Sorption of Arsenate from Soil-Washing Leachate by Surfactant-Modified Zeolite

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SURFACTANT-MODIFIED ZEOLITE

Surfactant-modified zeolite (SMZ) is an effective and economical sorbent for nonpolar organics, inorganic anions, and inorganic cations dissolved in water (Haggerty and Bowman, 1994; Bowman et al., 1995). Due to its low unit cost of about $400 per ton, SMZ is an attractive alternative to activated carbon and ion exchange resins. Oxyanions that are sorbed by SMZ include chromate, nitrate, selenate and sulfate (Bowman et al., 1995; Li et al., 1998). SMZ was tested in batch studies to remove arsenate from a leachate generated during a soil-washing treatability study. The SMZ was prepared from a pure clinoptilolite zeolite from the St. Cloud mine in Winston, New Mexico. The raw zeolite was treated with hexadecyltrimethylammonium bromide (HDTMA-Br) surfactant to a level of 150 meq/kg (42.6 g HDTMA per kg of zeolite). The surfactant forms a stable organophilic coating on the zeolite surface. Further details on the preparation and properties of SMZ are found in Haggerty and Bowman (1994).

Soil Leachate Characteristics and Treatment

Soil washing is an ex-situ remediation treatment technology that utilizes wet classification, mechanical separation, and chemical extraction processes to remove contamination from soil. Byproducts include fluids or a concentrated residue containing high concentrations of contaminants, fine particulates, and organic carbon. A synthetic soil leachate was prepared from Kennet "A" glacial till-type soil. Clean soil (5 x 150 g) was leached with 750 ml of 0.1N NaOH solution (pH >14) to yield a humate-rich solution. The leachate fractions were combined and diluted to 6 L with deionized water, filtered, then spiked with $As_2O_5^{2-}$ as the sodium salt to approximately 500 mg/L as arsenic. Batch isotherms using variable leachate:SMZ ratios from 40:1 to 4:1 were run at pH 12 and two temperatures, 25°C and 15°C, respectively. The supernatants and solids were analyzed using EPA methods 7060 (dissolved and total solution arsenic), EPA method 7060 with digestion (total arsenic-solid fraction), and EPA method 9060 (TOC).

Results

Dissolved versus total arsenic results were similar. At each temperature, sorption reached a plateau or maximum, then decreased at the highest solution concentration (corresponding to the lowest amount of zeolite added, 2.5 g). Sorption maxima of 5540 mg of arsenic per kg of SMZ were observed at 25°C, and 3150 mg at 15°C. Total arsenate recoveries varied from 74% to 125%. SMZ effectively decolorized the leachate solutions, proportional to the amount of SMZ. The maximum TOC removed varied from 94 to 97 percent. The linearized form of the Langmuir equation was fitted to the As data, with a coefficient of determination of 0.997 for the 25 °C batch (0.906 for the 15°C batch). Sorption of arsenate likely results from two mechanisms: anion exchange with bromide on the external portion of the surfactant bilayer on the zeolite surface, and adsorption of organically complexed arsenate via hydrophobic interactions with the surfactant moiety at the zeolite surface.

Haggerty, G.M, Bowman, R.S., 1994. ES&T, 28, 452-458.
Bowman, R.S., Haggerty, G.M., Neel., D., Flynn, M., 1995. ACS Symposium Series 594, pp.54-64.
Li, Z., Anghel, I., and Bowman, R.S., 1998. J. Dispersion Science and Technology, 19(6&7), 843-857.

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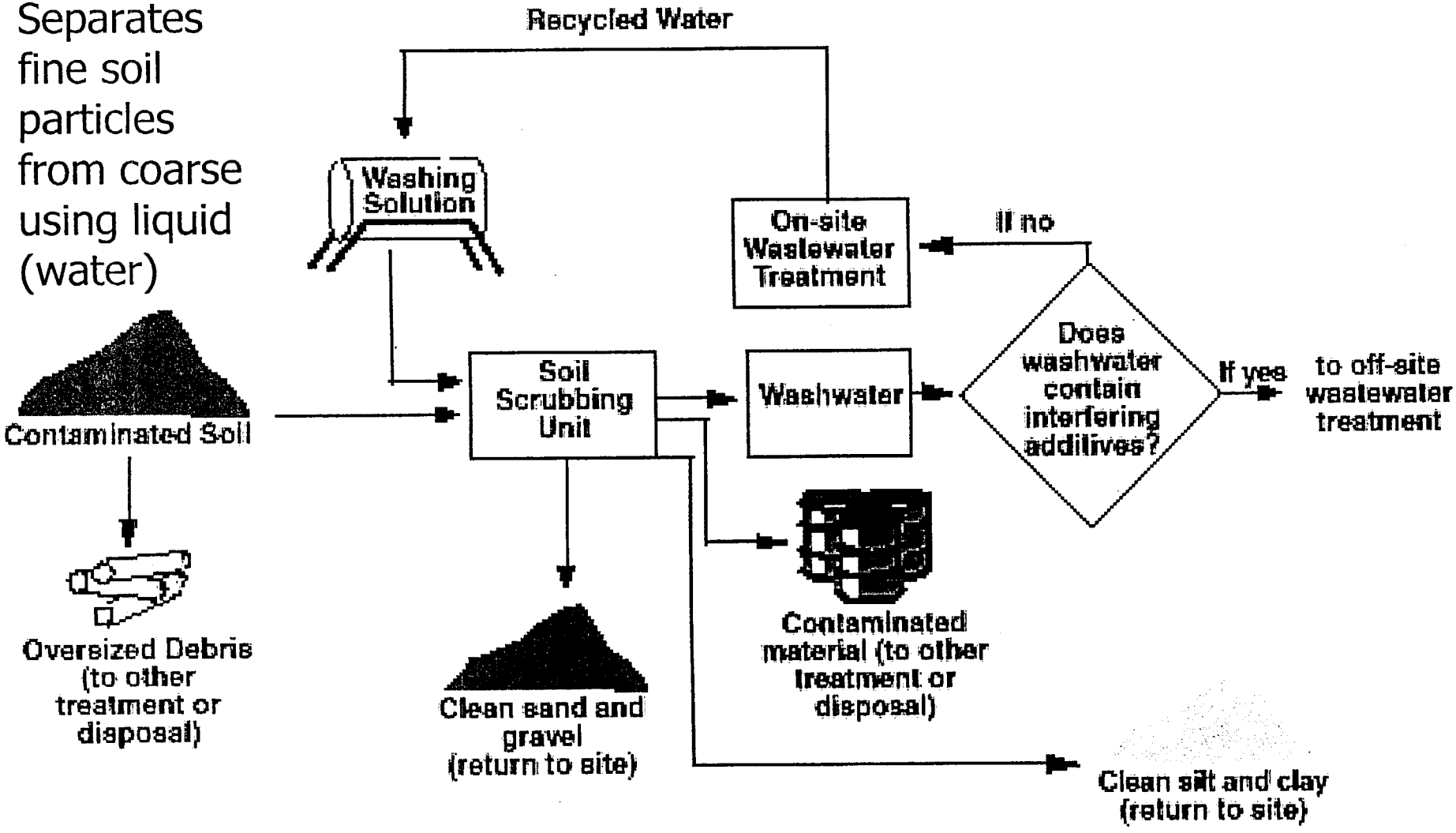
Research Focus

- Is SMZ potentially useful as a sorbent for secondary treatment of soil flushing leachate?
- Can SMZ adsorb arsenate?
- Can SMZ adsorb residual organic carbon?
- Can this occur under high pH conditions? What are temperature effects?
- Is the process efficient and cost-effective?

Soil Washing Technology

Separates fine soil particles from coarse using liquid (water)



Reduces contaminated soil volume
Produces fine soil, liquid streams

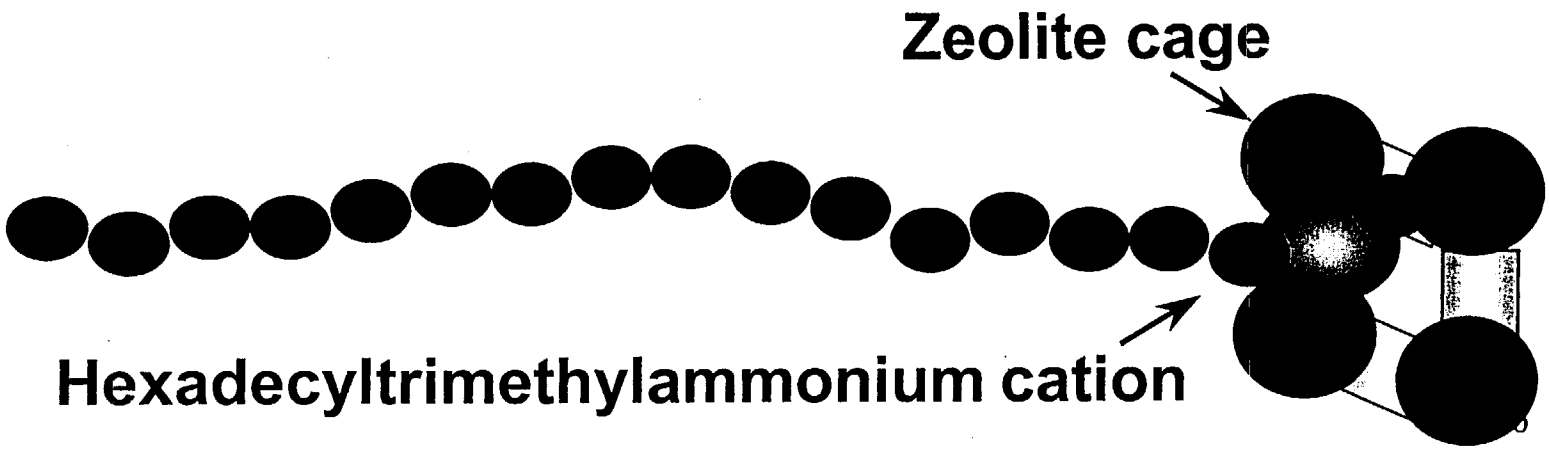
From U.S. EPA, 2001. *A Citizen's Guide to Soil Washing.*

Zeolite Characteristics

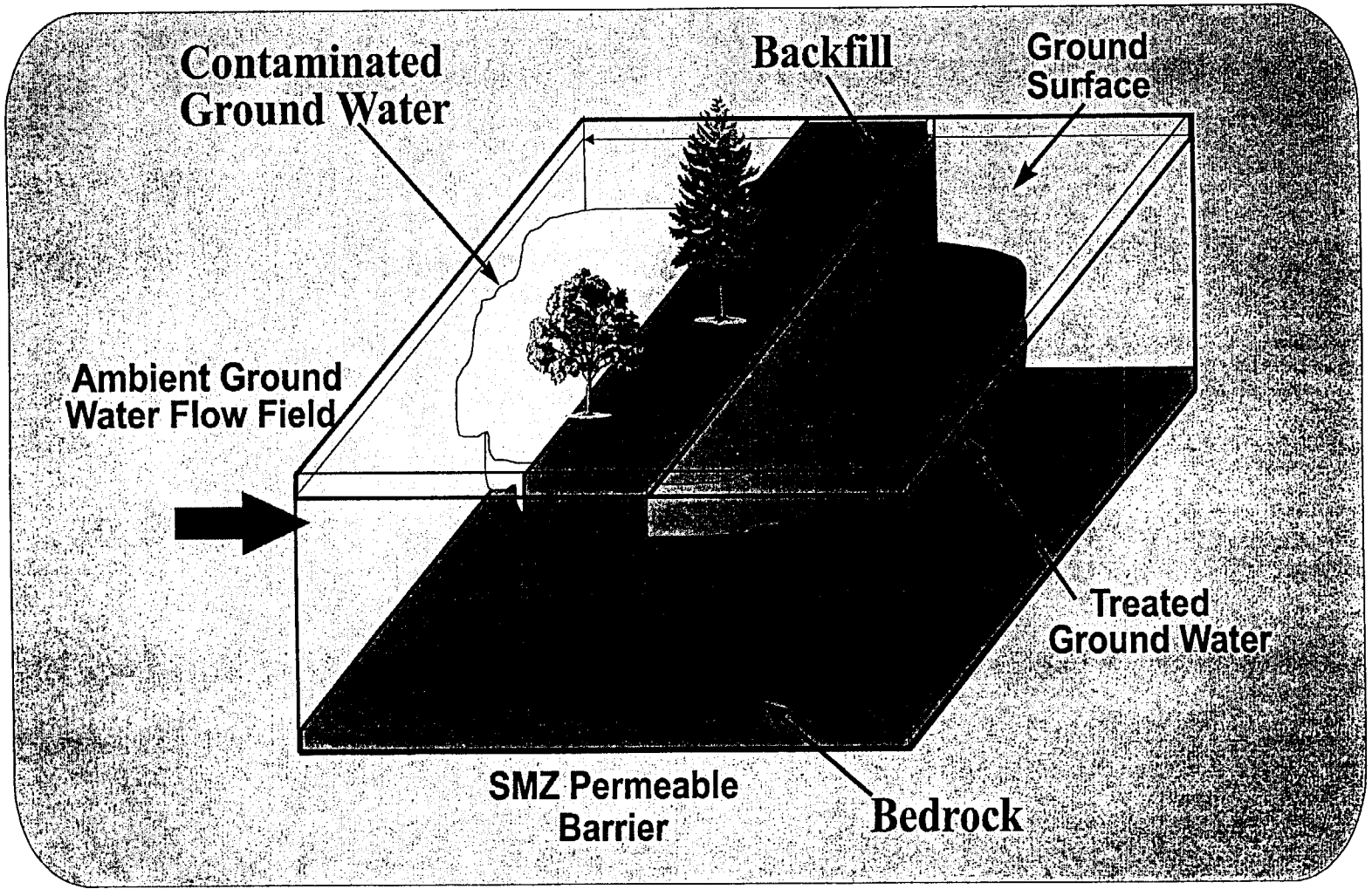
- hydrated aluminosilicate minerals
- surface chemistry similar to smectite
- distributed cation exchange capacity
  - external CEC = 90 meq/kg
  - total CEC = 300 meq/kg
- fixed structure with internal channels
- molecular sieve properties

HDTMA Characteristics

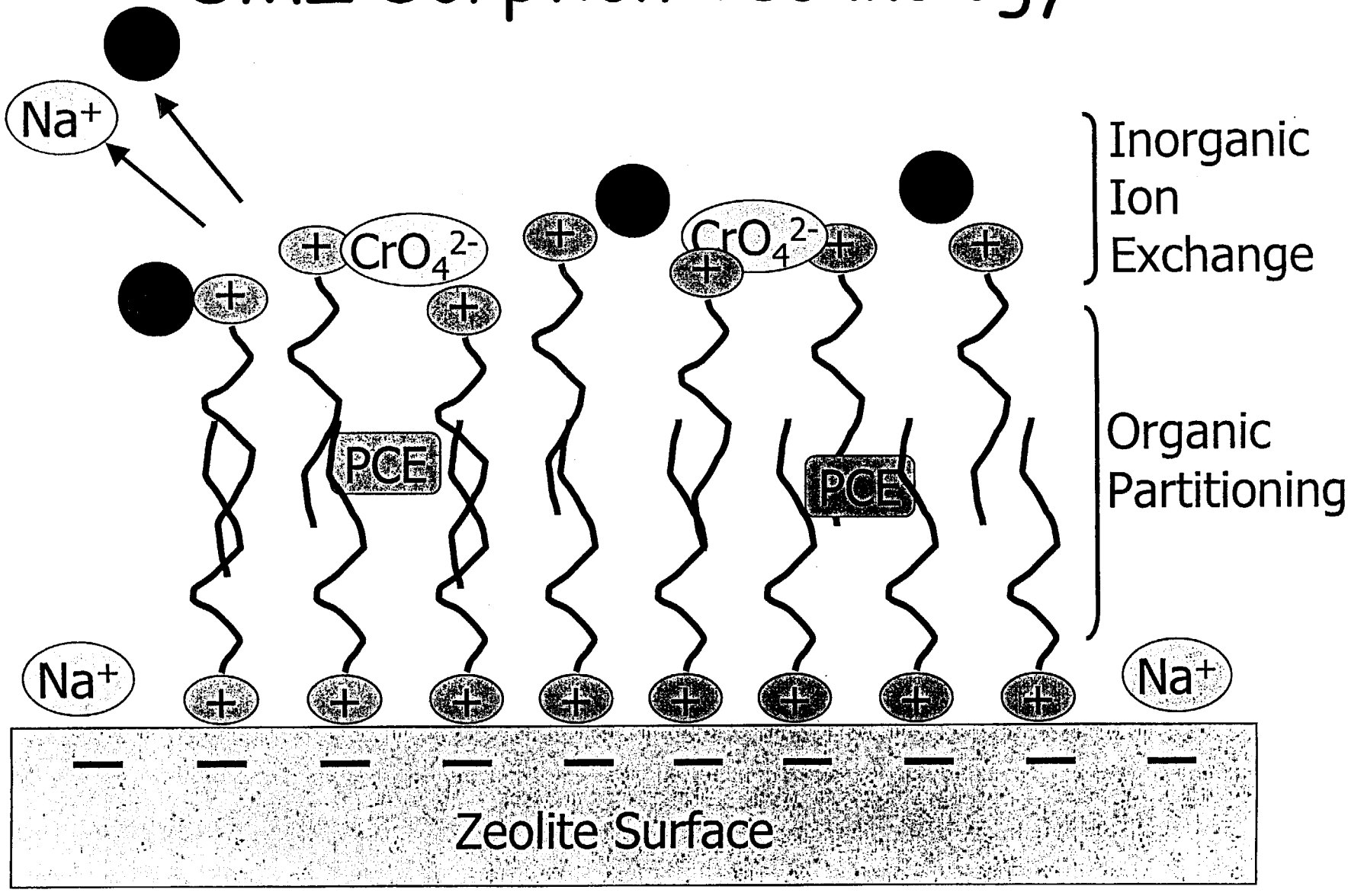
- hydrophobic/hydrophilic properties
- permanent +1 charge on head group
- 16-carbon chain tail group
- forms micelles in solution at critical concentration
- interacts similarly with zeolites and smectites



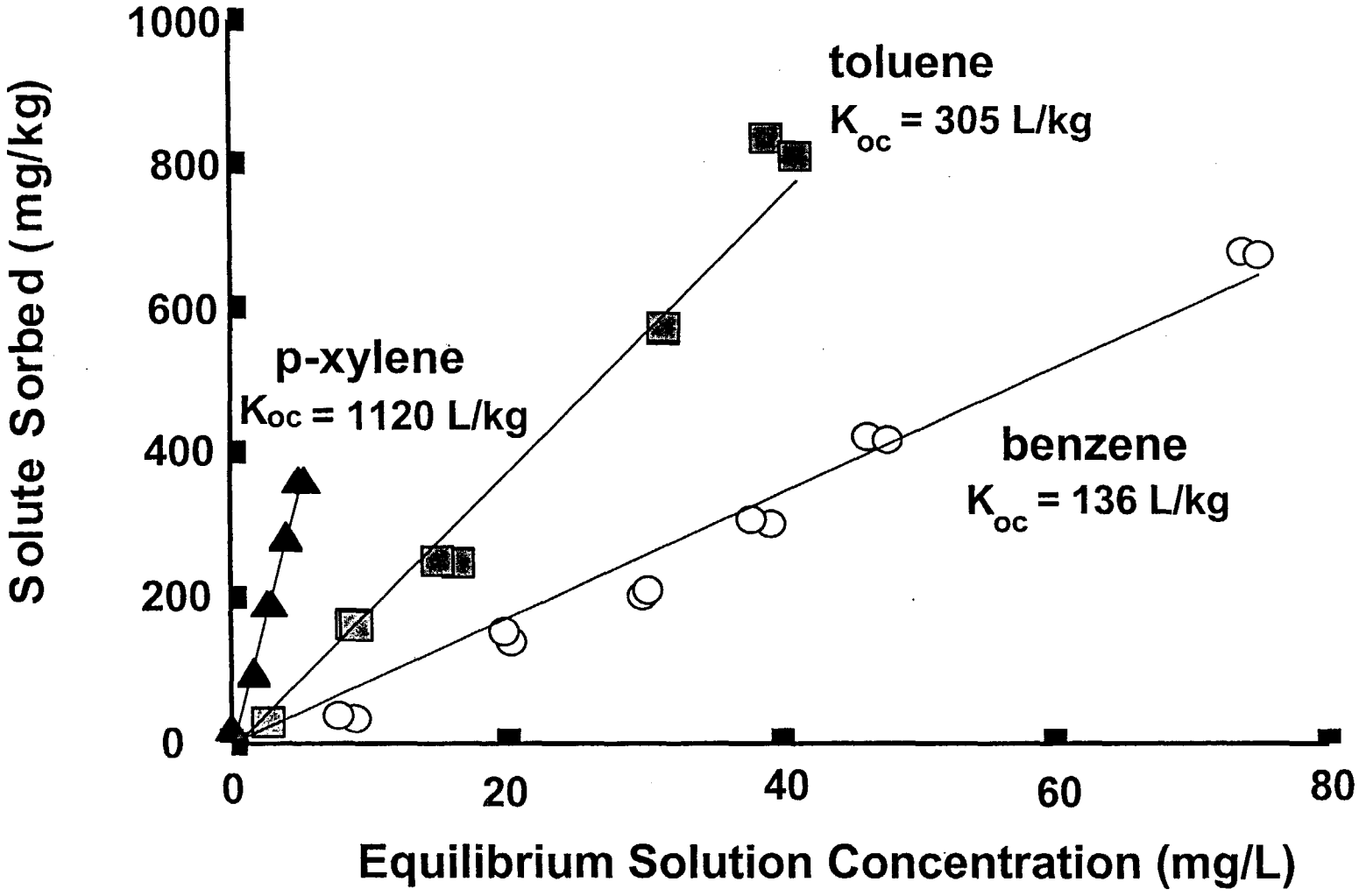
Permeable Barrier Technology



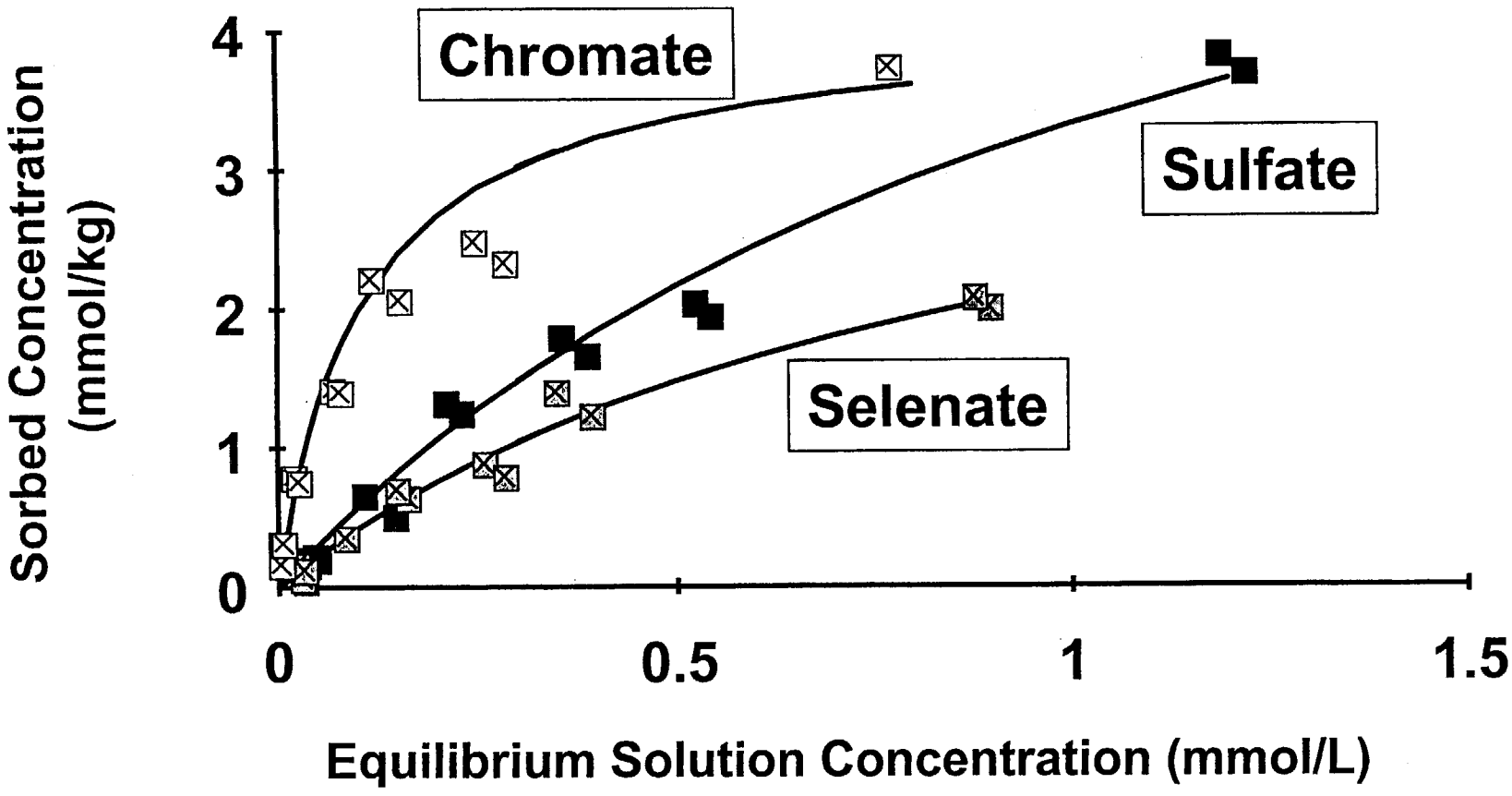
SMZ Sorption Technology



Organic Partitioning Batch Studies



Oxyanion Sorption
Batch Studies



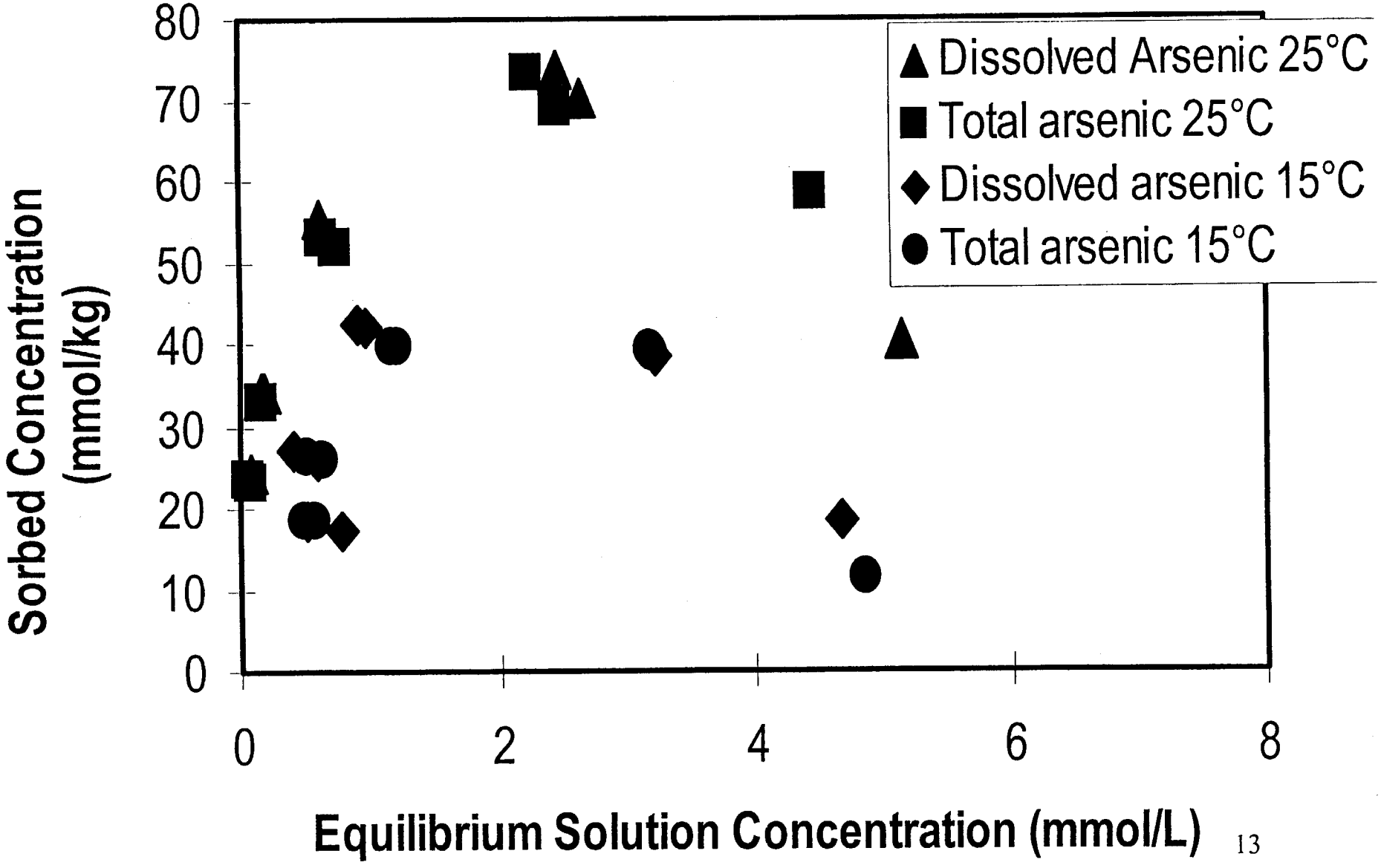
Synthetic Leachate

- Kennet "A" glacial till soil
- 5 x 150 g batches leached with 750 ml each of 0.1 N NaOH (pH>14)
- Fractions combined and diluted to 6L
- Spiked with $Na_2As_2O_5$ to ~500 mg/L As
- pH readjusted to >12 immediately before batch studies began

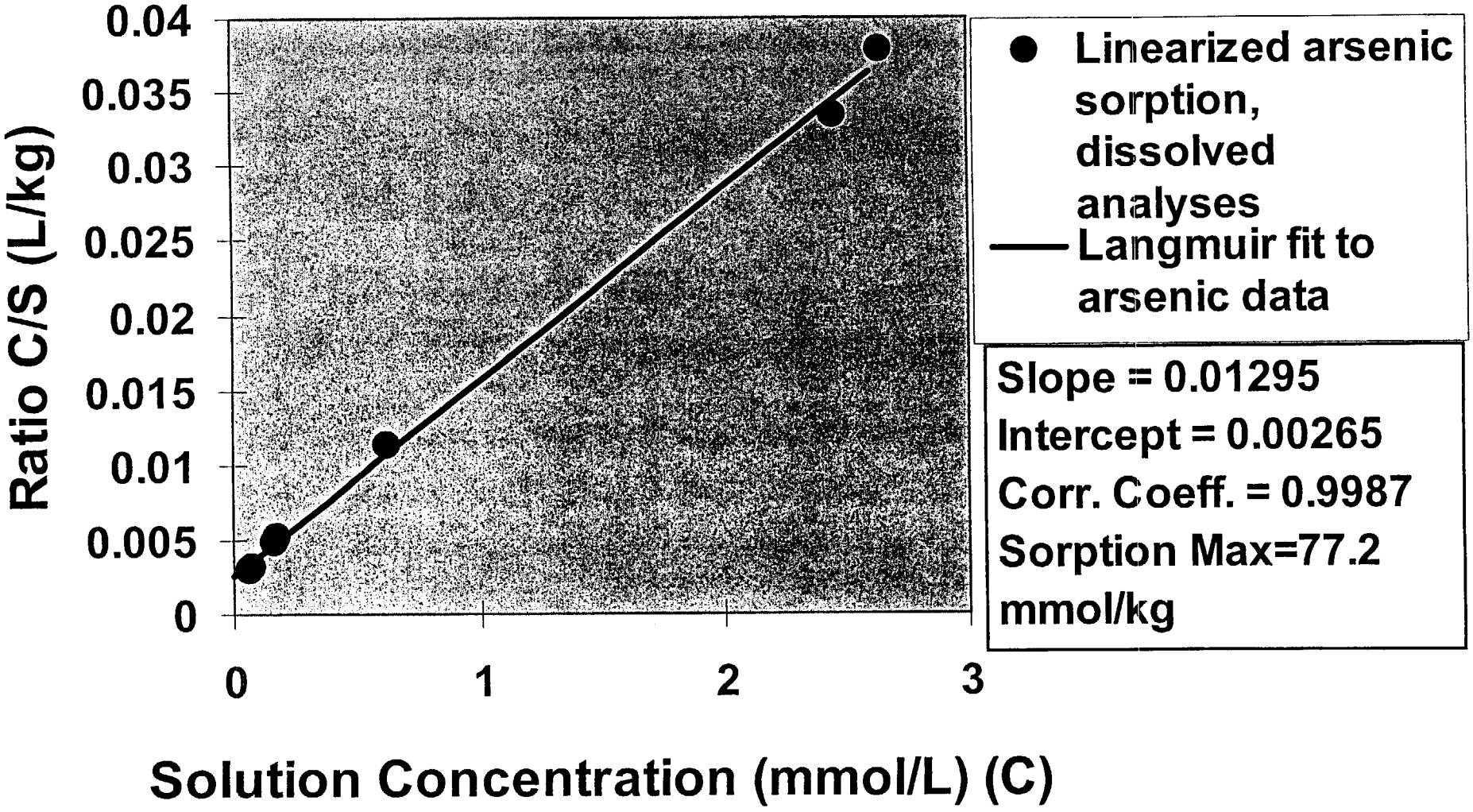
Batch Study Methods

- Variable leachate:SMZ ratios
  - 40:1 to 4:1
  - SMZ prepared to 150 meq/kg zeolite with HDTMA-Br
  - Appropriate DI blanks and duplicates
- Temperatures 15C and 25C
- pH 12 (initial), final pH = 11.8-12.6
- Equilibration time 24 hours
- Centrifuge at 19800x*g* for 45 minutes
- Analyses (Conoco Analytical Labs):
  - EPA 7060 for dissolved and total As in Solution
  - EPA 7060 with digestion for total As on solids
  - EPA method 9060 for TOC in solution

Arsenic Sorption at 15°C and 25°C

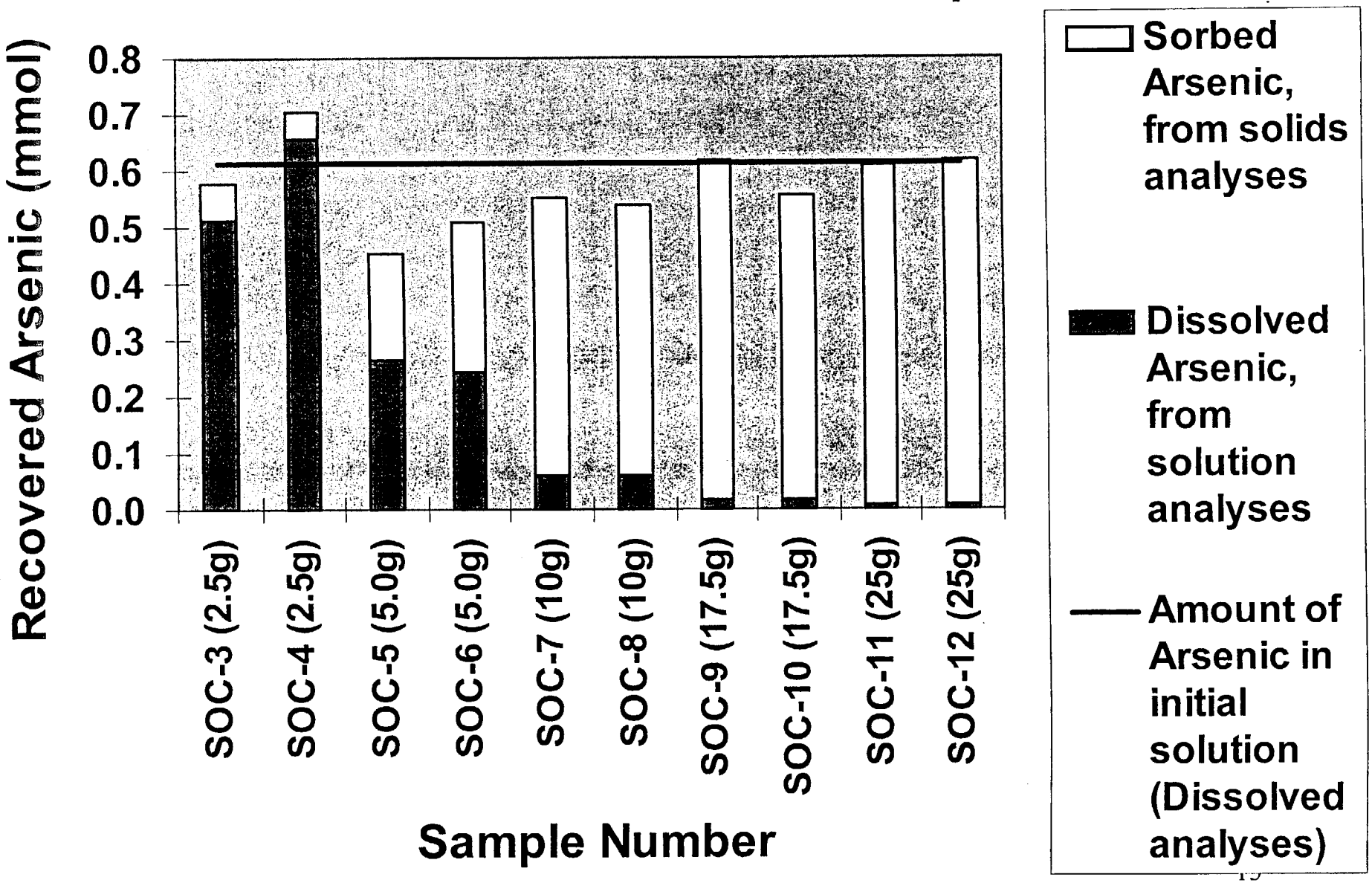


Langmuir Analysis for Sorbed Arsenic, 25C Batch Study

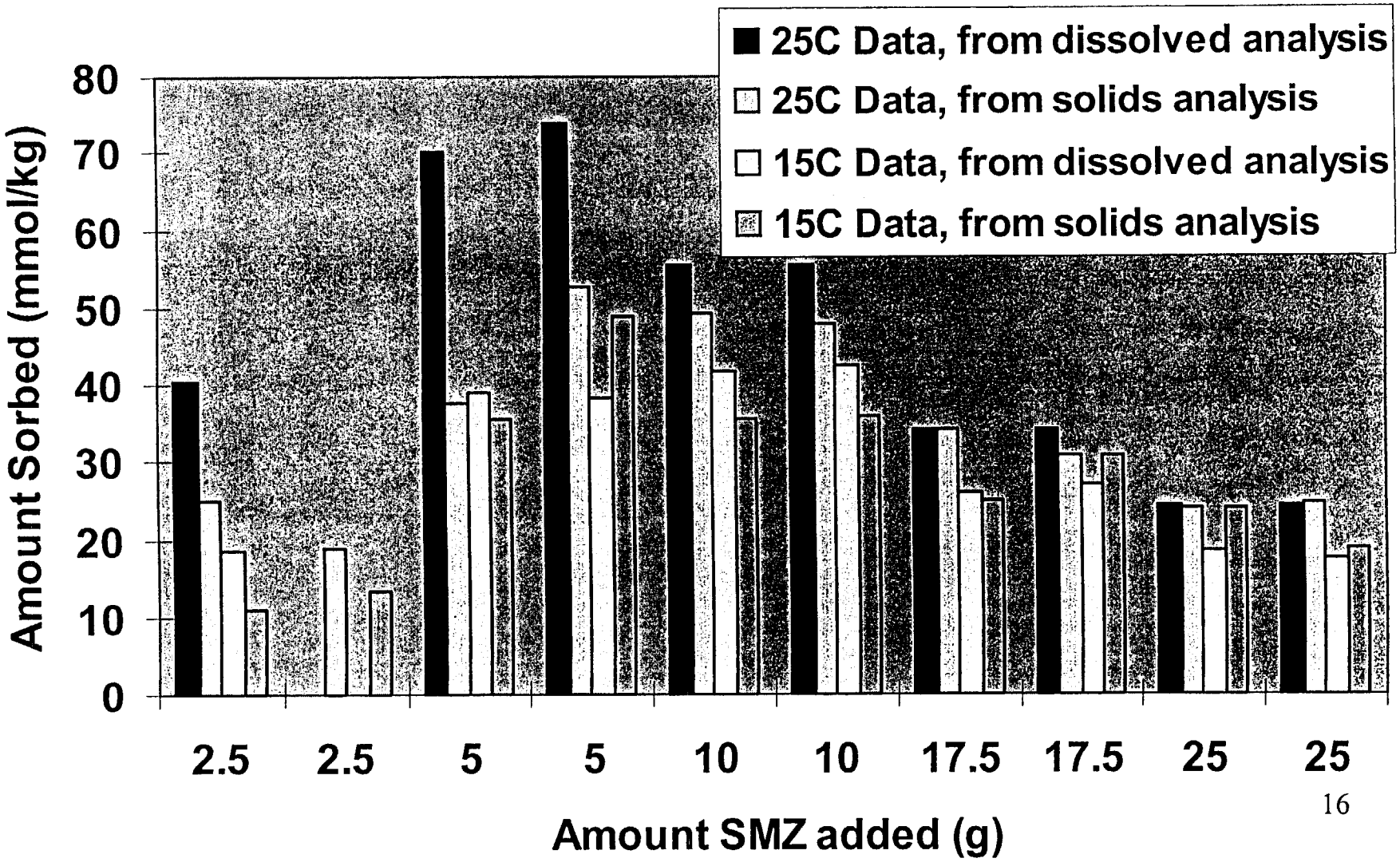


Data for samples containing 2.5 g SMZ omitted.

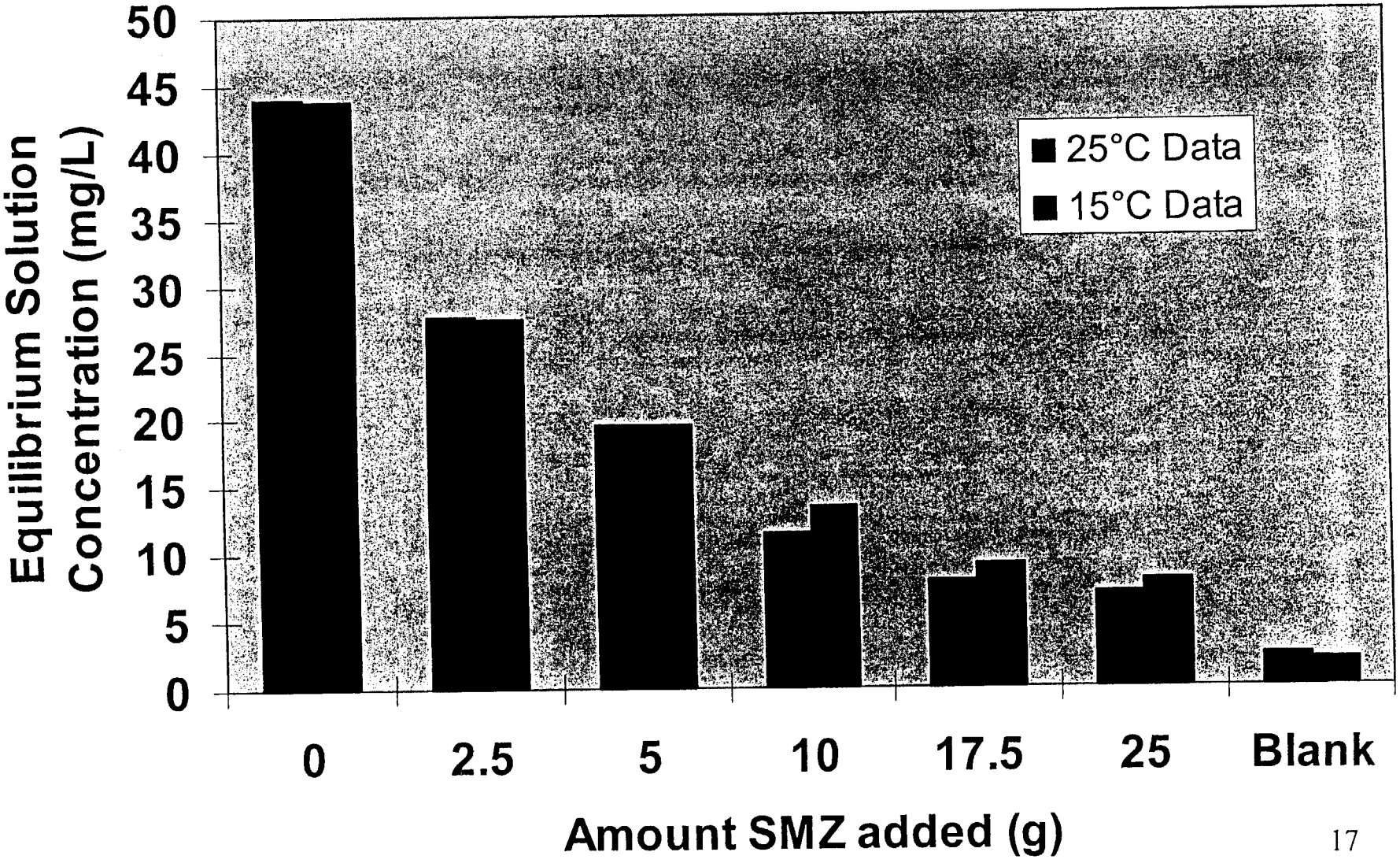
Arsenic Recovered in Batch Samples, 25°C



Arsenic adsorbed on SMZ solids corrected for wet weight and solution contributions



Total Organic Carbon Content of Leachate after Treatment with SMZ



Study Conclusions

- SMZ successfully sorbs arsenate from solution; mechanism are anion exchange, possibly partitioning for OC-complexed As
- Also sorbs organic carbon/decolorizes (partitioning)
- Higher temperature shows more complete sorption
- No negative effects from high pH
- Prediction of maxima, mechanism is feasible
- Costs therefore can be predicted
- Future work should include column tests