Addressing Water Quality Impacts of Oil Shale Development – Modern Approaches for an Old Problem

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State-of-the-Science, 1980

- Detailed characterization of shale underway
- Effect of retort method on chemical and physical properties
- Leach tests – static and flow through aimed to derive steady state condition
- Chemical speciation/saturation established
- Reaction path, groundwater, and solute transport models emergent and enabled by development of new numerical techniques
Thirty years on…

- Superfund (CERCLA: Dec 1980), National Laboratories, Department of Energy, Military branches, Nuclear Regulatory Commission
  - Investigated causes, dispersal, and mitigation of diverse environmental contaminants
  - Superfund alone invested >$60billion
  - Stimulated emergence and maturation of fields of environmental geochemistry and contaminant transport
  - Demonstrated clear need for appropriate and sufficient pre-development background conditions in hydrology, geology, ecology

Photo: Brian Ray, Craig Daily Press
Pre-development Baseline

- Seasonal, annual, and decadal variability must be documented.
- Baseline developed using data prior to 1980 would have been inadequate.
Remote and Continuously Sensed Data

• Instrumentation and communications technology developed for continuous monitoring, remote sensing and imagery, and remote sampling of wide range of hydrologic and biogeochemical parameters AND wide range of time and space scales.

• Aids in establishing pre-development background and in project monitoring.

• CUAHSI’s Hydrologic Measurement Facility (Consortium of Universities for the Advancement of Hydrologic Science) is a good resource.
Geophysical Methods

- Refined from deep-earth methods to capture hydrologic and near-surface subtleties.
- Multi-method, cross-scale approach necessary.
- Schematic represents space and time process scales over which 1) x-band, 2) LIDAR, 3) LAS/SODAR, 4) EC/isotope sensor, 5) networked sensors, 6) TDR, and 7) GPR operate.

Jacobs et al., 2006
Mapping intra-sedimentary faults with aeromagnetic data, Albuquerque basin

Semi-linear, generally northerly-striking anomalies (2-10 nT amplitude) in the high-resolution aeromagnetic image (a) are primarily due to faults that offset different strata within the sedimentary basin fill. A map of these aeromagnetically inferred faults (b) substantially increases the information on faults known previously only from surface evidence (c). Improved fault knowledge directly improves hydrologic models

Blue cells - primary property inferred, Pink cells - secondary properties that might be inferred. (Grauch et al., 2001; Robinson et al., 2006)
Dynamic and scale-dependent fluid-rock reactions

- Molecular probes developed to examine surface and bulk chemistry, bonding environments, ligand geometries, valence states, and interactions:
  - High energy radiation (XPS, Auger, XANES, EXAFS) probe bonding environments
  - Lower energy radiation (IR, FTIR) combined with magnetic field (NMR, ESR)

- Microscopic techniques improved to provide spatially-resolved data at $\mu$m to nm scale, including hydrated and volatile species and living materials in natural fluid media
  - TEM, HR-TEM, STEM, ESEM, STM, AFM
What have we learned?

- Adsorption at mineral surfaces is complex:
  - not always a simple electrostatic force related to Zpc
  - specific functional groups govern organometallic adsorption

- Continuum from mononuclear adsorption of ions in solution to surface precipitation of a new phase

- Mineral surfaces participate actively
  - Dissolve, provide ions, electrons, control oxidation state
  - Surface micro-structural details localize reactions and organisms

- Microorganisms participate through intracellular and extracellular reactions

- Macroscopic chemical thermodynamic approach describes system behavior incompletely in low T biologically-mediated environments
Iron Sulfides in Mahogany Zone

- Low surface area As-bearing pyrite octahedra inter-grown with high surface area Mn-bearing pyrrhotite.
- Macroscopic surface and groundwater interactions with sulfides, as well as their behavior during retorting, is summation of reactivity of two phases.

Harrison et al., 1991)
Heterogeneous minor element distributions

- Complexities in leach test interpretations
- Time-dependent variations in chemical signatures

False-color electron microprobe wavelength dispersive elemental maps showing localized distribution of As-rich domains (bright areas) in pyrite in Alabama coal samples

(Kolker and Huggins, 2007)
Secondary minerals often control geochemistry

- Weathering of mine waste rock produces new phases and complex textures with high reactivity
- Pyrrhotite alters to native sulfur
- Pyrite and sulfur coated by Fe-HOXY
- Arsenic incorporated into scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$
- Batch leach tests give uncertain process information

(BSE image: Jeong and Lee, 2003)
Secondary soluble minerals

- Common in disturbed environments in arid climates
- Reactive and fugitive, complex crystallization sequences
- Many have strong affinity for trace metal sorption/desorption

- Alunite \( \text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 \)
- Alunogen \( \text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O} \)
- Copiapite (C) \( \text{Fe}^{2+}\text{Fe}^{3+}_4 \text{SO}_4\text{OH}_2 \cdot 20\text{H}_2\text{O} \)
- Coquimbite (Cq) \( \text{Fe}^{3+} \text{(SO}_4)_3 \cdot 9\text{H}_2\text{O} \)
- Epsomite \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \)
- Gypsum (G) \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)
- Halotrichite \( \text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O} \)
- Hexahydrite* \( \text{MgSO}_4 \cdot 6\text{H}_2\text{O} \)
- Jarosite \( \text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2 \)
- Melanterite \( \text{Fe}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O} \)
- Rhomboclase* (Rh) \( \text{HFe}^{3+}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \)
- Rozenite* (R) \( \text{Fe}^{2+}\text{SO}_4 \cdot 4\text{H}_2\text{O} \)
- Szomolnokite* (Sz) \( \text{Fe}^{2+}\text{SO}_4 \cdot \text{H}_2\text{O} \)
- Voltaite \( \text{K}_2\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O} \)

Rio Tinto, SW Spain; Buckby et al., 2003
Biogeochemical Coupling

- Microbes serve as catalysts, create intercellular micro-chemical environments, and may incorporate elemental components in biomineralization

- Oxidation of As$^{3+}$ and Fe$^{2+}$ leads to mixed valence Fe-As precipitates

Morin et al., 2003
And so.....?

- Microscopic and molecular scale processes govern rates and paths of environmental reactions

- Very careful, detailed characterization required to document spatial and temporal distribution of all relevant fluid-solid interactions

- Simple leach tests mask the longer term geochemical processes

- Kd approach is a lumped process parameter, presenting difficulties for risk assessment and forward prediction

- Upscaling from surface molecular and biochemical reactions to macroscopic approaches amenable to simulation and field-scale problems remains one of the *Grand Challenges* of both reactive transport modeling and molecular environmental geochemistry
Short event and seasonal variations in surface water chemistry

- Snow melt runoff and recharge, short precipitation events
- Variations in mixing components
- Dissolution of secondary phases

Alamosa R., CO (Rupert, 1997)

St. Kevin Gulch, CO (Kimball et al., 1999)
Seasonal variations in groundwater chemistry

- Snowmelt dissolves soluble sulfates and flushes metal-rich groundwater residing over winter.

- Snowmelt recharge introduces organic carbon and nitrogen and organic compounds into the groundwater.

Herbert, 2006
Computational Science

- Emergent in late 1970s
- Fully developed as the third scientific method
- State-of-the-practice to apply numerical simulation in evaluation of source, fate, and transport in surface and groundwater
- Short time periods characterize research to application transfer
- Look closely at cutting edge in model development as this has relevance to pre-development data collection
An Example: Reactive Transport

• Theory well constrained
• Processes operate from atomic to field scale over multiple time increments
• Geoscience research needs related to:
  “capture of scale-dependence of reactive transport processes, describing chemical microenvironments, coupling mechanical and chemical effects, reconciling field and laboratory reaction rates….,” (Steefel et al., 2005).
• Regulators expectations of the research community include
  “...more flexible, sophisticated, and user-friendly models..”
  “...access to realistic ranges of parameters relevant to field conditions..” “...guidance documents...common pitfalls...illustrative approaches...” (Nuclear Regulatory Commission, 2006).
• Interface between researchers and end-users is an implementation problem not clearly responsibility of either party
The Technology Transfer Dilemma

- During early development, many PIs and different organizations build targeted models. Limited to research applications.
- With time, a small number become more comprehensive and widely adopted.
- Efficiency of transfer, user training, broad applications.
- Feedback to scientific community, improved capabilities, better supporting data etc.
- However, contemporary, complex models need a more organized approach to achieve technology transfer.

Reaction Path/Chemical Model Development
(modified from Melchior and Bassett, 1990)
Numerical Models will be Community-based

- The Community Climate System Model is one way to organize scientific effort, accrue economy, and reach out to society.
- Improved focus for supporting research including databases, experimental and field test sites.
- Other models (Community Land Model, Community Atmospheric Model) interface easily.
- Multiple agency interest in these capabilities is leveraged to implement this approach.
- A robust solution to technology transfer from science to policy makers and regulators.

http://www.cccsm.ucar.edu/
Reactive Transport Simulation

- Approaches based on Yucca Mt., Hanford, and in limestone are relevant to in-situ and modified in-situ oil shale retort
- Matrix, fracture, and conduit components have distinctive flow and chemical reaction characteristics
- Matrix characterized by near-equilibrium kinetics or equilibrium chemistry
- Fractures characterized by higher flow rates and far-from-equilibrium reaction kinetics
- Preferential flow paths readily develop, creating larger conduits, turbulent flow and sediment transport
- Components combine to define water chemistry
- Seasonal variations in recharge change proportions of flow regimes and thus create seasonal variations in water chemistry
Reactive transport – Yucca Mt. example

- Unsaturated zone model
- Calculation of chemical reactions resulting from surface water infiltration
- Establish time needed to create pre-development steady-state background
- Calcite volume fractions at initialization and at simulation times of 100,000 yr. for matrix and fracture continua.
- Calcite precipitation in matrix is minimal, but is significant in fractures.
- Higher flow velocity of Ca-enriched groundwater enhances calcite precipitation rates in fractures, relative to matrix.

Browning et al., 2003
The Cutting Edge

- Coupling of atmospheric, land surface, hydrologic and biogeochemical processes to predict response to meteorological forcing
- “What are the effects of regional climate change on the dynamics of element cycling”? 
- NCAR community land model (CLM3) provides input to a variably saturated groundwater model (TOUGH2, TOUGHREACT (LBL))
- Preliminary results show improved water table predictions
- An important step towards sensitivity of groundwater to climate

Oldenburg et al., 2006; Pan et al. 2007
Lessons Learned from Summitville

August 12, 1999
Modern Summitville Mining History

1984  Galactic Resources Ltd. permitted for open-pit cyanide heap-leach Au mine. Mine permit included a water assessment of evaporation >precipitation.

1986  Mining and leach operations commenced. Cyanide detected leaking through avalanche damaged heap-leach liner.

1987  First reported release of cyanide-contaminated fluids into Wightman Fork. Assumption of "Zero-discharge" discarded. Galactic required to install water treatment facility.

1989  Cracks detected in earthen dike holding back leach pad ores. Water treatment capacity inadequate.

1992  Galactic declared bankruptcy, abandoned site water management activities

1995  Mining district declared a US-EPA Superfund Site; continued serious environmental impacts

1996-98

2005  Site and watershed remediation largely completed - $210m
What were missing links with science at Summitville?

• Inadequate watershed model – climate, geochemistry, surface/groundwater, regional background
• Poorly known infiltration behavior of clay-rich ore on leach pad
• Lack of risk analysis in geoengineering design
• Insufficient tools provided to regulators
• Pro-mining political environment
• Contemporary science must be more proactive at the oil shale policy and technology transfer interface
Today’s Summitville

• Restoration to a pre-mining condition will never be possible; hydrology and near-surface materials are permanently altered

• Off-the-shelf remediation does not work well
  – Recontouring, reseeding, and revegetation
  – Porous wall barrier clogs with Fe-HOxy
  – Higher maintenance costs than projected
  – Unattainable remediation standards

• Need innovative chemical and biological approaches to in-mountain pool remediation rather than mechanical “band-aids on a cancer patient”

A.N. Buckingham, CDPHE, pers. comm., 8/24/07
Best Practices for the Future

• *Mining Megasites: Lessons Learned* (National Academy of Sciences, 2005)
  – large, complex sites cannot be restored and must be managed in perpetuity
  – human health risk can be reduced; ecosystem impairment may be permanent
  – restoration of ecologic function (biocritiera) more realistic than reduction of chemical concentrations below specified concentrations

• Design data collection, evaluation and decision-making processes to be focused on a durable process for long-term site management

• Active involvement of all stakeholders – state, federal, community, private

• Define biological performance goals that include future land use and waive specific ARAR requirements if appropriate

• Appoint an advisory, independent, multidisciplinary science review panel

• Encourage alternative and innovative technologies

• Establish a trust fund to provide long-term support for stewardship of the land