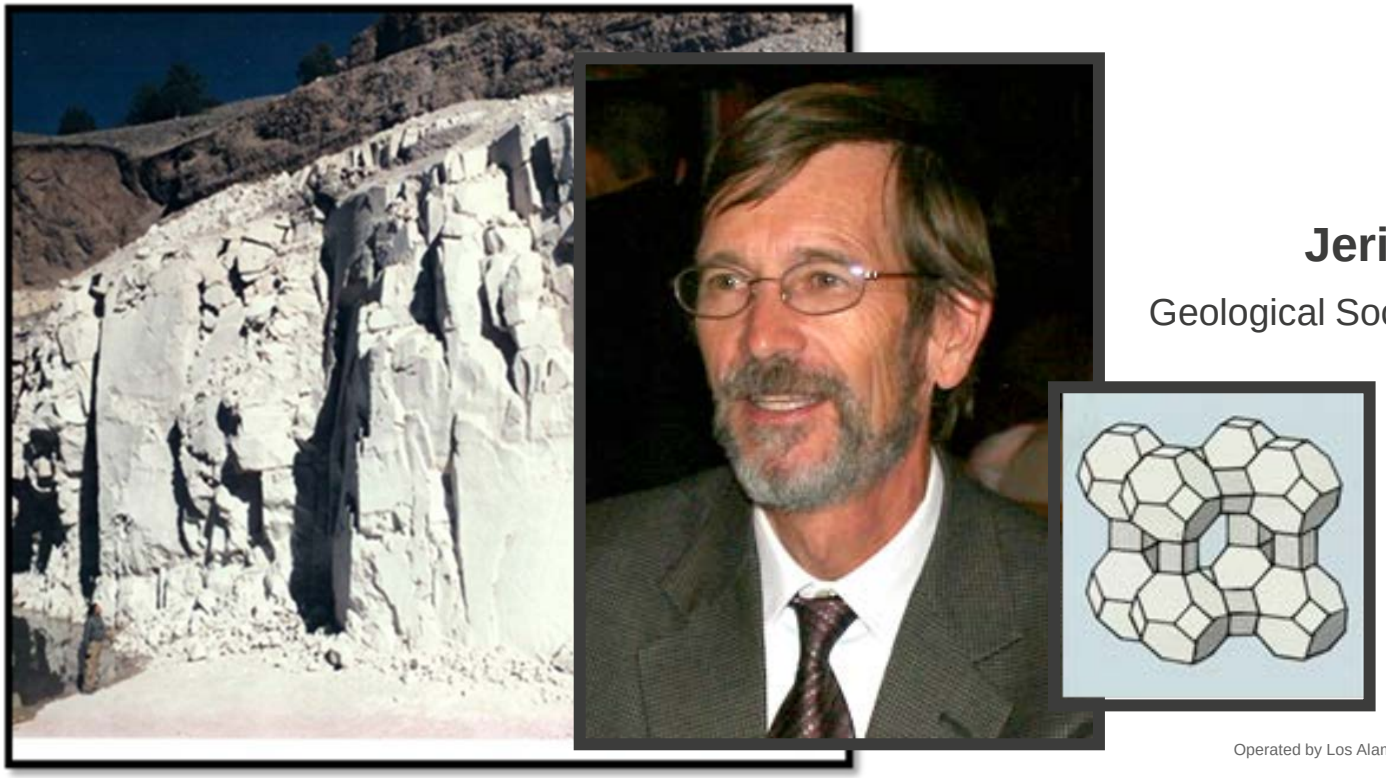
Rob Bowman and the Advent of Surfactant-Modified Zeolites

T104. From Pores to Mountains, and Minutes to Millennia: Session Dedicated to the Contributions of Rob Bowman, Fred Phillips, and John Wilson



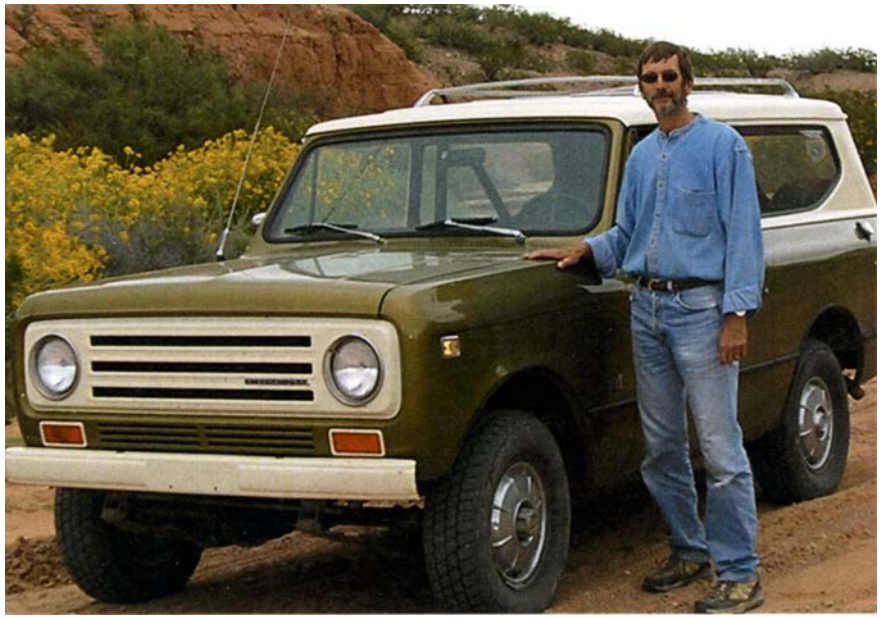
Jeri Sullivan Graham

Geological Society of America, Denver

September 28, 2016

Outline

- Some History…
- What is SMZ?
- What did Rob and his students find out about it? (Hint: a lot….)
- Multiple uses
- St. Cloud Mine
- IX Power
- Recollections
- Collaborations



Some History

- Rob's original idea?
- New sorbent for environmental contaminants
- First major publication-ES&T
- Original tests on organics
- Inorganics included for "completeness"
- Surprise-anion interactions
- Next steps: Why? How? Mechanisms?

Environ. Sci. Technol. **1994**, *28*, 452–458

Sorption of Chromate and Other Inorganic Anions by Organo-Zeolite

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Department of Geoscience and Geophysical Research Center, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801

We performed batch sorption experiments that showed a significantly enhanced removal of inorganic oxyanions from aqueous solution by clinoptilolite-dominated zeolite modified by the quaternary amine hexadecyltrimethylammonium (HDTMA). Since HDTMA is too large to enter into the internal portion of the zeolite, sorption of the amine only occurred on the zeolite's external exchange sites. HDTMA was exchanged with extrastructural cations of the zeolite up to the external cation-exchange capacity. The HDTMA-modified surface was stable when exposed to extremes in pH and ionic strength and to organic solvents. While the natural zeolite had no affinity for the oxyanions, the HDTMA-modified zeolite showed significant removal of chromate, selenate, and sulfate from 0.005 M $CaCl_2$ aqueous solution. Sorption data for each anion were well-described by the Langmuir isotherm equation. We found that anion sorption was highest when the zeolite was modified such that HDTMA satisfied 100% of its external cation-exchange capacity. The mechanism of anion retention appears to be the formation of an HDTMA-anion precipitate on the zeolite surface.

Introduction

Zeolites are hydrated aluminosilicate minerals characterized by cage-like structures, internal and external surface areas of up to several hundred meters squared per

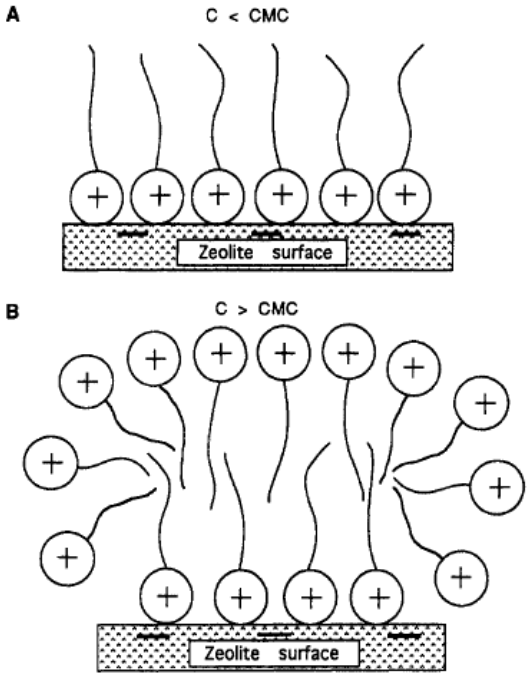
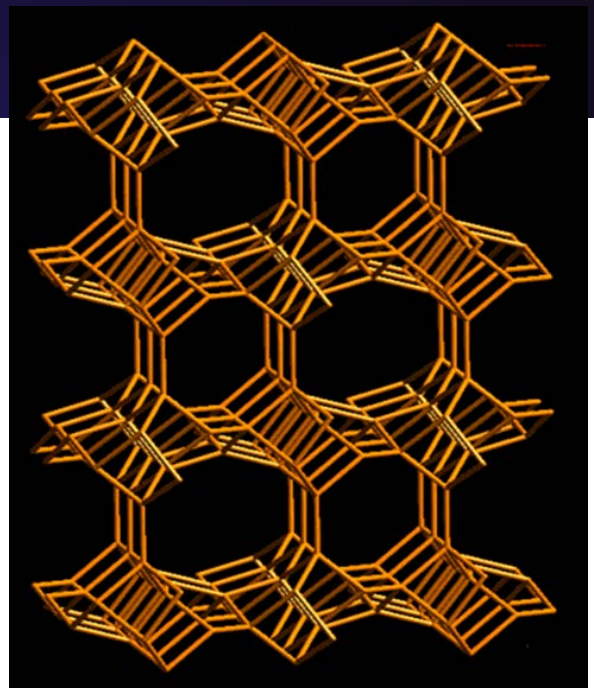
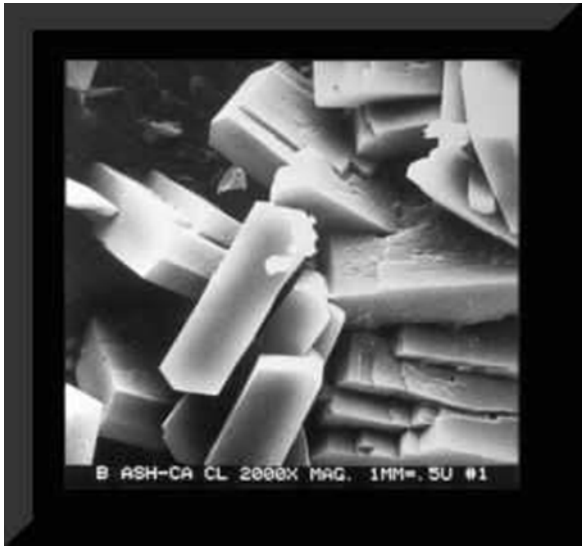


Figure 1. Hemimicelle (A) and admicelle (B) formation by cationic surfactants on zeolite surface.

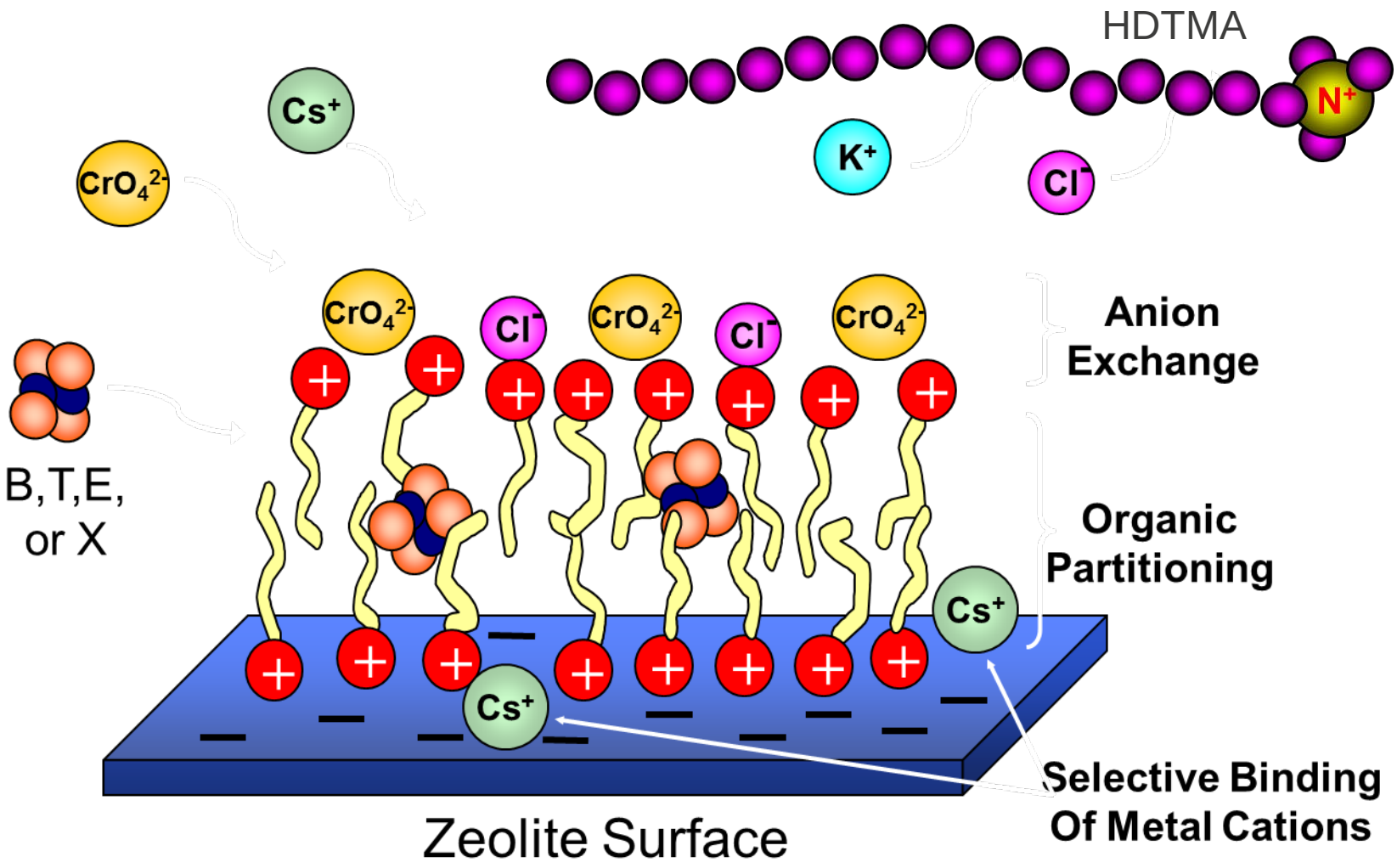
What is SMZ?
Properties of Zeolites

- Hydrated aluminosilicates, e.g. clinoptilolite, heulandite, chabazite
- $(Ca, Na_2, K_2)(Al_6Si_{30}O_{72})\cdot 24H_2O$
- Cage-like structures with Angstrom-sized pores
- Crystals on the ~1cm scale or smaller
- High cation exchange capacities (~1meq/g)
- High internal and external surface area (100's m^2/g)
- No shrink-swell behavior
- Natural zeolites have about 45 known structures
- Occur as aggregates in deposits worldwide
- Derived from hydrothermal weathering of volcanic tuffs
- CHEAP! $0.05-0.20/kg
- Mined in New Mexico, Mountain West, Internationally (Italy, China, S. Korea, Japan, Turkey, Jordan)



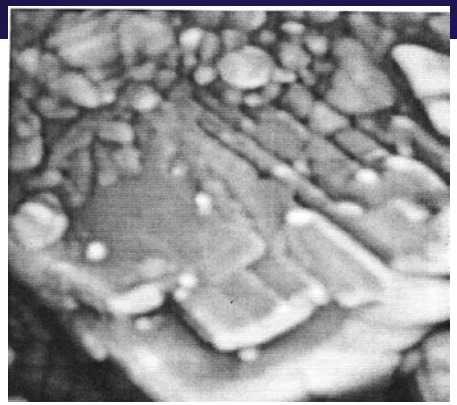


What is SMZ?
Properties of Surfactants



What did they find out about SMZ?

- Structure
- Composition
- Sorption
- Function
- Multi-ion interactions
- Durability
- Reusability
- Regeneration
- Microbial interaction
- Counterion effects



JOURNAL OF COLLOID AND INTERFACE SCIENCE 206, 369–380 (1998)
ARTICLE NO. CS985764

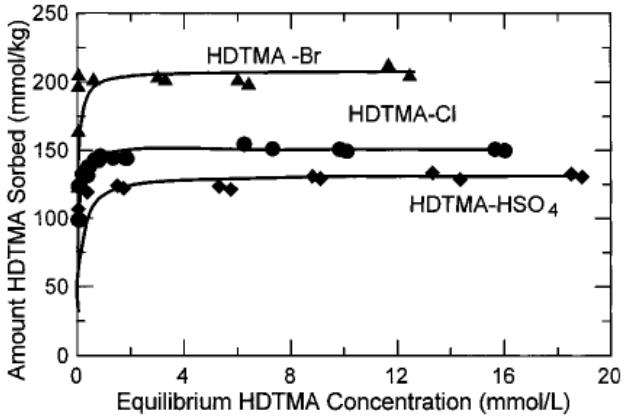


FIGURE 1. Effect of counterions on HDTMA sorption to zeolite. Solid lines are Langmuir fits to the observed data using the parameters in Table 1.

Thermodynamics of Cationic Surfactant Sorption onto Natural Clinoptilolite

E. J. Sullivan,*,[1] J. W. Carey,† and R. S. Bowman*

*Department of Earth and Environmental Science and Geophysical Research Center, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801; †Los Alamos National Laboratory, EES-1, Los Alamos, New Mexico 87545

Received January 31, 1997; revised July 6, 1998; accepted July 21, 1998

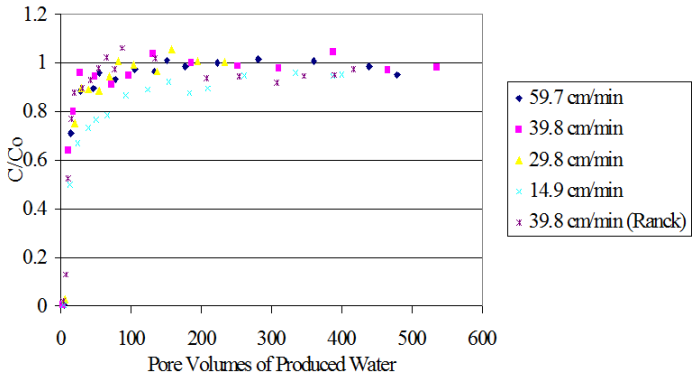
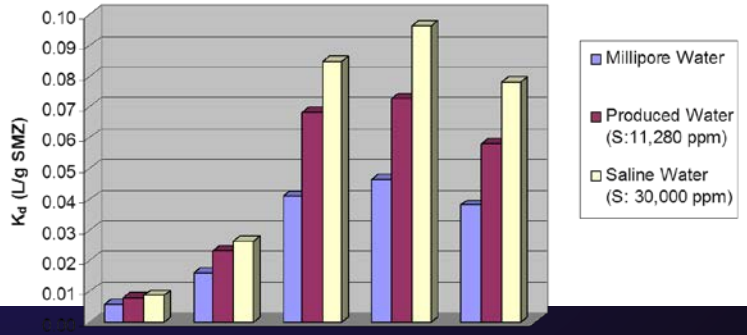
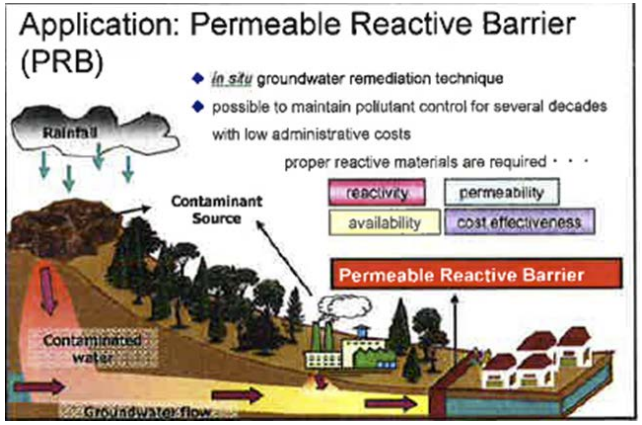


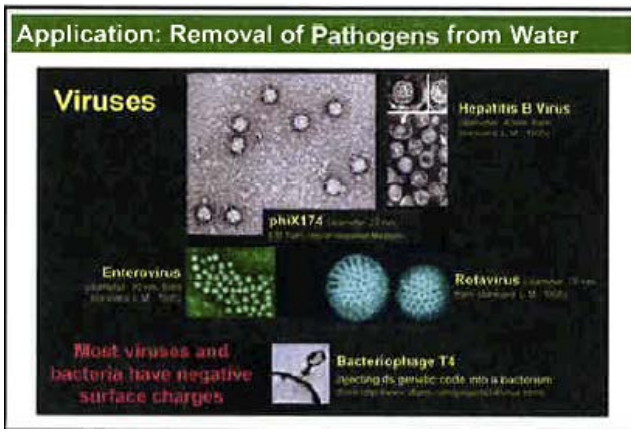
Figure 2. Benzene sorption on virgin SMZ

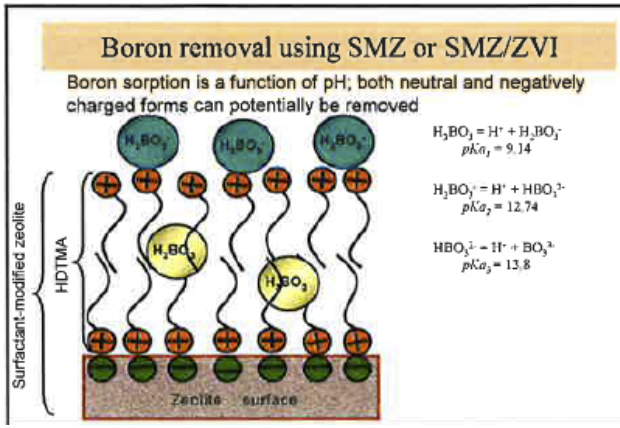


Multiple Uses

- Organic (nonpolar) adsorption
- Inorganic adsorption-cations, anions
- Microbial interactions and antimicrobial function
- Surface water remediation
- Ground water remediation-permeable barriers for PCE, Chromate
- Well protection
- Treatment of challenging wastewaters-mine drainage, produced water
- Engineered system designs
- Costs to use and treat







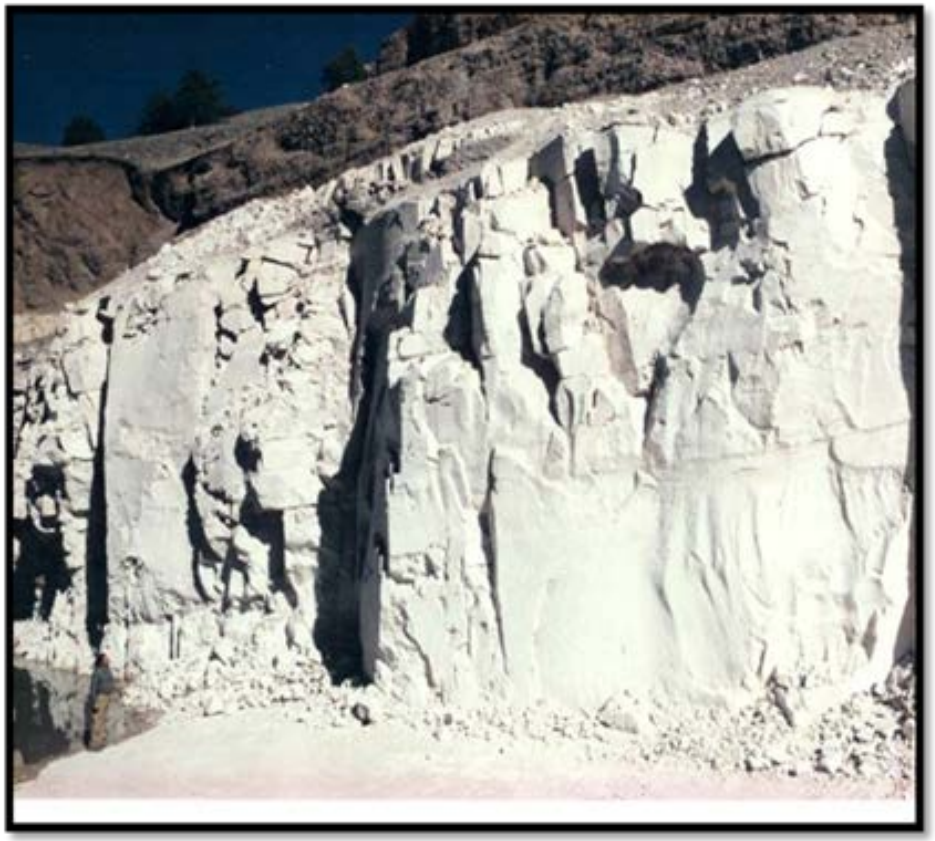
St Cloud Mining

Winston, NM Clinoptilolite

- **Primary Exchangeable Cations**: Calcium, Potassium, Magnesium
- **Major Markets**: Animal Feed, Water Treatment, Odor Control

Bowie, Arizona Chabazite

- **Primary Exchangeable Cation**: Sodium or Calcium
- **Major Markets**: Radionuclide Capture, Desiccants, Specialty Applications



Ash Meadows, Nevada Clinoptilolite

- **Primary Exchangeable Cations**: Sodium, Potassium
- **Major Markets**: Water Treatment, Turf Products, Animal Feed

St Cloud Applications

- **Fukushima Daiichi plant cleanup (Tc^{99} and oil)**
- **Oily wastewaters and produced water**
- **In situ mine wastewater cleanup**
- **Nitrogen recovery from wastewaters**

Passive AMD And Metals Removal: SCM Zeolites have been successfully used in active and passive systems around the US. Currently Thallium at the Kendall Mine in Montana, Uranium at the Homestake Uranium Mill in Grants, New M and AMD and heavy metals From the Lead Queen Mine near Patagonia, Arizona are in service.

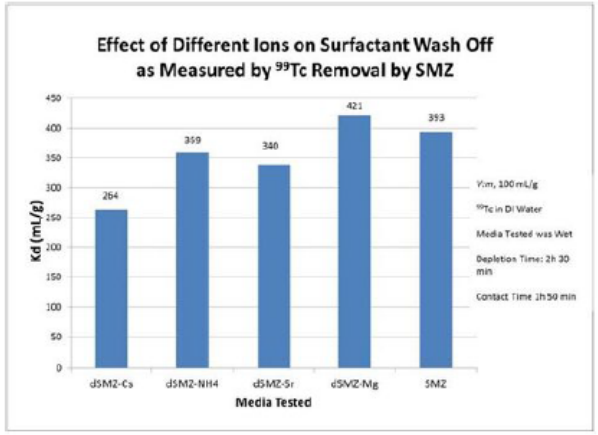


Figure 7.a) Qualitative determination of media oil uptake by fluorescence b) quantitativ determination of surfactant retention of oil by the indirect removal of Tc 99.

KURION PROCESS AND SKID DESIGN Source: Denton et al. 2011

IX Power

- Licensee for the SMZ-VPB-MBR patent
- Multiple products for wastewater treatment
- >$5M venture capital investment

http://www.ixwater.co/ix-water-products/

US007767078B2

(12) **United States Patent**
Sullivan et al.

(10) **Patent No.: US 7,767,078 B2**
(45) **Date of Patent: Aug. 3, 2010**

(54) **SYSTEM FOR TREATING PRODUCED WATER**

(75) Inventors: **Enid J. Sullivan**, Los Alamos, NM (US); **Lynn Katz**, Austin, TX (US); **Kerry Kinney**, Austin, TX (US); **Robert S. Bowman**, Lemitar, NM (US); **Soondong Kwon**, Kyungbuk (KR)

(73) Assignee: **Los Alamos National Security, LLC**, Los Alamos, NM (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **12/202,007**

(22) Filed: **Aug. 29, 2008**

(65) **Prior Publication Data**

US 2009/0101572 A1 Apr. 23, 2009

Related U.S. Application Data

(60) Provisional application No. 60/999,463, filed on Oct. 17, 2007.

(51) **Int. Cl.**
C02F 3/00 (2006.01)

(52) **U.S. Cl.** **210/150**; 210/151; 210/220; 210/269; 210/416.1

(58) **Field of Classification Search** 210/150–151, 210/220, 269, 416.1

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International Search Report for PCT/US08/80262, International Searching Authority, May 5, 2009, pp. 1-9.

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Primary Examiner—Chester T Barry
(74) *Attorney, Agent, or Firm*—Samuel L. Borkowsky; Samuel M. Freund

(57) **ABSTRACT**

A system and method were used to treat produced water. Field-testing demonstrated the removal of contaminants from produced water from oil and gas wells.

Commercialization

- **IX Power awarded global license to LANL SMZ technology in 2013**
- **Began 2 year product development in consult with O&G industry**
  - Field testing and commercial field trials
  - Deep-dive into regulatory and field operations
- **Backed by private equity and founders**
  - IX Power has 25 years of DOE tech commercialization & product development experience
- **To date ~$5M raised and expended with $5M more anticipated for future development of the IP.**

Current Product Line

- **IX Water OG**
  - PW solution
- **IX Water Blü**
  - Drinking water (metals, As)
- **Both are**
  - Modular: 60 to 1,200 gpm
  - Reusable media
  - 99% effective: metals, organics, TSS, scalants
  - $0.23 to $0.47 / bbl

Students-in their own words….

- Grace Haggerty
- Jeri S. Graham
- George Li (postdoc)
- Julia Whitworth
- Emily Keene
- Ioana Witkowski
- Steve Roy
- Kirk Jones
- Craig Altare
- Mike Ranck
- Alana Fuierer
- Elaine Darby
- Mike Owen
- Soondong Kwon (UT-Austin)
- Jaron Andrews
- ***And others…….***

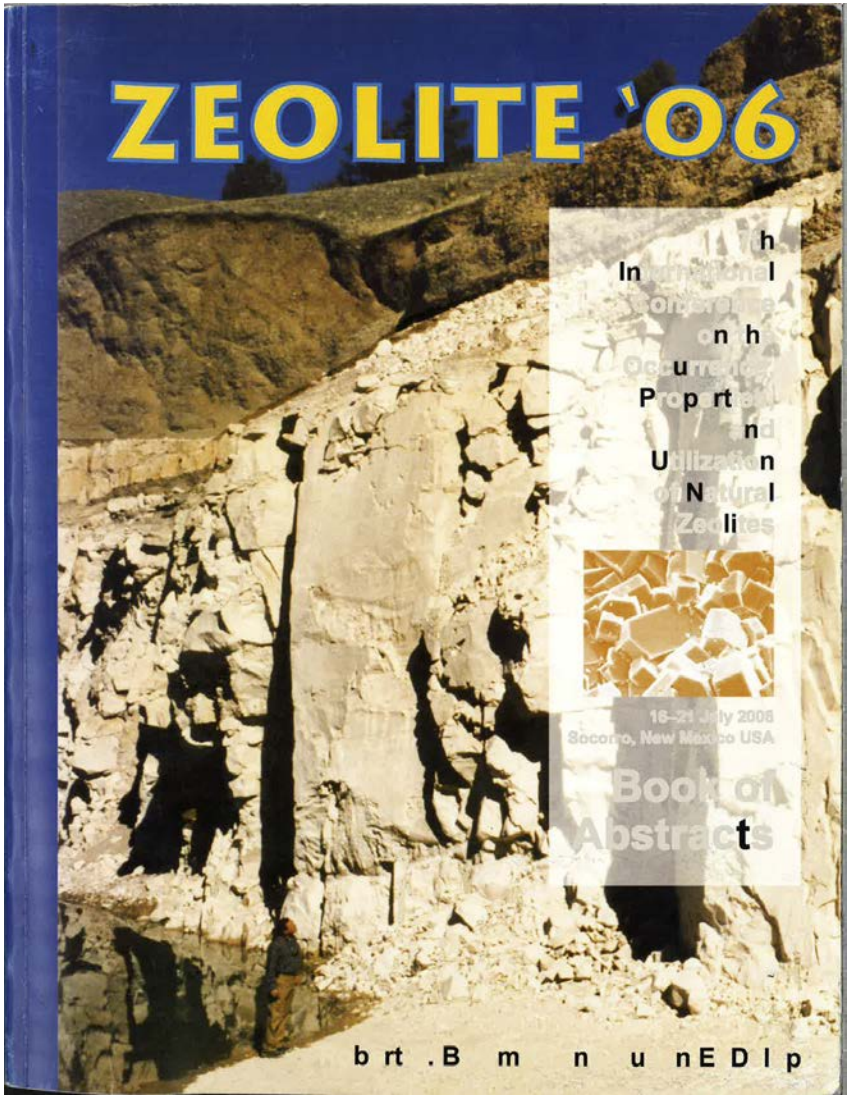
George Li*: "I took a postdoc position with Rob from 1995 to 1998. During a phone interview, Rob said: "This project will deal with technical details of practicality and applicability of SMZ and may not involve in cutting edge research that results in high impact publications that are required for a postdoc to find a teaching job. However, these daily routine works may also lead to important discovery if you have an inquisitive mind and trustful experimental results." This latter emphasis helped me to extract valuable information from our initial screening of different surfactants for zeolite modification. Our first paper "**Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite"** published in ES&T in 1997 resulted in more than 200 citations per Web of Science."*

Ioana Witkowski*: "Rob gave me the opportunity to do a column research study on chromate removal by surfactant modified zeolite (SMZ). He was my thesis advisor at New Mexico Tech. I am very grateful for the time he took in teaching, guiding and supporting me through my research. His knowledge and dedication to the SMZ field brought many advances in the permeable barrier technology field. Because of Rob and his passion for his work, I became interested in geochemistry and that led me to a position at Los Alamos National Lab. I also became an amateur mineral collector. I am forever grateful for what Rob Bowman did for my career."*

Julia Whitworth: "*Rob was my MS thesis advisor for a study of surfactant-modified zeolites (SMZs). Although we probably had too-robust a modified zeolite production method (involving a paint mixer and a lawn mower blade!), Rob was a thoughtful and supportive adviser, always ready with good advice but also willing to let me find my own way of solving problems – which should be one of the primary goals of education, after all. Today, I frequently see papers on the removal of contaminants from groundwater using SMZs, including BTEX, phenols, toxic elements such as As, and even biological pathogens….Rob was definitely a leader in this field that has born great fruit in various applications today."*

Zeolite ‘06

- 7th International Conference on Occurrence, Properties and Utilization of Natural Zeolites
- July 16-21, 2007 Socorro, NM, USA
- Rob headed local organizing committee and edited abstracts with Susan Delap
- Session on the Legacy of Fred Mumpton
- 8 invited papers and 128 contributed papers
- Mine tours, a barbecue, and a rodeo!



National and International Collaborations

- Japan: Dr. Keiko Sasaki, Kyushu University (2007) 6-week sabbatical visit by Rob to Kyushu
- NEDO PRB System proposal for Boron and Fluoride removal from groundwater (2008) with D.W. Blowes, UW (Canada) and K. Sasaki
- M. Hashimoto, Kurita Water Industry-field site characterization
- Chihuahua, Mexico-Pathogen removal from groundwater –field site testing of well-bore SMZ packing
- Many U.S. and European collaborations and “cross-pollinations”-Texas, New York, Greece, Italy, Slovenia, UK…….

- Special collaboration and patents with UT researchers Lynn Katz and Kerry Kinney

Many Thanks to:
Karen Bowman, Dan Eyde, Grizz Deal, George Li, Ioana Witkowski, and Julia Whitworth for their contributions.