WATER TREATMENT TECHNOLOGY FOR OIL AND GAS PRODUCED WATER

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ABSTRACT

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 US (Allen and Rosselot, 1994). Whereas reinjection (for enhanced recovery or disposal) accounts for as much as 95% of this water (IOGCC, 1993), the remaining fraction is still considerable. Reinjection is not always feasible because of geographic and cost considerations. In the case of offshore waters (Gulf of Mexico), for instance, discharge is the most practical and cost-effective means of handling the waste stream. Some on-shore waters of lower salinity, for example, in areas of east Texas, are exempt from required reinjection and are frequently used for beneficial uses such as stock or crop watering. In these situations, however, it may be desirable, and often necessary from a regulatory viewpoint, to treat produced water before discharge. It also may 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.

In the case of lower-salinity water, the removal of organic compounds becomes more important to meet requirements or esthetic considerations for beneficial re-use. Low-cost, simple technologies are desirable so that small producers or isolated production areas can use the process easily. Sorption of organics by surfactant-modified zeolite (SMZ) followed by air stripping and subsequent treatment of the off-gas by a vapor-phase bioreactor (VPB) has been shown to be effective at removing BTEX from produced water and is a simple, cheap process that is cost-competitive with other sorption-based technologies. Figure 1 shows the removal of benzene over a number of sorption/desorption cycles from a produced water stream. Regeneration using air stripping was found to remain effective throughout the cycles. Air stripping using a simple, commercially available air compressor strips the volatile compounds from the SMZ column. The air stream is routed to the VPB where bacteria use the BTEX as a food source. Figure 2 shows the removal of BTEX from a laboratory air stream in a VPB.

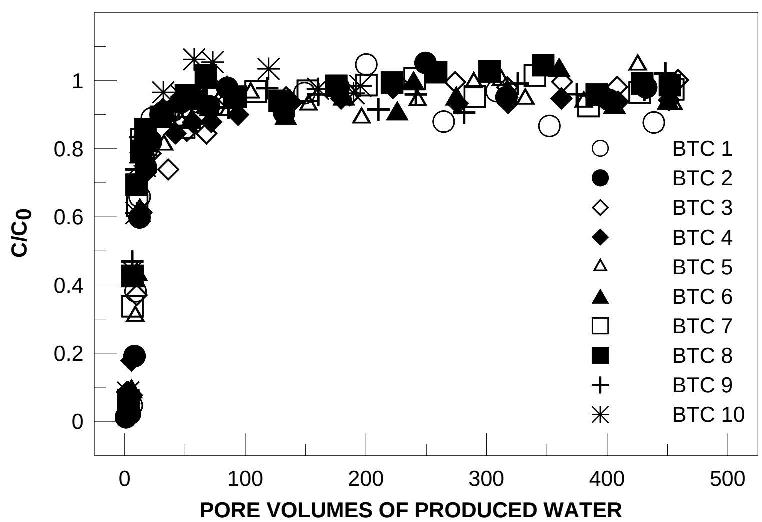

Figure 1. Repetitive sorption of benzene on and SMZ column, with air sparging between breakthrough curves (BTCs) (Ranck, in press). Similar results were seen for toluene, ethylbenzene, and xylenes.

A cost analysis (Carrico, 2002) comparing SMZ with other organic treatment processes indicates that SMZ can be cost-competitive on a per-gallon basis. Costs evaluated included membrane filtration, carbon adsorption, chemical oxidation (hydrogen peroxide and ozone), air stripping, UV oxidation, and reinjection. Costs for these treatment processes ranged from $0.20 to $8.33 per 1000 gallons of water, with capital costs of up to $300,000. SMZ coupled with air sparging was estimated to cost as little as $0.49 per 1000 gallons after one year of operation, with a low initial capital cost of $18,500 for an Industrial system. Further cost data for incorporation of the VPB is being developed during the current study phase.

Field testing of the SMZ column has been successful (summer 2002); field testing of the combined system will occur in summer 2004. At this time a variety of test sites and produced waters are being sought for field-test facilities to provide more data on continuing cycles and field robustness of the system.

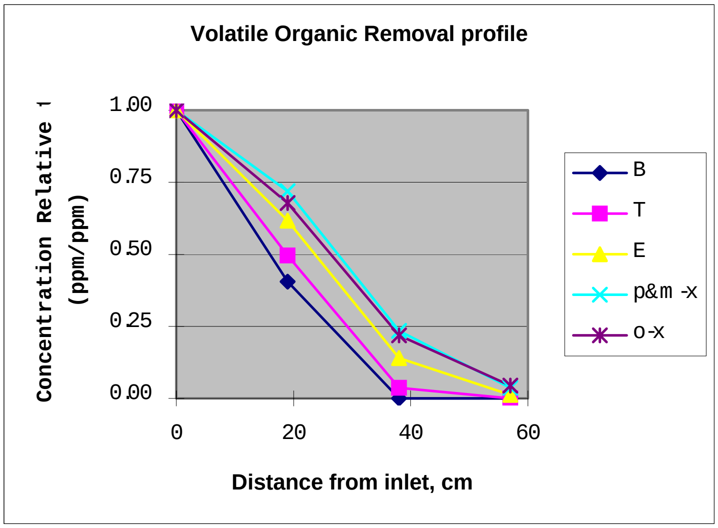

Figure 2. Organic removal profile from inlet to outlet on prototype VPB. (Kinney, unpub data).

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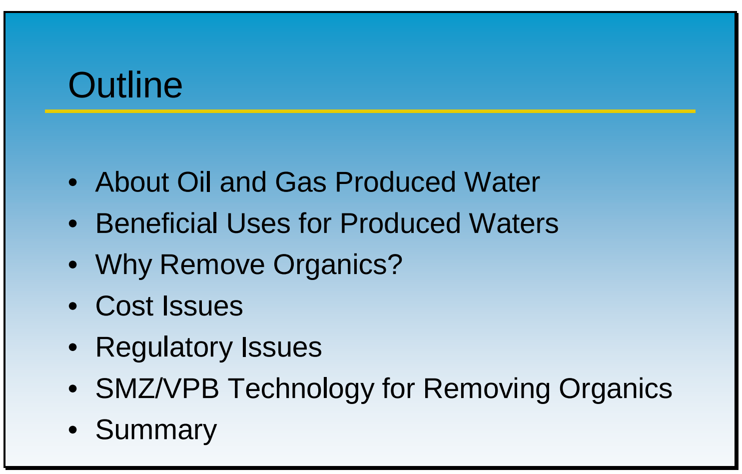


Produced Water Factoids

- Sources:
  - oil and gas Exploration & Production
  - coal-bed methane, coal mining
- 1 barrel oil = up to 10 barrels water (5-7 typical)
- 5.67 mb/d crude in U.S. in March 2004 (API)
- 3+ billion tons of waste per year
- Fresh to high salinity (100 to 100,000 ppm TDS)
- Semivolatile and volatile organic compounds, NORM
- Surfactants, methanol, barium salts
- 95% is reinjected – disposal, enhanced oil recovery

Produced water is a very large waste stream within the US. Most is reinjected; however, a portion of the waste stream could be re-used for specific purposes such as agricultural, industrial, or treated water use. This remaining portion is still considerable and may be of value in water-poor regions.

Surface discharge site, east Texas

Reinjection facility

The picture (top left) is from an oil production facility in Flatonia (Arnum Field), in east Texas. Oil in this region is from shallow production zones, and the produced water is very fresh. Surface discharge is allowed and is used for stock watering and agriculture. The picture (lower left) is of a reinjection facility. Water is gathered from a number of wellheads either by truck or pipeline and moved to a central facility where it is usually pumped to a former producing zone for disposal, or pumped to a producing zone for enhanced oil recovery.

Fate of Remaining 5%

- Offshore Discharge (Gulf of Mexico)
- Fresh Water use
  - Stock watering
  - Irrigation
  - Recharge to aquifers or river base flow additions (Pecos)
- Salt Water use
  - Road application
- Industrial use
  - Electric power production
    - Salinity tolerant: ash wetting
    - Salinity intolerant: cooling tower make-up

Some of the produced water is fairly fresh and is readily re-used. The most important treatment processes are to remove excess oil, dissolved organics, and removal of chemicals added during production. Other treatments might include pH adjustment. For higher salt waters, organics must be reduced before the RO filtration process to prevent filter clogging.

Another photo from Flatonia. The pond on the right has some floating oil (note the black rim around the edge). This is retained and the skimmed water is routed via a subsurface pipe to the pond on the left. The production well is just off the photo to the right.

Disposal Cost Issues (Boysen, 2001)

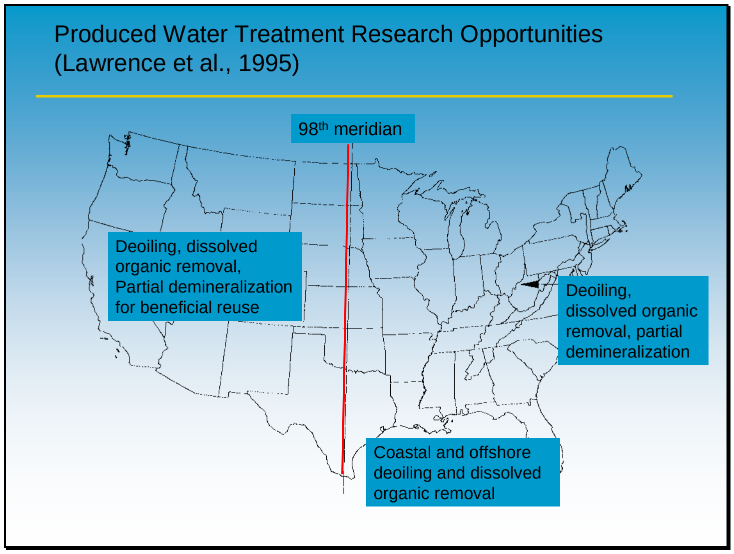
Location	Transport Cost ($/bbl water)	Disposal Cost ($/bbl water)	Total ($/bbl water)*
San Juan Basin, NM	0.70 to 3.20	0.50 to 1.10	0.50 to 4.30
Las Animas Arch, CO	0.50 to 1.86	0.21	0.71 to 1.07
Denver Basin, CO	Unknown to 1.00	1.00 to 1.75	Unknown to 2.75
Anandarko, OK	0.05 to 0.27	1.25 to 2.25	1.25 to 2.52
San Juan, CO	Unknown	0.30 to 1.50	Unknown to 1.50

*On-site disposal does not require transport.
Costs are site and region-specific, often fixed

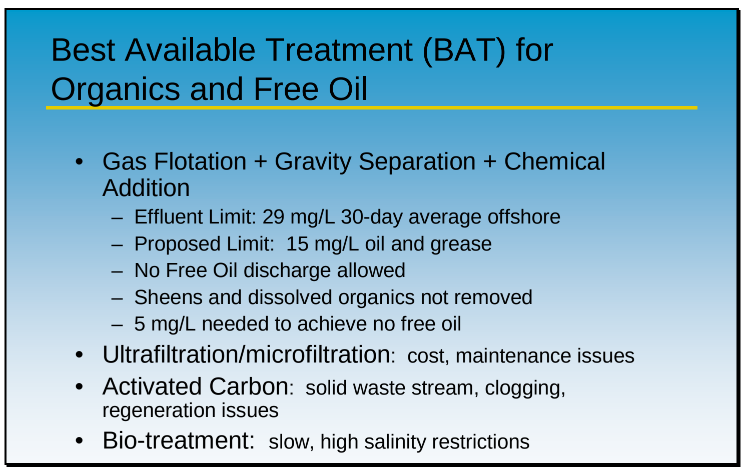
REFERENCES: Information from personal communication with D. Boysen, Crystal Solutions, Inc. Data are also contained in the following:

Boysen, D.B., "Cost Factors Associated with Managing Produced Water at CBM Properties in the Rocky Mountain Region;" 10th Annual Internatl. Petroleum Environmental Conf. (CD); Houston, TX; Nov. 2003.

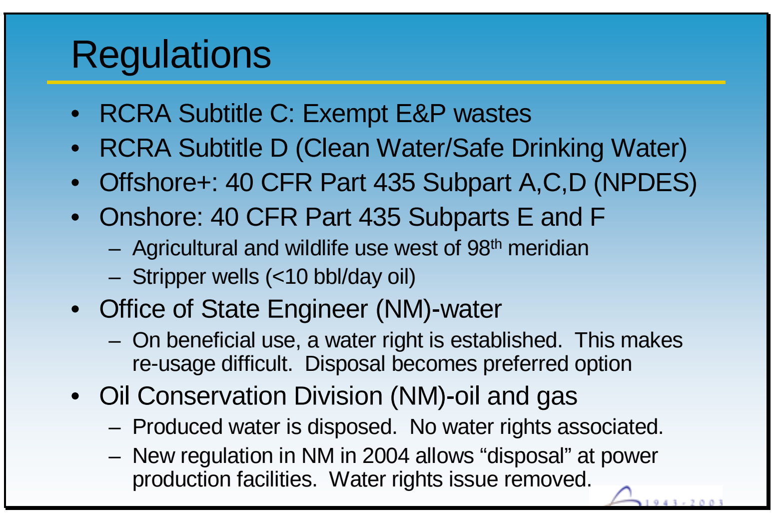
Boysen, D.B, J.E. Boysen, and T. Larson, "Regional, Technical, Regulatory and Economic Trends in Produced Water Management," *Gas Research Institute Publication #02/0222*, Chicago, IL, Nov. 2002.



REFERENCE: 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. In: SPE/EPA Exploration and Production Environmental Conference, Houston, Texas, March 27-29, pp. 373-392.



This slide lists some (not all) technologies that are currently in use for organic removal.

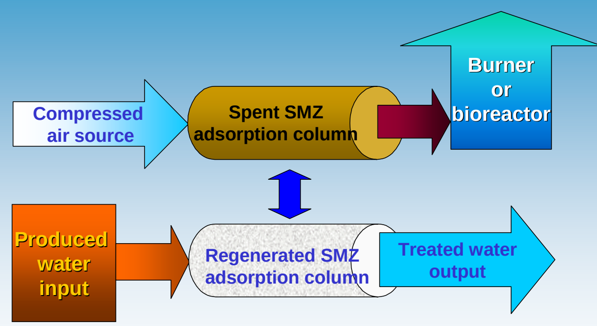


Need for Organic Treatment

Objectives: Low cost, usable at point source, simple, low maintenance

- Meet offshore/onshore regulatory requirements
- Treat dissolved organic constituents
- Insensitive to salt/mineral content, clogging, bacteria
- Regeneration critical to sorption processes
- Low cost off-gas treatment needed (air regulations!)
- Combine SMZ sorption with air-sparge to vapor-phase bioreactor (VPB) off-gas treatment

Schematic of SMZ/VPB System



Objectives: Evaluate SMZ Sorption, SMZ Regeneration, and VPB Performance

Input water flows through one or more SMZ adsorption columns. Treated water is output. In a multi-column setup, one column at a time would be removed from the flow for regeneration by air sparging. The sparged air (from an inexpensive compressor) would be sent to a Vapor Phase bioreactor to remove BTEX compounds. The regenerated column would be returned to use and another column cycled out for regeneration.

Zeolite (Clinoptilolite)

Crystalline aluminosilicate

Pore size: 4.0x5.5, 4.4x7.2 & 4.1x4.7 Å

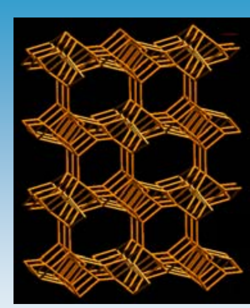
Surface area 15.7 m^2/g

High cation exchange capacity

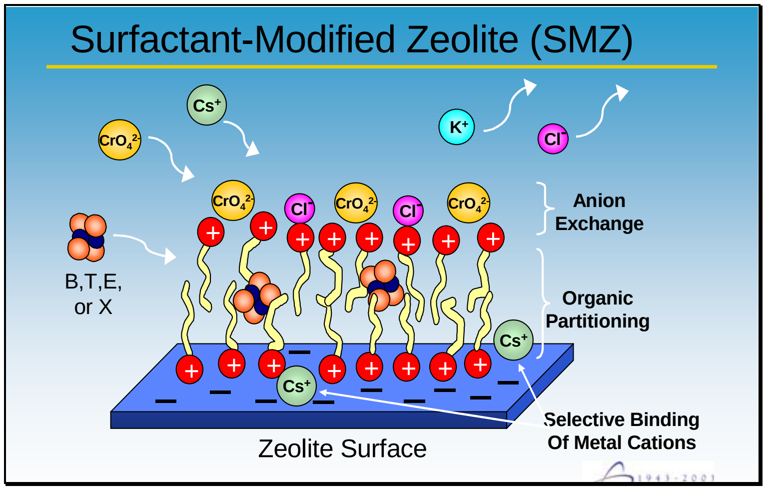
- **Internal – 800 meq/kg**
- **External – 100 meq/kg**

Can be ground to desired particle size

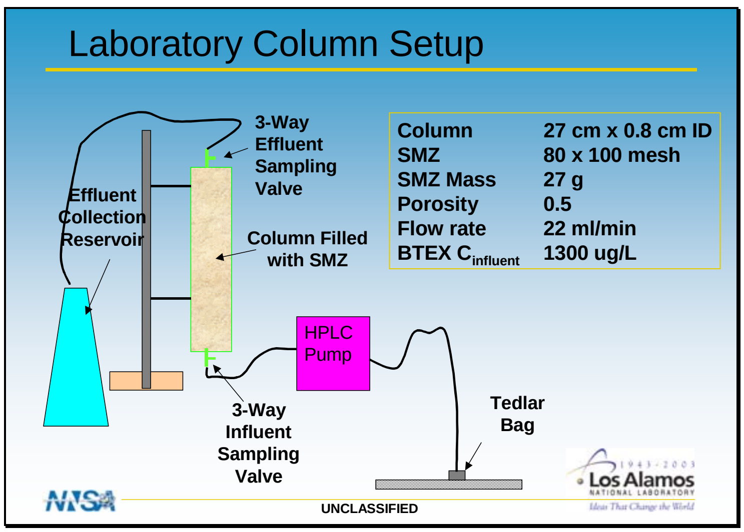
- **14-40 mesh (1.4 – 0.4 mm)**
- **80-100 mesh (0.18 – 0.15 mm)**



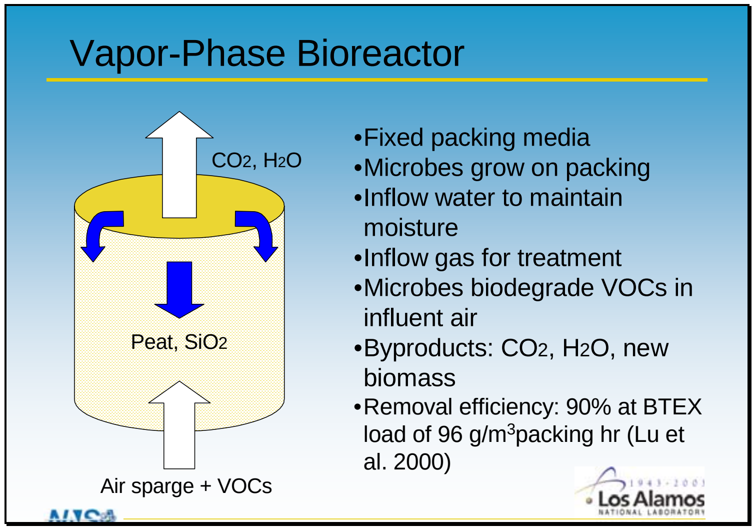
The base material for the sorbent in the SMZ/VPB system is clinoptilolite zeolite. This mineral is mined in areas such as southwest New Mexico, central Idaho, and Wyoming. It is abundant, inexpensive, and frequently used as an ion-exchange medium or molecular sieve-filter medium in water treatment processes.



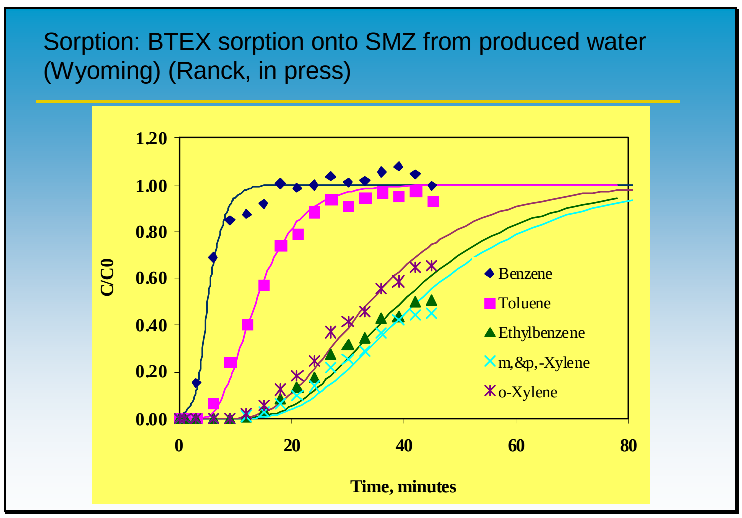
Although this appears complicated, the important part is the zone of organic partitioning. The surfactant molecules (red balls with yellow tails) are ion-exchanged to the clinoptilolite surface. In this illustration, the hydrophobic tails have formed a bilayer on the surface as the result of hydrophobic attraction between tail groups. BTEX compounds (left) are sorbed by the hydrophobic zone. Air stripping can remove these volatile organics from the hydrophobic zone easily.



The set-up in the laboratory.



Air sparge vapor from the regenerating SMZ is routed through the Vapor Phase bioreactor. Microbes grow on support media and degrade volatile organic compounds. Removal efficiencies have been tested and found to be equal to or greater than published efficiencies of 90%.



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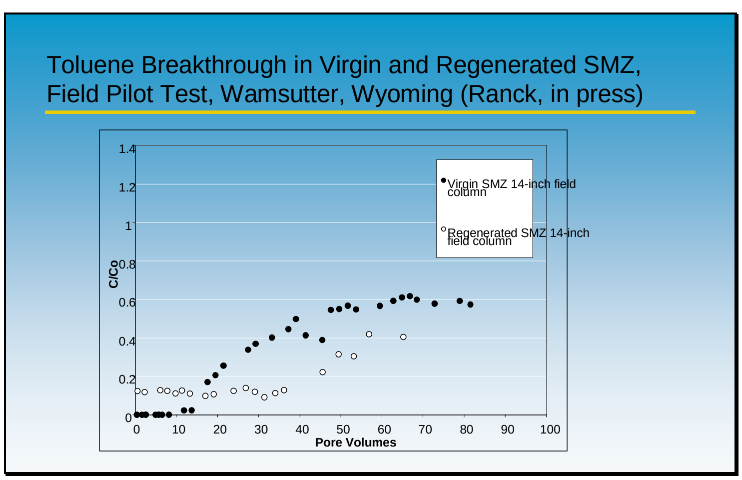

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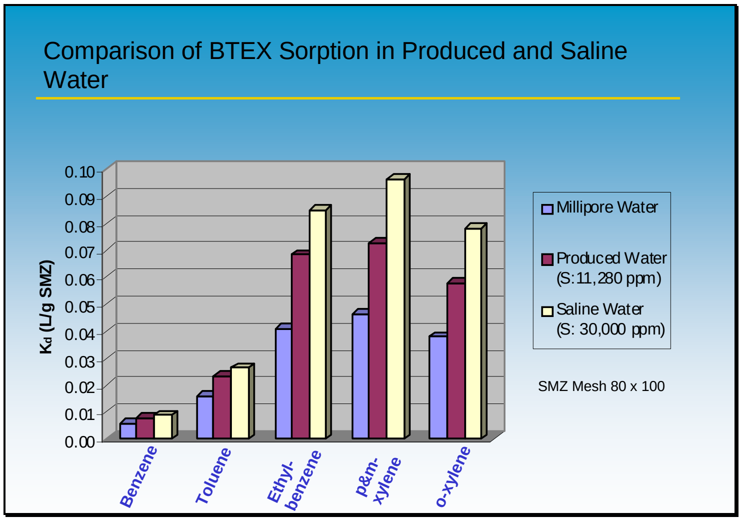
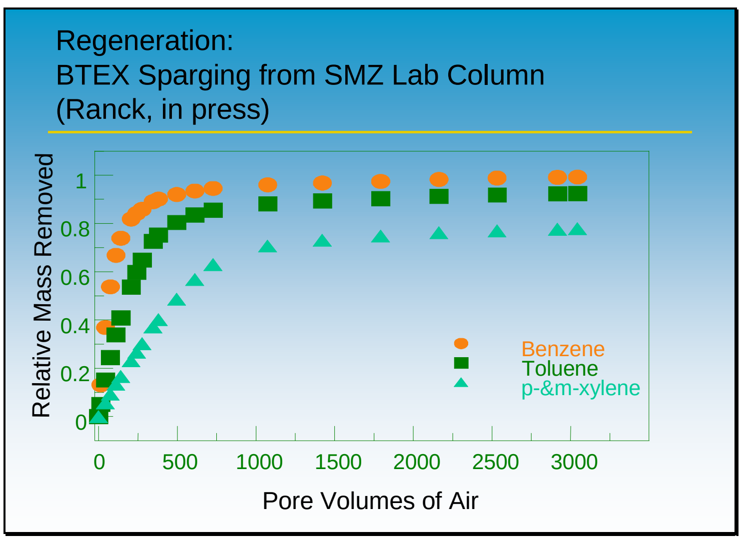


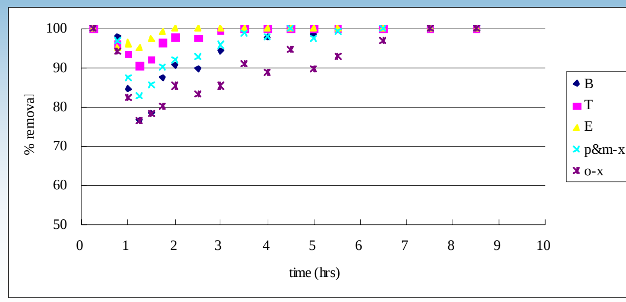
Note that saline water enhances sorption of BTEX compounds. This is an important advantage to the system, as other treatment methods are usually negatively impacted by increased salinity.



Note near complete removal of Benzene and good removal of toluene and xylenes using air sparging.
REFERENCE: Ranck, J.M., Bowman, R.S., Weeber, J.L., Katz, L.E., and Sullivan, E.J. (in press). BTEX removal from produced water using surfactant-modified zeolite. J. Environ. Engineering.

VPB Performance (Lab)

- No competitive inhibition among BTEX compounds
- 95% benzene removal efficiencies obtained
- Removal efficiency following reestablishment of the inlet BTEX feed after a 2.8 day shutdown period



Unpublished data, K. Kinney, 2004.

Summary

- Current lab work is promising
- Future work to include field site testing Summer 2004, beyond?
- Potential for beneficial re-use is expanding, if cost-effective treatments available
- Caution: regulatory hurdles! Industry resistance!