SAND2010-6545P

Improving ISR Safety

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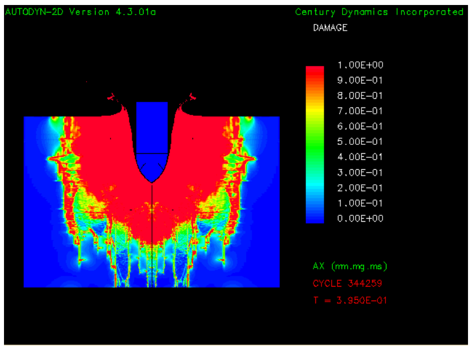
EPA Region 8 Office

Jim Krumhansl
Geochemistry Department
Geoscience, Climate, and Consequence Effects Center
Sandia National Laboratories*

*505-844-9093
jlkrumh@sandia.gov

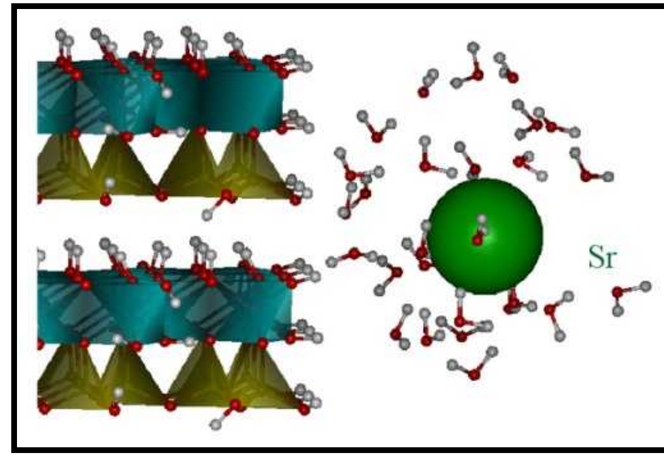
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia Earth Science Capabilities: Multiple Geoscience Resources Available to Address Problems

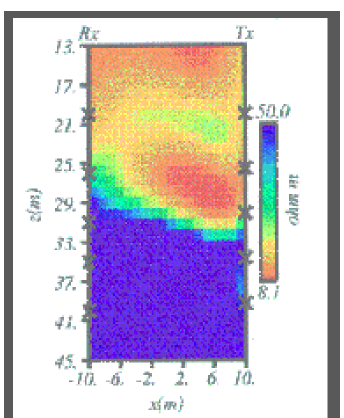


Geomechanics

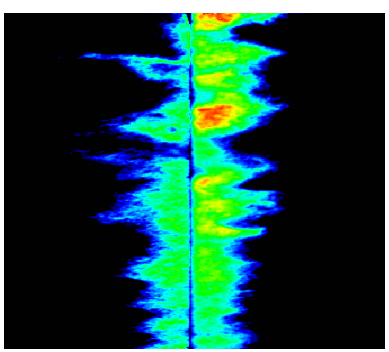
Geotechnology



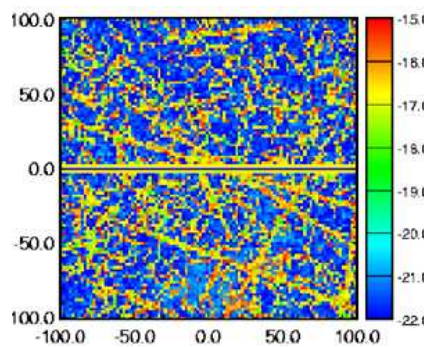
Geochemistry



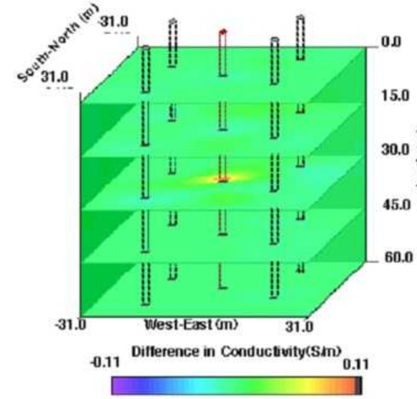
Geophysics



Geohydrology



Geostatistics



Numerical Modeling

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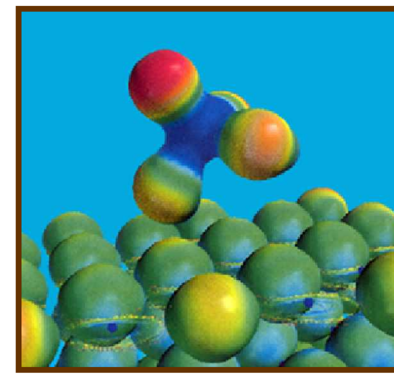
Earth Science Related Programs At Sandia

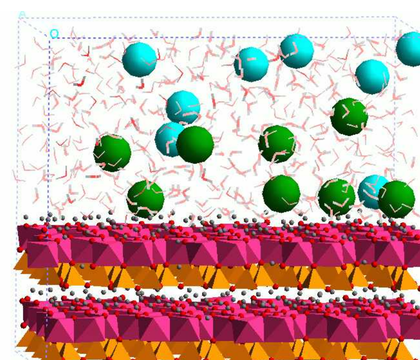
- WIPP and YMP – Radioactive Waste Disposal
- DOE Site Cleanup – Hanford, Savannah River etc.
- Strategic Petroleum Reserve
- CO_2 Sequestration – NETL Collaboration, Regional Collaborations, LDRD internally Sandia-funded programs
- Water Treatment – As Removal, SiO_2(aq) removal, desalinization, integrated water use studies
- BLM Delaware Basin Gas Migration Project
- DOE-BES basic research – EFRC, CFSES, Actinide Chemistry etc.
- Hence, over time Sandia has developed a significant level of understanding regarding interactions between man-made intrusions and the natural environment.

SNL Capabilities Applicable to U Resource Development

- Characterization of groundwater flow and radionuclide transport
  - Well tests and well test analysis
  - Tracer tests
  - Subsurface flow and transport modeling
  - Monitoring network design



- Water treatment
  - In-situ and Ex-situ Removal of Contaminants
  - Novel Membrane Technologies
  - Desalination and Water Reuse



- Integrated Geochemical Studies: Modeling, Laboratory and Field
  - Natural and engineered attenuation/sequestration of metals and contaminants
  - MD Simulations: sorption of radionuclides and interactions at water-mineral interfaces

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Challenges Associated with Current ISR Processes

- **Mobilization of Se, Mo, As, V, along with the Uranium in oxidizing environments**
- **General increases in groundwater salinity**
- **Mobilization of Rn and Ra**
- **Introducing complex organic compounds into the groundwater.**

- **U-Rich Lixiviant Water Chemistry (Air-CO_2-$NaHCO_3$ type leach)**
- Constituent Typical Concentration Range
- Calcium 100 - 350 - mg/l Magnesium 10 - 50 - mg/l
- Sodium 500 - 1600 - mg/l Potassium 25 - 250 - mg/l
- Bicarbonate 0 - 500 - mg/l Sulfate 100 - 1,200 - mg/l
- Chloride 250 - 1,800 - mg/l Silica (SiO2 aq) 25 - 50 - mg/l
- 226 radium 500 - pCi/l Uranium 50 - 250 - mg/l
- Conductivity 2,500 - 7,500 - µS/cm l pH 7-9
- Total Dissolved Solids 1,500 - 5,500 - mg/l

(From: Pelizza, 2008)

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Improvements in ISR technology may allow for more specific targeting of U – and less mobilization of other constituents

- **Suppress oxidation of non-U constituents**

  Phosphate can greatly slow pyrite oxidation but how will it impact U mobility?

- **Novel Use Of Complexing Agents**

  Carbonate is inexpensive but other options may serve provide additional benefits that outweigh costs

- **Target U^{+4} extraction and leave oxy-anions behind.**

  Isosaccharinic (ISA) and Gluconic Acids target tetravalent actinides.

sandstone uranium mineralization Showing natural mobilization of Uranium and associated elements.

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Models vs. Experiments vs. Field Tests

$ $ $

- Costs dictate the order in which questions such as this should be addressed.
- Reaction path codes (REACT, EQ3/6, PHREEQE) are particularly useful in providing an early understanding of chemistry-based performance envelopes.
- These codes basically compute the equilibrium states which evolve as constituents are mixed.
- Databases typically require modification and building informative models requires considerable process knowledge.

Typical REACT run script

```
Swap Calcite  for Ca++
100 g free Calcite
pH = 7.0
Na+ = 1600 mg/kg
Cl- = 2800 mg/kg
HCO3- = 500 mg/kg
ISA- = 1e-2 molal
SiO2(aq) = 30 mg/kg
Suppress Quartz Tridymite
Uraninite Chalcedony
Swap U++++  for UO2++
U++++ = 1e-20 molal
Swap O2(g) for O2(aq)
log  f  O2(g) = -64.2
React 10 g  Coffinite
go
```

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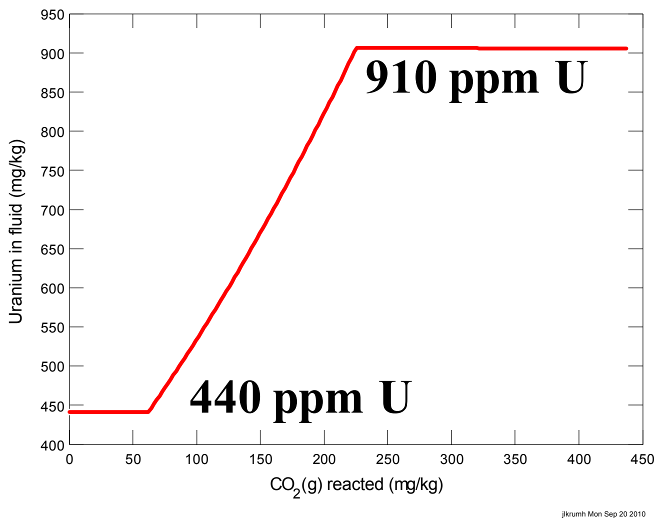
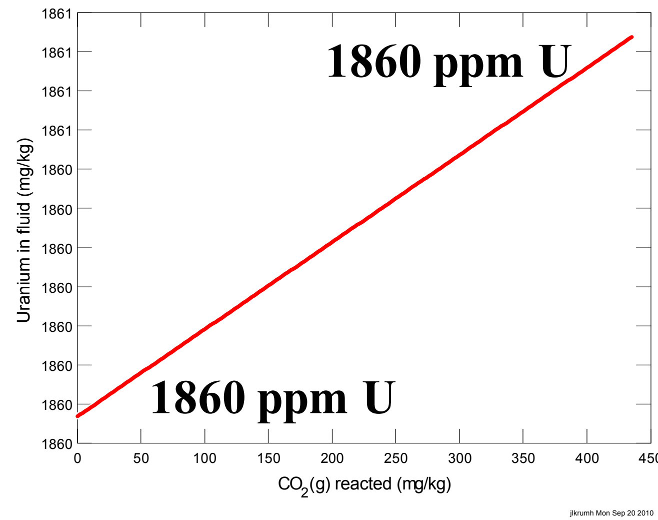
Phosphate may actually Help; REACT Model:

Calcite + Schoepite + CO_2(0.01 mole/l) in dilute fluid:
Na (1583 pm), Cl(2527 ppm), HCO_3(199 ppm)

- **No Phosphate**



0.01 Molal Phosphate



No exotic U-phosphate complexes enhanced solubility so the differences lie in which phases suppressed uranium solubility:

Final Minerals:	No PO_4	With PO_4
$(UO_2)_3(PO_4)_2$:$4H_2O$	-------	0.004999
$CaUO_4$	0.008049	-------
Calcite	0.9953	0.9914
Schoepite	0.3031	0.2808
UO_2CO_3	0.004846	-------

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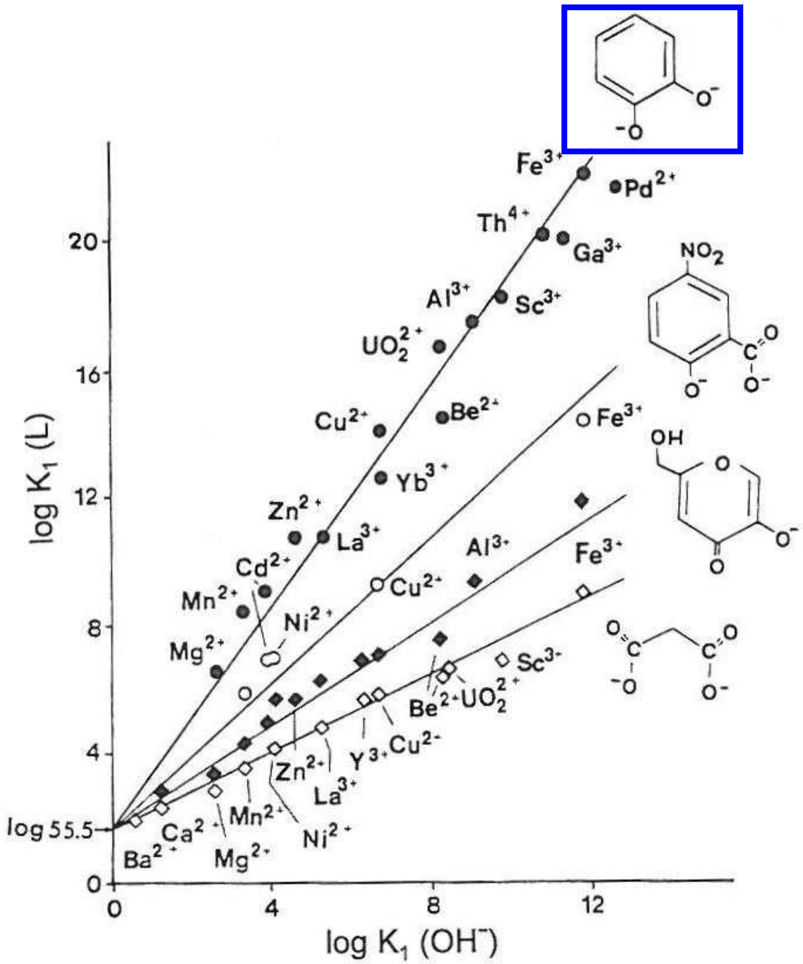
Novel Complexes May Enhance U-Recovery



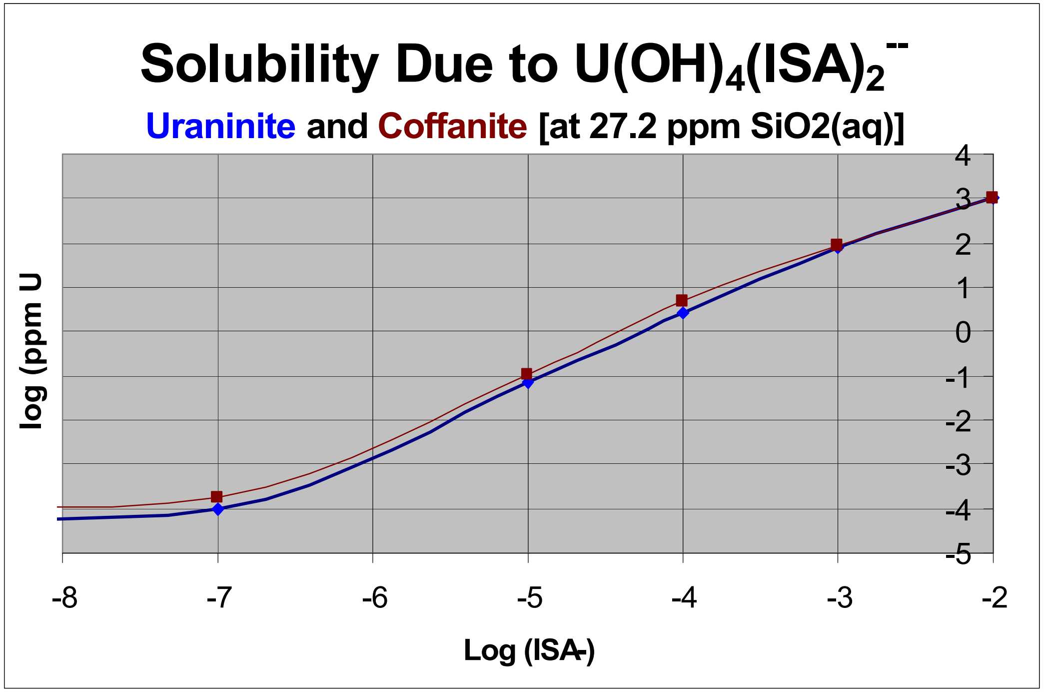
(From: Martell and Hancock, 1996)

The literature contains numerous systematic listings of potentially useful complexing agents – often with not very complex structures.

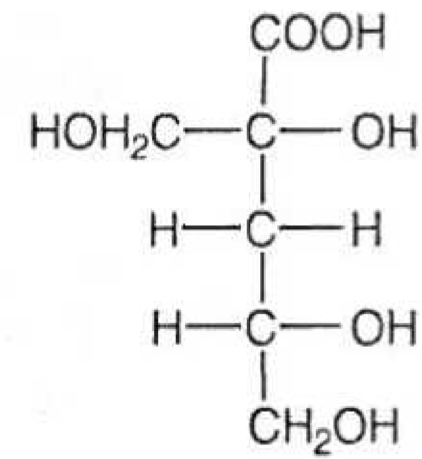
Catechol is an example: it is both the strongest complexing agent in its family and has a preference for higher-valent metals: Th^{+4}>UO_2^{+2}, <u>*also Silica*</u>!

Catechol may provide a significant advance in leaching ores rich in coffinite ($USiO_4$) without oxidation or mobilizing divalent metals.

Nuclear waste programs historically are concerned about Isosaccharinic Acid (ISA)



Based on Gonya et al., 2008



Ca-ISA is easily made by boiling a solution of lime and lactose-monohydrate.

ISA is another low cost option for putting U^{+4} into solution while maintaining a reducing environment.

UO_2^{++} hydroxide and carbonate complexes dominate in oxidizing environments.

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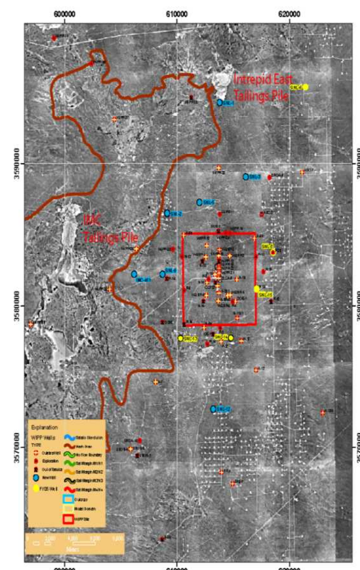
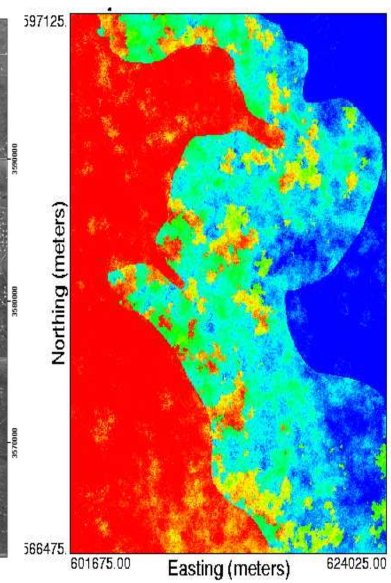
Another Approach Optimizes Hydrologic Design for *In Situ* Recovery

- **Unique SNL mobile hydraulic testing data acquisition capabilities for aquifer testing**
- **Unique SNL aquifer test analysis software**
- **Incorporate hydrogeologic facies and heterogeneity into 3D groundwater model**
- **Tracer test characterization of in-situ solute transport processes**
- **Stochastic modeling of subsurface flow and transport**
- **Optimized design of production and monitoring well networks**
- **Reduce and quantify uncertainty in production and remediation phase life cycle costs**

mobile aquifer testing trailer



geologic map



transmissivity map

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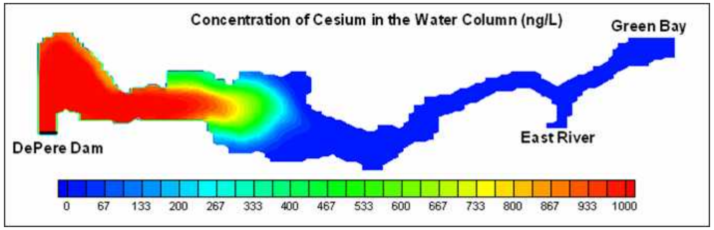
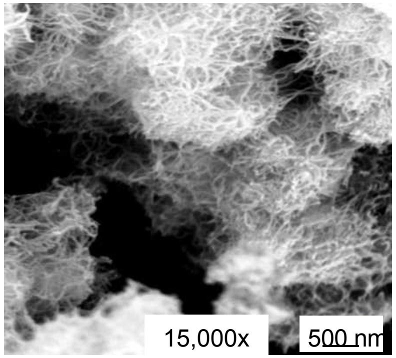
Additional SNL Capabilities Applicable to U Resource Development

- Disposal cell/landfill cover design and analysis
  - Geomechanical testing and analysis
  - Cell landfill cover design and analysis
  - Probabilistic, risk-based performance assessment
  - Sampling, site characterization, long-term monitoring



- Soil and Sediment Transport
  - Erosion and transport measurements
  - Contaminated sediment transport modeling
  - Habitat impacts

- Materials Development
  - Radionuclide getters
  - High capacity, rapid exchange materials that are element selective



Modified titanate: selective for U, Pu, Ac

- Performance Assessment
  - Probabilistic modeling
  - Sensitivity and uncertainty analysis

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Summary and Conclusions

- **Creative use of non-standard chemistry may provide new ways of targeting the extraction of uranium minerals while also providing environmentally friendly approaches that don't liberate oxy-anions or heavy metals.**
- **Sandia also has significant hydrologic capabilities for developing efficient well designs using advanced data collection systems coupled with fluid flow modeling.**

Patents pending.

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