min, pressurization time 1.0 min, loop fill time 1.0 min, loop equilibration time 0.5 min, injection time 0.09 min.

The BTEX concentrations in gas samples from both lab and field air-sparging were analyzed by direct injection into the HP 5890A GC. Calibration standards in Milli-

Q water were prepared in 10-mL headspace vials fitted with Teflon face butyl septum. Based on the Henry's constants and the known aqueous concentration, the BTEX mass removed from the headspace and injected into the GC was calculated. All GC operating conditions were the same as above, with the split flow increased to 63 mL/min.

Aqueous BTEX concentrations in samples from the field columns were measured using a Tekmar 7000 headspace sampler attached to a HP Model 5890 gas chromatograph with a 30-m, 0.53-mm I.D. Restek capillary column (RTX-624) and flame ionization detector. The carrier gas (He) had a flow rate of 36 mL/min and nitrogen was added as a makeup gas. No split flow was utilized. The analyses were performed with an initial temperature of 40°C for 1 minute, followed by a 20°C/min ramp to 85°C, and then increased at 0.5°C/min to a final temperature of 90°C held for 1 minute. The injector temperature was 250°C and detector temperature was 275°C. The GC was calibrated during each run with eleven BTEX standards of varying concentrations over a linear response range up to 1.5 mg/L of each BTEX compound. *p*-xylene and *m*-xylene were not resolved by this method and were treated as a single compound. For headspace analysis, a 50-μL sample was diluted with 5 mL of Milli-Q water and sealed in a 22-mL headspace vial fitted with a Teflon-faced butyl septum. The headspace sampler run conditions were as follows: Oven temperature 80°C, loop temperature 170°C, transfer line temperature 170°C, equilibration time 15.0 min, mixing time 10.0 min, pressurization time 1.0 min, pressure equilibration time 0.25 min, loop fill time 1.0 min, loop equilibration time 0.25 min, injection time 1.0 min.

2.2 Vapor Phase Bioreactors

The experimental vapor phase bioreactors for this project have been designed and are currently being assembled to treat the off-gas from the SMZ regeneration process. The bioreactor design selected for this project is a hybrid system that combines features of both biotrickling filters and biofilters. Similar to a biotrickling filter, the experimental bioreactor will be packed with a synthetic media and nutrients such as nitrogen will be supplied externally via a liquid spray system. However, the nutrients will be sprayed over the bed for only 30 minutes per day instead of continuously as occurs in biotrickling

filters. This periodic nutrient supply will minimize the liquid film on the packing material since excess water can hinder the mass transfer and ultimately the removal rate of relatively hydrophobic hydrocarbon pollutants. This design also allows easier control over bioreactor conditions and enables adjustments such as increased nitrogen supply or pH control to be accomplished easily. The experimental bioreactor is also similar to classical biofilters since the liquid phase will be essentially immobile throughout most of the bioreactor operation.

The experimental bioreactor column (I.D. 16 cm) consists of three individual sections bolted together (Figure 1). Each section will be packed with polyurethane foam cubes (1.5 cm) to a height of approximately 19 cm. Polyurethane foam is attractive for this application since it has a relatively high surface area, is light weight and can be compressed to remove excess biomass. A 2 cm plenum located between each packed section will allow for gas sampling and redistribution of the contaminant stream between sections. This design has been used successfully in previous experiments to treat VOC mixtures containing both hydrophobic and hydrophilic constituents.

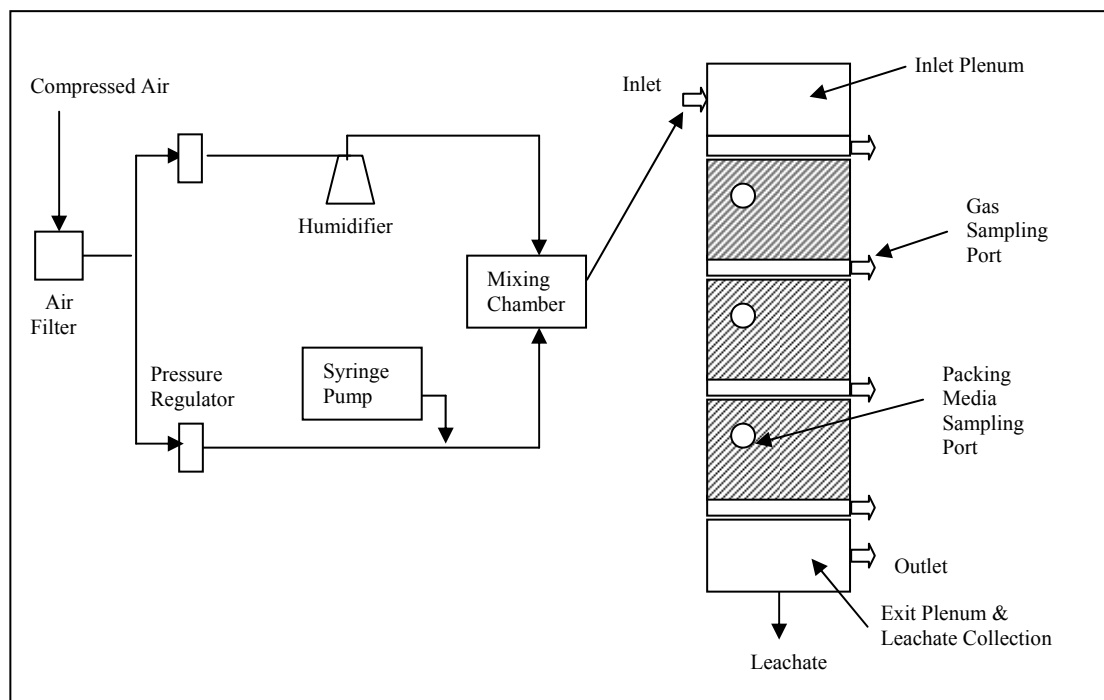


Figure 1. Schematic diagram of experimental vapor phase biofilter design

3. Results and Discussion

During the first twelve months of this project, we focused on work in Phases 1 and 2 of this project as described in section 1. Results for each task as outlined in section 1 are discussed below.

3.1 Phase 1. Optimize SMZ Regeneration Process

Task 1.0 Determine SMZ Sorption Characteristics for Volatile and Non-Volatile Components of Produced Waters

Subtask 1.1 Determination of Produced Water Composition. We have characterized the produced water composition (from the Wyoming test site) for organic compounds and their concentrations as part of the effort in Phase 1 (Table 1). The analytical results showed that in addition to the BTEX compounds, phenol and naphthalene compounds provided significant contributions to the organic content. These results will be employed to select the synthetic water for VPB and regeneration studies.

Subtask 1.2 Characterization of Organics Sorption in SMZ Batch Reactors. Sorption capacity for BTEX compounds onto SMZ had previously been determined using virgin SMZ under a range of conditions. In this project, we compared BTEX sorption onto SMZ as a function of regeneration cycle. The batch sorption study performed on virgin SMZ, SMZ that had experienced 5 sorption/regeneration cycles, and SMZ that had undergone 10 sorption/regeneration cycles confirmed that the SMZ had not lost any sorption capacity for benzene sorption after 5 and 10 cycles.

Batch experiments of BTEX on SMZ were also conducted with saline water, phenol, or naphthalenes, compounds that will be added as part of the synthetic produced water fed to the biofilters. Figure 2 shows BTEX isotherms in 10,000ppm salt water with all initial BTEX, phenol, and naphthalenes concentrations equal (0 to 75,000 ug/L). With the exception of benzene, all other isotherms had greater slopes than those in 10,000 ppm salt water with no phenol or naphthalenes. All of the isotherms, however, had lower

slopes than those prepared in 100,000 ppm salt water with no phenol or naphthalenes. A ten-fold increase in salt caused greater BTEX sorption than the presence of the other organic chemicals.

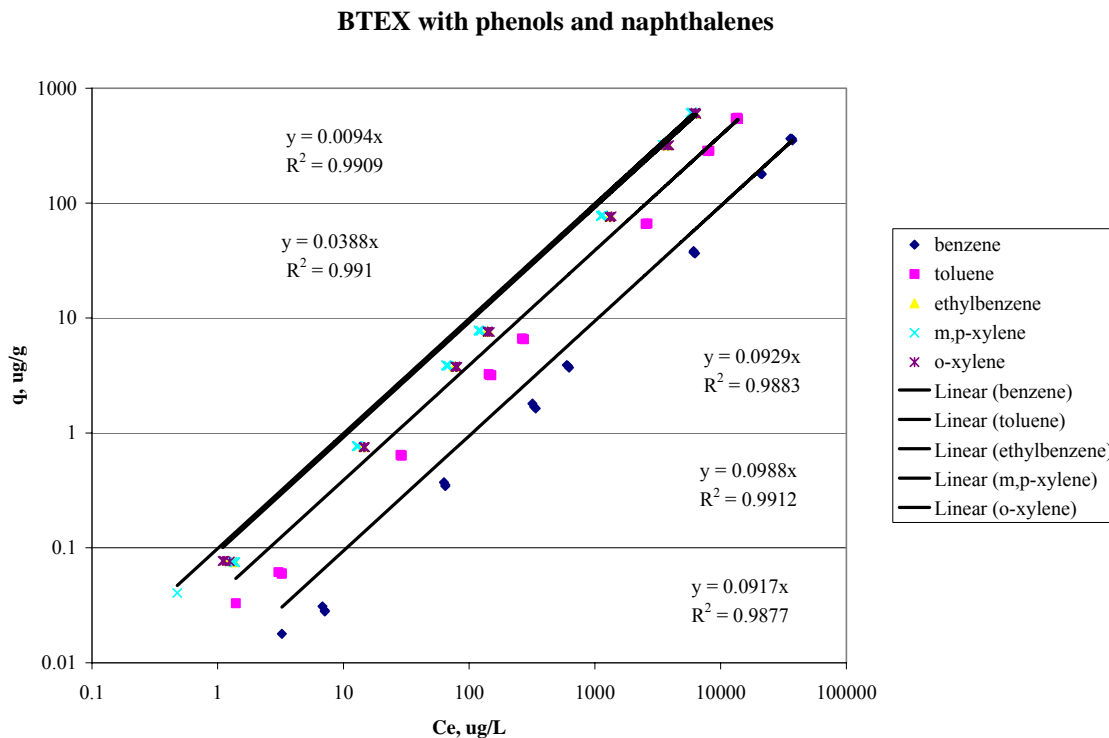


Figure 2. BTEX Isotherms in Synthetic Produced Water

Subtask 1.3 Characterization of Organics Retention Capacity in SMZ Column Reactors. The results from our column study show that benzene breakthrough occurs first because of its high solubility in water and low octanol-water partition coefficient K_{ow} , while the other compounds elute in order of increasing K_{ow} . The breakthrough curves (BTCs) of ethylbenzene and xylenes are similar due to their similar K_{ow} . Benzene begins to elute from the column after approximately 8 PV of produced water have been injected, while the xylenes and ethylbenzene do not rise above initial effluent concentrations until after 50 PV of water have been injected. The BTCs for each BTEX compound changed little over these 10 cycles, indicating little reduction in the sorption capacity of SMZ upon repeated saturation and air-stripping.

Using a regression coefficient significance test (Edwards 1984), the K_d values for benzene and toluene showed no statistically significant trends throughout the first nine sorption/regeneration cycles, while there was a decreasing trend in K_d for ethylbenzene and xylenes. The average decrease in K_d for ethylbenzene and the xylenes was approximately 2.7 L/kg per sorption cycle in Column 10a and 7.2 L/kg per sorption cycle in Column 10b. T-tests showed that the mean K_d values for each BTEX compound were statistically equivalent (95% confidence level) between replicate columns 10A and 10B throughout the first nine sorption cycles.

Task 2.0 Optimize Regeneration Schemes for All Produced Water Components

Subtask 2.1. Regeneration for Volatile Components. Experiments were conducted over ten sorption/regeneration cycles in laboratory scale. Data was collected for both BTEX sorption (discussed above) and air stripping. The sorption data was modeled using a bicontinuum advection/dispersion/retardation model.

BTEX Sorption in Laboratory Columns

Tritium breakthrough curves were developed to characterize the hydrodynamics of the columns. The tritium BTCs for the columns were well described by the simple 1-dimensional advection-dispersion equation:

$$R \frac{\partial C^*}{\partial p} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (2)$$

where:

$$C^* = \frac{C}{C_0} \quad (3)$$

$$P = \frac{vL}{D} \quad (4)$$

$$R = 1 + \left(\frac{\rho}{\theta} \right) K_d \quad (5)$$

$$p = \frac{vt}{L} \quad (6)$$

$$X = \frac{x}{L} \quad (7)$$

and C is the effluent solute concentration (M/L^3), C_0 is the influent solute concentration (M/L^3), C^* is the dimensionless solute concentration, D is the dispersion coefficient (L^2/T), v is the pore-water velocity (L/T), x is the distance (L), L is the column length (L), p is dimensionless time (pore volumes), ρ is bulk density (M/L^3), θ is volumetric water content, K_d is the linear equilibrium sorption constant (L^3/M), P is the Peclet number, and R is the retardation factor.

Equation 2 was fitted to the observed tritium data using the nonlinear least-squares optimization program CXTFIT 2.1 under flux-type boundary conditions (Toride et al. 1999). The pore-water velocity v was treated as a fixed value and R and D were fitted. All four columns yielded similar tritium BTCs with symmetrical shapes and R values in the range 0.955 to 1.13. The BTC for column 10A is shown in Figure 3. A dip in C^* was observed at about 2 PV for all columns, corresponding to the time at which flow through the columns was interrupted to change the influent from tritiated to non-tritiated brine.

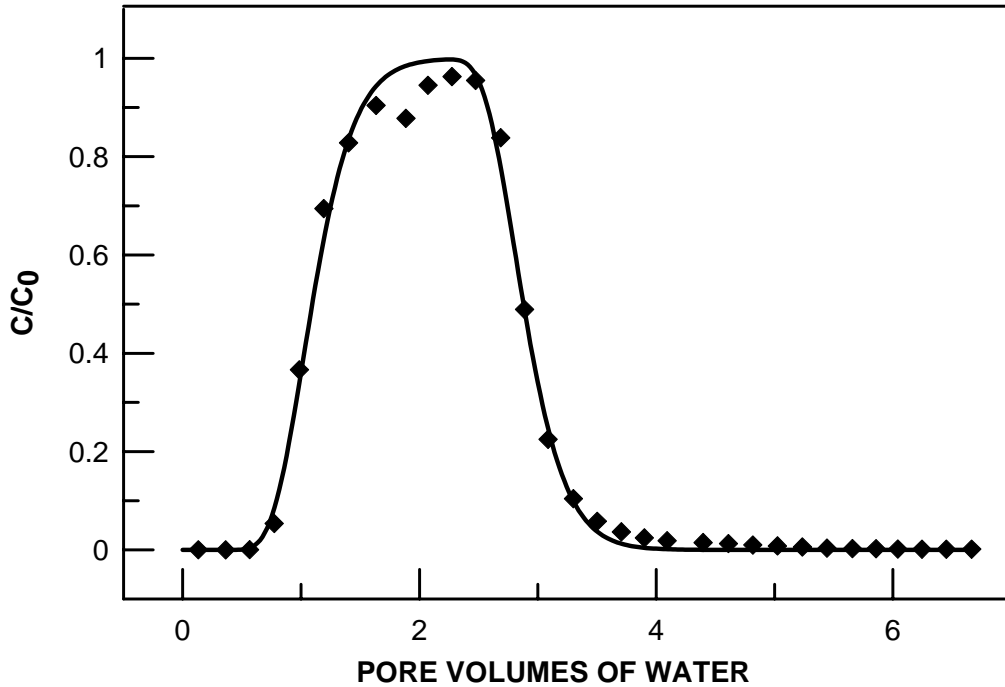


Figure 3. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 10A

Figure 4 shows the results of BTEX breakthrough on virgin SMZ in column 1. The equilibrium one-dimensional advection-dispersion equation (Eq. 2) did not adequately fit the observed data, so sorption of BTEX in the column experiments was analyzed with a bicontinuum model.

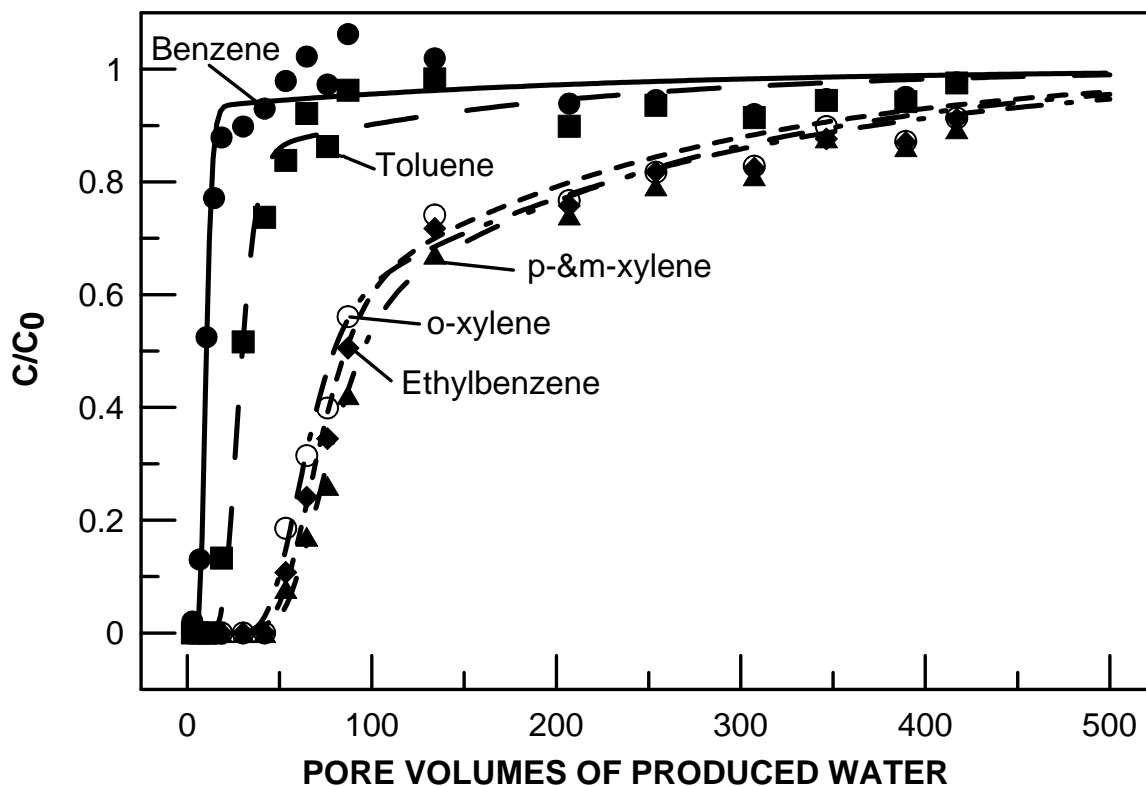


Figure 4. Observed and fitted BTEX breakthrough curves on virgin SMZ (Column 10A). The lines were based on the best fit of Eq. 10 to the observed data, as described in the text.

The bicontinuum model can be used to describe both physical and chemical nonequilibrium. Because the tritium BTCs did not exhibit early breakthrough or significant tailing, physical nonequilibrium was likely not significant and the processes causing nonequilibrium behavior in the BTEX BTCs are probably related to sorption nonequilibrium (Brusseau and Rao 1989). The mechanisms behind slow sorption are not fully understood, but it is often attributed to diffusion control (Pignatello and Xing 1996).

We assume slow sorption involves diffusion of BTEX within the hydrophobic region created by the surfactant molecules on the surface of SMZ. Under the first-order mass transfer model described by Brusseau et al. (1991), sorption occurs in two regions characterized by either instantaneous or rate-limited sorption:

$$S_1 = FK_d C \quad (8)$$

$$\frac{dS_2}{dt} = k_f S_1 - k_r S_2 \quad (9)$$

where S_1 is the sorbed concentration (M/M) in the instantaneous sorption region, S_2 is the sorbed concentration (M/M) in the rate-limited sorption region, F is the fraction of instantaneous sorption sites, t is time, and k_f and k_r are forward and reverse first-order rate constants (1/T), respectively.

The 1-dimensional advective-dispersive transport equation accounting for kinetically limited sorption and assuming steady-state water flow and a homogeneous porous medium, leads to the following equations (Brusseau et al. 1991):

$$\frac{\partial C^*}{\partial p} + (\beta R - 1) \frac{\partial C^*}{\partial p} + (1 - \beta) R \frac{\partial S^*}{\partial p} = (1/P) \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (10)$$

$$(1 - \beta) R \frac{\partial S^*}{\partial p} = \omega (C^* - S^*) \quad (11)$$

where:

$$S^* = \frac{S_2}{(1 - F)} K_d \quad (12)$$

$$\beta = \frac{\left[1 + F \left(\frac{\rho}{\theta} \right) K_d \right]}{R} \quad (13)$$

$$\omega = \frac{k_2 (1 - \beta) R L}{v} \quad (14)$$

S^* is the dimensionless sorbed concentration in the rate-limited domain, ω is the Damkohler number, the ratio of characteristic sorption time to hydrodynamic residence time.

The solution to Eqs. 10 and 11 requires estimation of four parameters (P , R , ω , and β). The value of P was determined from the tritium BTCs using Eq. 4. The value for R was determined from Eq. 5 by estimating K_d directly from the BTEX breakthrough

curves, using the areas between the influent and effluent BTEX concentrations to determine S ($S=S_1+S_2$). The parameter S was then related to K_d by Eq. 8 assuming equilibrium had been reached and $F=1$. Benzene and toluene had reached equilibrium and the actual value of C was used in Eq. 8 for these compounds. For ethylbenzene and the xylenes, which had not reached equilibrium by the end of each sorption cycle, we used the average of the final values of C and C_0 as a measure of C . The other two sorption parameters, ω and β , were optimized by fitting Eq. 10 to the experimental data with CXTFIT 2.1.

As shown in Figure 4, benzene breakthrough occurs first because of its high solubility in water and low octanol-water partition coefficient K_{ow} (Table 1), while the other compounds elute in order of increasing K_{ow} . The BTCs of ethylbenzene and xylenes are similar due to their similar K_{ow} values (Table 1). Benzene begins to elute from the column after approximately 8 PV of produced water have been injected, while the xylenes and ethylbenzene do not rise above initial effluent concentrations until after 50 PV of water have been injected.

Reproducibility between the BTCs for replicate columns was good. Figures 5a and 5b show the BTCs for benzene and p-&m-xylene during the first and fifth sorption cycles in duplicate columns.

Figures 6a and 6b show the breakthrough of benzene and p-&m-xylene, respectively, in Column 10A over 10 sorption/regeneration cycles. The BTCs for each BTEX compound changed little over these 10 cycles, indicating little reduction in the sorption capacity of SMZ upon repeated saturation and air-stripping. In fact, the BTC during the first injection shows the earliest breakthrough (least sorption and retardation) for each compound. The removal efficiency may have increased because of the retention of low volatility components in produced water during regeneration which could create an additional sorption medium for the partitioning of BTEX (Jaynes and Vance 1996). During these 10 cycles, approximately 4500 PV of water passed through each column.

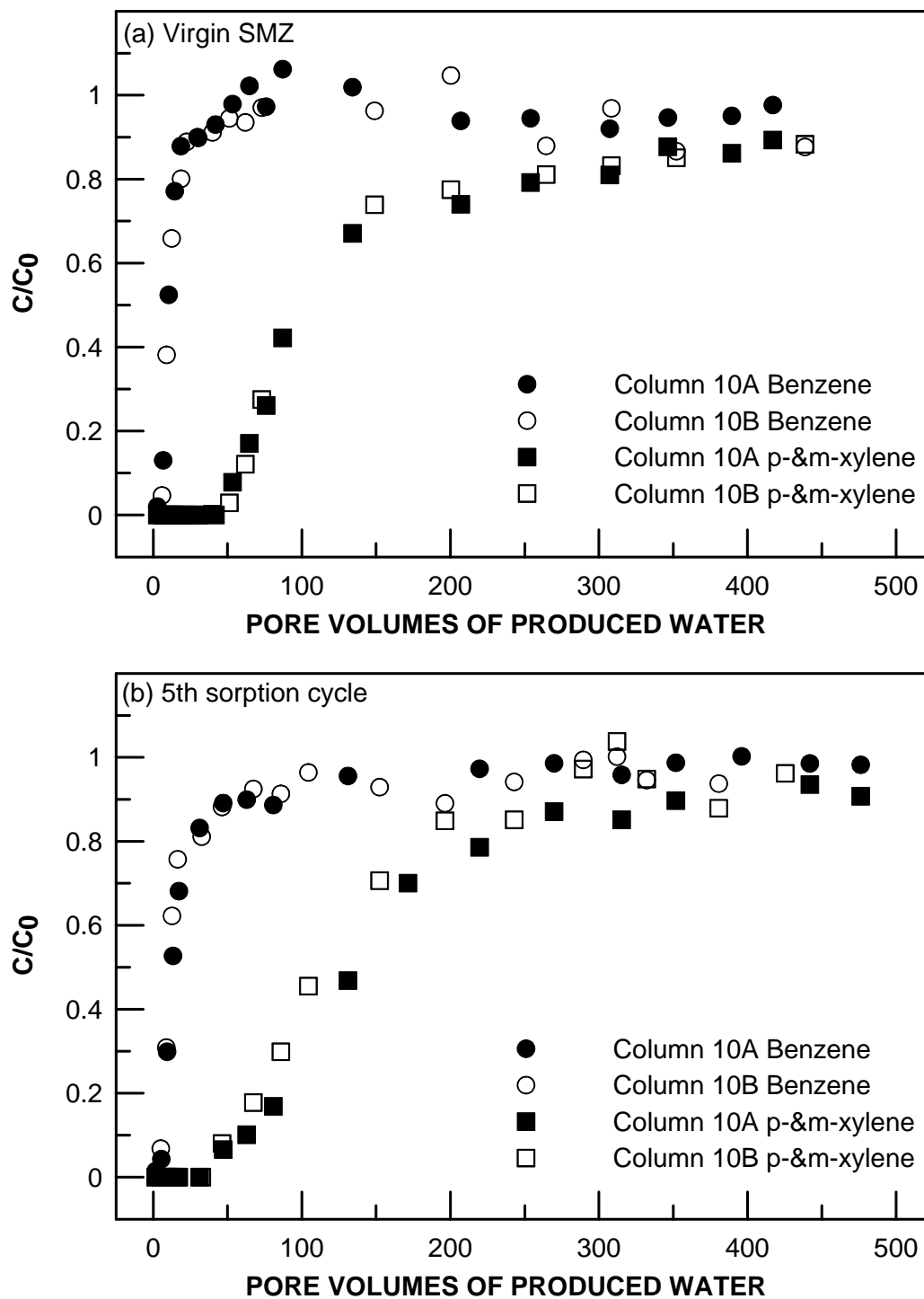


Figure 5. BTCs of benzene and p-&m-xylene in Columns 10A and 10B for (a) virgin SMZ and (b) during the fifth sorption cycle in columns 10A and 10B

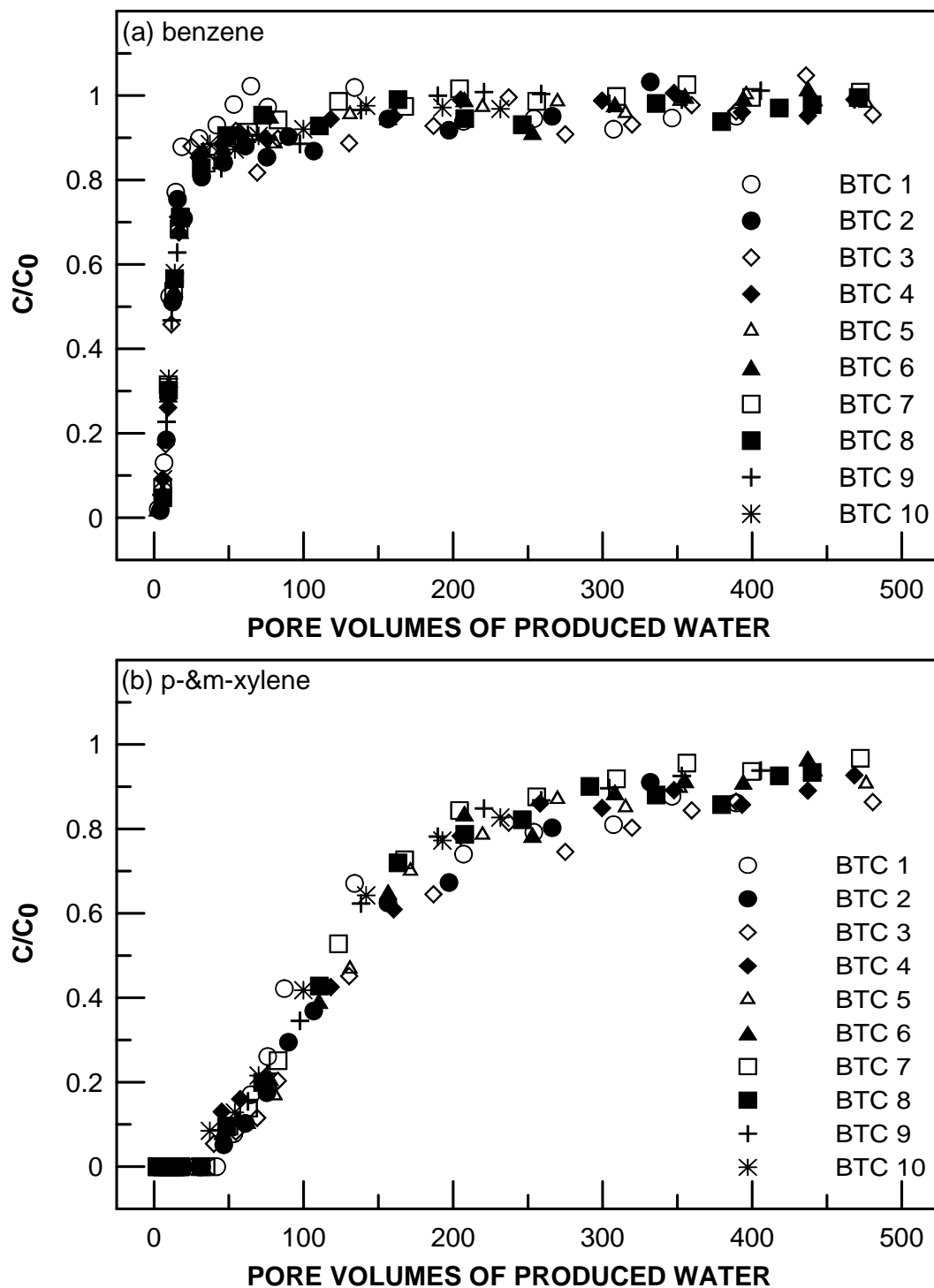


Figure 6. (a) Benzene BTCs for Column 10A over 10 sorption/regeneration cycles and (b) p-&m-xylene BTCs for Column 10A over 10 sorption/regeneration cycles

With repeated sorption cycles, backpressures increased in each column. This was investigated after completion of the ten sorption/regeneration cycles by examining virgin SMZ and SMZ from Columns 10A/10B and 5A/5B with a scanning electron microscope (SEM). The SEM results showed that the SMZ particles were breaking apart, creating finer particles which reduced column permeability and increased backpressure. Many particles from Columns 10A/10B were 10% of the size of the virgin SMZ grains. The cause of the particle breakdown is not understood and could be either mechanical or chemical in origin. With no significant reduction in sorption capacity after 10 sorption/regeneration cycles, the breakdown of SMZ particles and subsequent increase in column backpressure may play the largest role in determining the lifetime of SMZ in a produced-water treatment system.

Results from Regeneration via Air-Sparging

In addition to examining BTEX concentrations in the effluent during the sorption phase of each cycle, samples of off-gas were analyzed during the regeneration phase. The mass of BTEX removed from Column 10A by air-sparging after the first injection of BTEX is shown in Figure 7. The compounds with the highest aqueous solubility were the most readily removed. Air-sparging effectively stripped approximately 100% of the benzene from the columns, 90% of the toluene, and 75% of the lowest solubility BTEX compounds (only p-&m-xylene shown). Air-sparging results throughout the remaining nine regeneration cycles showed similar patterns as in Figure 7. Duplicate columns showed comparable sparging results.

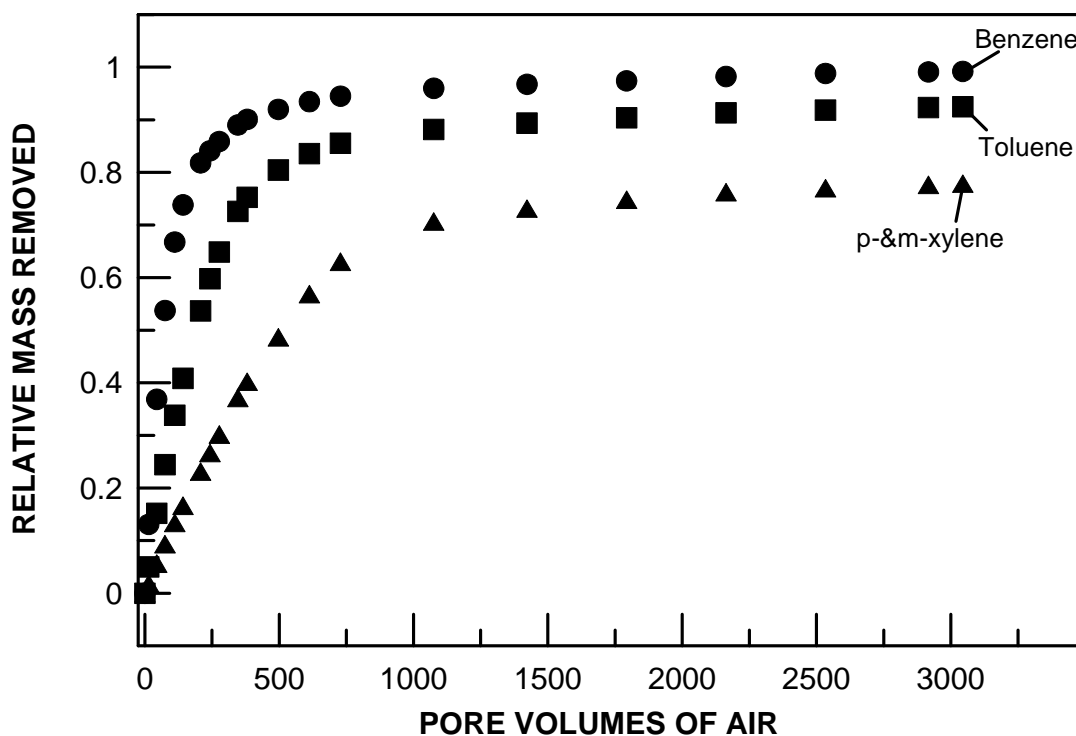


Figure 7. Cumulative masses of benzene, toluene, and p-&m-xylene removed relative to masses sorbed during first regeneration in Column 10A

Sorption Characteristics of Virgin and Regenerated SMZ

The batch sorption study performed on virgin SMZ (no prior BTEX exposure), SMZ that had experienced 5 sorption/regeneration cycles, and SMZ that had undergone 10 sorption/regeneration cycles confirmed that the SMZ had not lost any significant sorption capacity for BTEX after 5 and 10 cycles. Sorption data for each SMZ batch were well-described by the linear sorption model (Eq. 8 with $F = 1$), with all $R^2 \geq 0.77$ and most $R^2 \geq 0.92$. The K_d s for each BTEX compound on virgin and exposed SMZ were statistically indistinguishable. The means and standard deviations of K_d for each BTEX compound are shown in Table 3. These batch sorption results are consistent with our column results showing SMZ does not lose sorption capacity for BTEX over 10 sorption/regeneration cycles (> 4500 PV of exposure to produced water). Table 3 shows that K_d values determined from batch experiments were, however, significantly lower than K_d values determined from column experiments. Results from other studies have shown disagreement in K_d between batch and column experiments. Several different

Table 3. Mean K_d values determined by laboratory column and batch experiments. Standard deviations are shown in parentheses. “n” indicates the number of measurements for each mean.

Compound	Mean Column K_d (L/kg)	Mean Batch K_d (L/kg)
	(n=18)	(n=6)
Benzene	18.3 (4.70)	6.71 (0.57)
Toluene	37.5 (5.27)	15.6 (1.32)
Ethylbenzene	88.0 (10.9)	33.5 (2.87)
p-&m-xylene	95.0 (11.3)	36.5 (2.61)
o-xylene	87.7 (11.5)	39.4 (3.37)

reasons for the differences have been hypothesized, including immobile water in the column (MacIntyre et al. 1991), failure to reach sorption equilibrium in batch experiments (Streck et al. 1995), destruction of particles while shaking (Schweich et al. 1983), reduction in column particle spacing (Celorie et al. 1989), and inappropriate application of an equilibrium sorption model (Altfelder et al. 2001). The reasons for the discrepancies between batch and column K_d s in our experiments are unclear.

Comparisons to the Field Test of a Prototype SMZ Treatment System

The breakthrough of benzene and toluene on virgin SMZ in the field column is shown in Figure 8. The effluent concentration of ethylbenzene and xylenes remained near zero after 80 PV (not shown in Figure 8). Figure 8 includes a comparison of the BTC for benzene and toluene on virgin SMZ in the laboratory columns. The field column exhibited later breakthrough and stronger retention of BTEX than the laboratory column. Although the two systems are scaled, the likely reason for this is that the 14-40 mesh SMZ used in the field column has a higher surfactant loading (180 mmol HDTMA/kg zeolite) than the 80-100 mesh SMZ used in the laboratory columns (157 mmol HDTMA/kg zeolite).

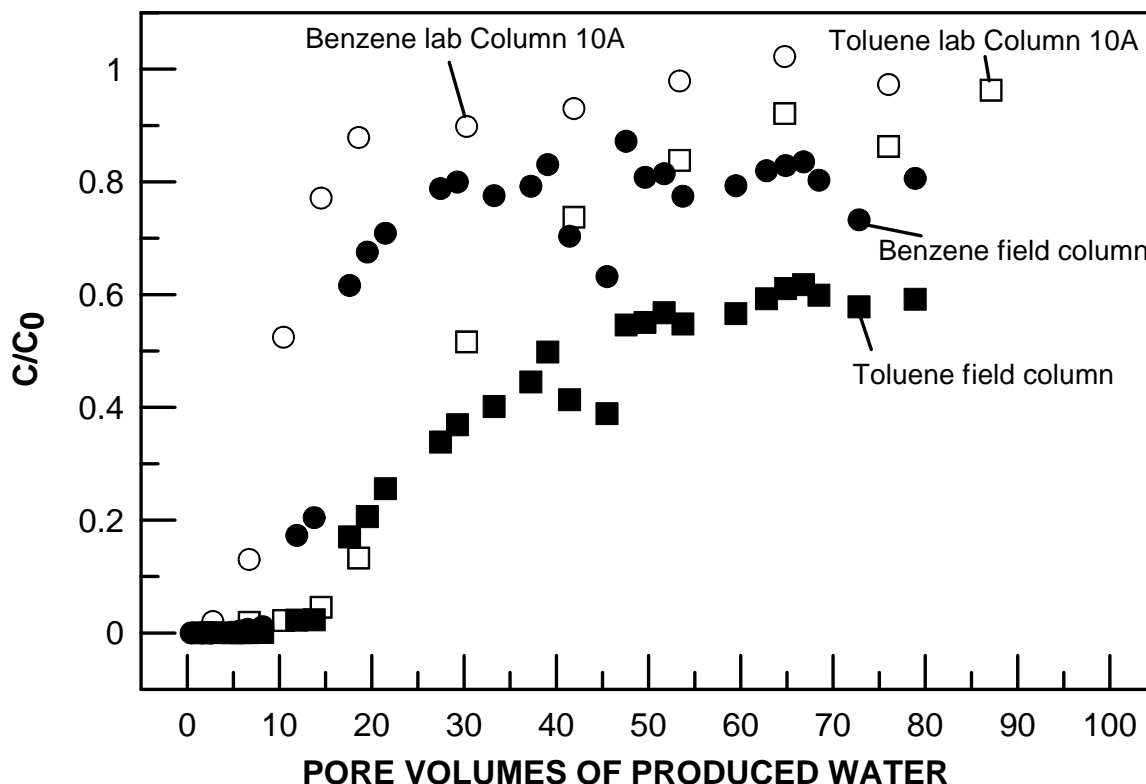


Figure 8. Comparison of benzene and toluene BTC for virgin SMZ in lab column 10A and field column

Figure 9 shows the BTCs for benzene and toluene on virgin and regenerated SMZ in the field column. The effluent concentrations for ethylbenzene and the xylenes were again very low and are not shown in Figure 9. The initial effluent concentrations of toluene (and ethylbenzene and xylenes) were above zero, which was higher than during any stage of the initial sorption experiment. These relatively high effluent concentrations were likely due to incomplete regeneration of the SMZ. During regeneration, air flow was in the same direction as water flow in the column, pushing the BTEX toward the effluent end of the column. The compounds with higher K_{ow} were likely not completely removed during sparging, but instead were concentrated toward the effluent end of the column. When produced water was reintroduced to the column for the second sorption cycle, these higher concentrations eluted. By reversing flow during air-sparging as in the laboratory columns, this problem could be eliminated as BTEX would be concentrated toward the influent end of the column if sparging was incomplete. Aside from the high

concentration of toluene initially, Figure 9 shows that the regenerated SMZ was even more effective at BTEX removal than the virgin SMZ, similar to the trend observed in the laboratory columns.

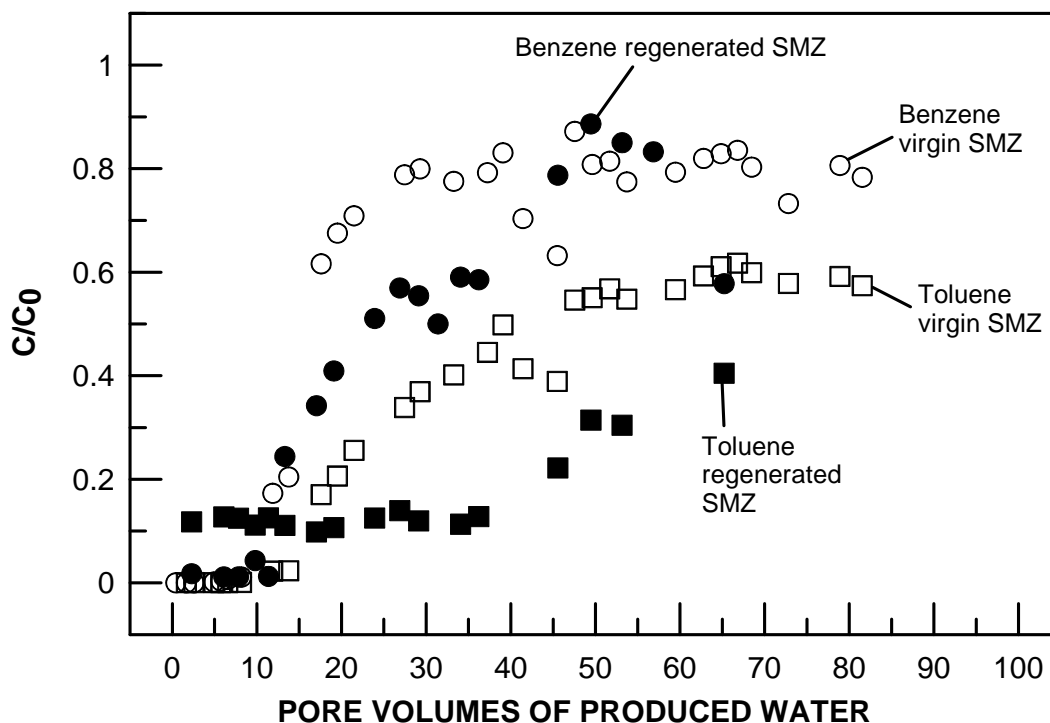


Figure 9. Benzene and toluene breakthrough on virgin and regenerated SMZ in field column

3.2 Phase 2. Optimize VPB for the Treatment of Waste Gases Expected from SMZ Regeneration (Lab-Scale)

Experimental studies for Phase 2 are underway at the University of Texas at Austin for designing vapor phase bioreactors that will treat the off-gas produced during regeneration of the SMZ column. We have designed and assembled a hybrid system that combines features of both biotrickling filters and biofilters and will test this system in conjunction with SMZ regenerating process.

The experimental vapor phase bioreactors that will treat the off-gas from the SMZ regeneration process is shown in Figures 1 and 10. The bioreactor design selected for

this project is a hybrid system that combines features of both biotrickling filters and biofilters. Similar to a biotrickling filter, the experimental bioreactor is packed with a synthetic media and nutrients such as nitrogen are supplied externally via a liquid spray system. However, the nutrients are sprayed over the bed for only 30 minutes per day instead of continuously as occurs in biotrickling filters. This periodic nutrient supply minimizes the liquid film on the packing material since excess water can hinder the mass transfer and ultimately the removal rate of relatively hydrophobic hydrocarbon pollutants. This design also allows easier control over bioreactor conditions and enables adjustments such as increased nitrogen supply or pH control to be accomplished easily. The experimental bioreactor is also similar to classical biofilters since the liquid phase is essentially immobile throughout most of the bioreactor operation.

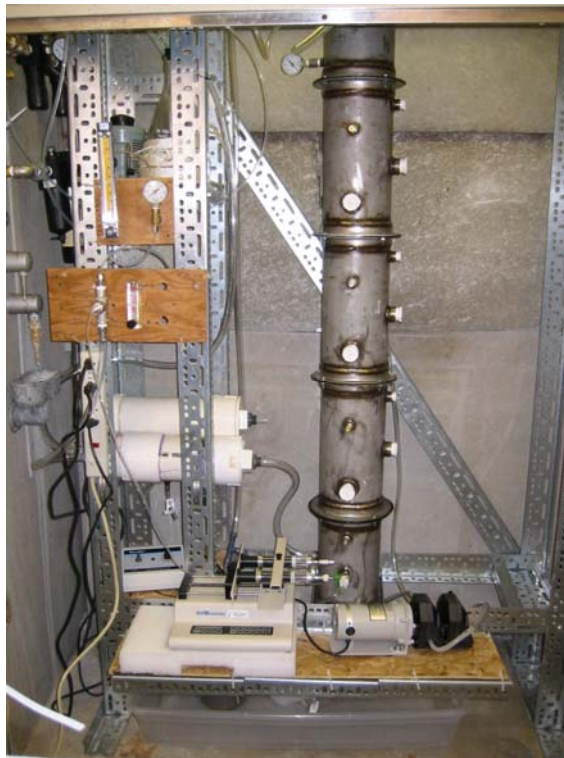


Figure 10. Experimental Bioreactor System

4. Conclusions and Future work

We found that in addition to BTEX, phenol and naphthalene compounds were also important organic pollutants in the produced water from the Wyoming test site. This information will be implemented to determine the composition of the influent stream for the vapor phase bioreactors that have been assembled in the mean time. For the SMZ regeneration phase, our preliminary results showed that BTEX retention in the SMZ column reactors increases with the number of regeneration cycles.

For the next six months of this project, we will focus on the following tasks to complete the proposed work in Phase 1 and Phase 2 of this project.

- i) Synthetic waters with different organic constituents as well as produced water will be fed into the SMZ reactors. Organic contents of both influent and effluent will be analyzed to determine the retention capacity in SMZ column reactors. Based on the composition of organic compounds in the produced water, phenols and naphthalenes will be added into the synthetic waters in addition to the BTEX compounds.
- ii) Regeneration will be conducted using high pH solutions for regeneration of non-volatile components and an air-sparging process for volatile components. The optimal conditions for the regenerating process will be evaluated and the ultimate useful life of SMZ will be determined.
- iii) Several hydrocarbon-degrading microbial cultures will be evaluated for the efficacy of degrading VOCs. Experiments will also be conducted to optimize a slip feed system to maintain VPB performance during periodic operation.
- iv) To assess the performance of VPBs, the composition and relative concentrations of key pollutants will be systematically varied. Laboratory scale experiments of VPBs will be conducted first with a simple BTEX mixture, then with a more complex waste gas stream representing the VOCs expected during the SMZ regeneration step.

5. References

- Altfelder, S., Streck, T., Maraqa, M. A., and Voice, T. C. (2001). "Nonequilibrium sorption of dimethylphthalate--compatibility of batch and column techniques." *Soil Sci. Soc. Am. J.*, 65(1) 102-111.
- API, 1987. Oil and gas industry exploration and production wastes.
- Bessa, E., Sant'Anna, G. L. Jr., and Dezotti, M. (2001). "Photocatalytic/H₂O₂ treatment of oil field produced waters." *Applied Catalysis B: Environmental*, 29(2) 125-134.
- Bowman, R. S., Haggerty, G. M., Huddleston, R. G., Neel, D., and Flynn, M. M. (1995). "Sorption of nonpolar organic compounds, inorganic cations, and inorganic oxyanions by surfactant-modified zeolites." *Surfactant-enhanced subsurface remediation*, D. A. Sabatini, R. C. Knox, and J. H. Harwell, eds., American Chemical Society, Washington, DC, 54-64.
- Bowman, R. S., Li, Z., Roy, S. J., Burt, T., Johnson, T. L., and Johnson, R. L. (2001). "Pilot test of a surfactant-modified zeolite permeable barrier for groundwater remediation." *Physicochemical groundwater remediation*, S. A. Burns, ed., Kluwer Academic/Plenum Publishers, New York, 161-185.
- Bowman, R. S., Sullivan, E. J., and Li, Z. (2000). "Uptake of cations, anions, and nonpolar organic molecules by surfactant-modified clinoptilolite-rich tuff." *Natural zeolites for the third millennium*, C. Colella and F. A. Mumpton, eds., De Frede Editore, Napoli, Italy, 287-297.
- Boysen, D. B., Boysen, J.E., and Boysen, J.A. (2002) "Creative strategies for produced water disposal in the Rocky Mountain region." *Proc., 9th Annu. International Petroleum Environmental Conference*, Integrated Petroleum Environmental Consortium, Albuquerque, NM.
- Breck, D. W., 1974. *Zeolite molecular sieves: structure, chemistry, and use*. John Wiley and Sons, New York, 771 p.
- Brusseau, M. L., Jessup, R.E., and Rao, P.S.C. (1991). "Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes." *Environ. Sci. Technol.*, 25(1), 134-142.
- Brusseau, M. L., and Rao, P.S.C. (1989). "Sorption nonideality during organic contaminant transport in porous media." *CRC Crit. Rev. Environ. Control*, 19(1), 33-99.
- Celorie, J. A., Woods, S. L., Vinson, T. S., and Istok, J. D. (1989). "A comparison of sorption equilibrium distribution coefficients using batch and centrifugation methods." *J. Environ. Qual.*, 18(3) 307-313.
- Code of Federal Regulations. (2002). Title 40. U.S. Government Printing Office, Washington, DC.
- Crittenden, J. C., Berrigan, J.K, and Hand, D.W. (1986). "Design of rapid small-scale adsorption tests for a constant diffusivity." *Journal WPCF*, 58(4), 312-319.
- Crittenden, J. C., Reddy, P. S., Arora, H., Trynoski, J., Hand, D. W., Perram, D. L., and Summers, R. S. (1991). "Predicting GAC performance with rapid small-scale column tests." *Journal AWWA*, 83(1), 77-87.
- Deeb, R. A. and Alvarez-Cohen, L (1999) "Temperature Effects and Substrate Interactions During the Aerobic Biotransformation of BTEX Mixtures by Toluene-

- Enriched Consortia and *Rhodococcus rhodochrous*." *Biotechnol. Bioeng.*, vol. 62, no. 5, 526-536.
- Deshusses, M. A. and Webster, T. S. (2000) "Construction and Economics of a Pilot/Full-Scale Biological Trickle Filter Reactor for the Removal of Volatile Organic Compounds from Polluted Air." *J Air Waste Manage. Assoc.*, vol. 50, no. 11, 1947-1956,
- Deshusses, M. A., Hamer, G. and Dunn, I. J. (1995) "Behavior of Biofilters for Waste Air Biotreatment." *Environ. Sci. Technol.*, vol. 29, 1048-1058.
- Edwards, A. L. (1984). *An Introduction to Linear Regression and Correlation*, 2nd Ed. W. H. Freeman and Co., New York.
- Gallup, D. L., Isacoff, E. G., and Smith, D. N. III. (1996). "Use of Amberlite MB3 mixed bed carbonaceous adsorbent for removal of BTEX compounds from oil-field produced water." *Environ. Progress*, 15(3) 197-203.
- Haggerty, G. M., and Bowman, R. S. (1994). "Sorption of chromate and other inorganic anions by organo-zeolite." *Environ. Sci. Technol.*, 28(3), 452-458.
- Huddleston, R. (1990). "Surface-altered hydrophobic zeolites as sorbents for hazardous organic compounds." MS Thesis, New Mexico Institute of Mining and Technology, Socorro, NM.
- Janks, J.S., and Cadena, F. (1992). "Investigations into the use of modified zeolites for removing benzene, toluene, and xylene from saline produced water." *Produced Water*, J.P. Ray and F.R. Engelhart, eds., Plenum Press, New York, 473-487.
- Jaynes, W. F., and Vance, G. F. (1996). "BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes." *Soil Sci. Soc. Am. J.*, 60(6), 1742-1749.
- Jutras, E. M., Smart, C. M., Rupert, R., Pepper, I. L. & Miller, R. M. (1997) "Field-Scale Biofiltration of Gasoline Vapors Extracted from Beneath a Leaking Underground Storage Tank." *Biodegradation*, vol. 8, 31-42.
- Kinney, K. A., Loehr, R. C. and Corsi, R. L. (1999) "Vapor-Phase Bioreactors: Avoiding Problems Through Better Design and Operation." *Environ. Prog.*, vol. 18, no. 3, 222-230.
- Lawrence, A. W., Miller, J.A., Miller, D.L., and Hayes, T.D. (1995). "Regional assessment of produced water treatment and disposal practices and research needs." *Proc., SPE/EPA Exploration and Production Environmental Conference*, Society of Petroleum Engineers, Houston, Texas, 373-392.
- Leson, G. and Smith, B. J. (1997) "Petroleum Environmental Research Forum Field Study on Biofilters for Control of Volatile Hydrocarbons." *J. Environ. Eng.*, vol. 123, no. 6, 556-562,
- Leson, G. and Winer, A. M. (1991) "Biofiltration: An innovative Air Pollution Control Technology for VOC Emissions," *J. Air Waste Manage. Assoc.*, vol. 41, no. 8, 1045-1054,
- Li, Z., and Bowman, R. S. (2001). "Regeneration of surfactant-modified zeolite after saturation with chromate and perchloroethylene." *Wat. Res.*, 35(1), 322-326.
- Lu, C., Chu, W. and Lin, M. 2000. "Removal of BTEX Vapor from Waste Gases by a Trickle Bed Biofilter," *J. Air & Waste Manage. Assoc.* **50**: 411-417.

- MacIntyre, W. G., Stauffer, T. B., and Antworth, C. P. (1991) "A comparison of sorption coefficients determined by batch, column, and box methods on a low organic carbon aquifer material." *Ground Water*, 29(6) 908-913.
- Mackay, D., Shiu, W. Y., and Ma, K. C. (1992). "Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals," Lewis Publishers, Chelsea, MI.
- Moe, W. M. and Irvine, R. L. (2001) "Effect of Nitrogen Limitation on Performance of Toluene Degrading Biofilters." *Water Res.*, vol. 35, no. 6, 1407-1414
- Neel, D., and Bowman, R. S. (1992). "Sorption of organics to surface-altered zeolites." *Proc., 36th Annual New Mexico Water Conference*, New Mexico Water Resources Research Institute, Las Cruces, NM, 57-61.
- Neff, J. M., and Sauer, Jr, T.C. (1996). "Aromatic hydrocarbons in produced water." *Produced Water 2: Environmental Issues and Mitigation Technologies*, M. Reed and S. Johnsen, eds., Plenum Press, New York, 163-175.
- Negri, M. C., and Hinchman, R. C. (1997). "Biotreatment of produced waters for volume reduction and contaminant removal." *Proc., 4th Annual International Petroleum Environmental Conference: Issues and Solutions, Production and Refining*. Integrated Petroleum Environmental Consortium, San Antonio, Texas.
- Otto, G. H., and Arnold, K. E. (1996). "U.S. produced water discharge regulations have tough limits." *Oil and Gas J.*, 94(29) 54-61.
- Park J, Kinney KA. (2001) "Evaluation of Slip Feed System for Vapor-Phase Bioreactors." *J. Environ. Eng.*, vol. 127, no. 11, 979-985.
- Pignatello, J. J., and Xing, B. (1996). "Mechanisms of slow sorption of organic chemicals to natural particles." *Environ. Sci. Technol.*, 30(1), 1-11.
- Santos, S. M., and Wiesner, M. R. (1997). "Ultrafiltration of water generated in oil and gas production." *Water Environ. Res.*, 69(6) 1120-1127.
- Schweich, D., Sardin, M., and Guedent, J. P. (1983). "Measurement of a cation exchange isotherm from elution curves obtained in a soil column: Preliminary results." *Soil Sci. Soc. Am. J.*, 47(1) 32-37
- Song, J. and Kinney, K. A. (2000) "Effect of Vapor-Phase Bioreactor Operation on Biomass Accumulation, Distribution, and Activity." *Biotechnol. Bioeng.*, vol. 68, no. 5, 508-516.
- Song, J. and Kinney, K. A., Boswell, J. T. and John, P. C. (2002) "Performance of a Compost-Based Hybrid Bioreactor for the Treatment of Paint Spray Booth Emissions." In *Proceedings of the Air & Waste Management Association's Annual Meeting & Exhibition*, 2002
- Stephenson, M. T. (1992). "A survey of produced water studies." *Produced Water*, J. P. Ray and F. R. Engelhart, eds., Plenum Press, New York, 1-11.
- Streck, T., Poletika, N. N., Jury, W. A., and Farmer, W. J. (1995). "Description of simazine transport with rate-limited, two-stage, linear and nonlinear sorption." *Water Resour. Res.*, 31(4) 811-822.
- Tao, F. T., Curtice, S., Hobbs, R. D., Sides, J. L., Wieser, J. D., Dyke, C. A., Tuohey, D., and Pilger, P. F. (1993). "Reverse osmosis process successfully converts oil field brine into freshwater." *Oil and Gas J.*, 91(38) 88-91.

- Thoma, G. J., Bowen, M. L., and Hollensworth, D. (1999). "Dissolved air precipitation/solvent sublation for oil-field produced water treatment." *Separation and Purification Tech.*, 16(2) 101-107.
- Toride, N., Leij, F.J., and van Genuchten, M.T. (1999). "The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, version 2.1." Research Report No. 137, U.S. Salinity Laboratory, USDA, ARS, Riverside, CA.
- U.S. EPA. (2000). "Profile of the oil and gas extraction industry." EPA/310-R-99-006, Washington, DC.
- van Groenestijn, J. W. & Hesselink, P. G. M. (1993) "Biotechniques for Air Pollution Control," *Biodegradation*, vol. 4, 283-301.
- Woertz, J. R., Kinney, K. A., McIntosh, N. D., Szaniszlo, P. J. (2001) "Removal of Toluene in a Vapor-Phase Bioreactor Containing a Strain of the Dimorphic Black Yeast *Exophiala lecanii-corni*." *Biotechnol. Bioeng.*, vol. 75, no. 5, 550-558.