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Geochemical Modeling: EQ3/6 and PHREEQC

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U.S. DEPARTMENT OF ENERGY NNSA

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History of Geochemical Codes on WIPP

- FMT (Fracture-Matrix Transport)(Babb and Novak, 1997)
  - Chemical equilibrium using the Pitzer aqueous model.
    - Transport was not supported in Version 2.0 used for WIPP actinide calculations
  - Only geochemical code approved by the EPA to perform actinide solubility calculations from the CCA to CRA-2014
- EQ3/6 (Wolery and Jarek, 2008)
  - Equilibrium-Speciation, reaction-path code for complex theoretical systems
  - Approved for WIPP since the CCA, approved for actinide solubility calculations since CRA-2014
- PHREECQ (Parkhurst and Appelo, 1999 and 2013)
  - Equilibrium-Speciation code with a multitude of capabilities
  - Some capabilities of Version 2.12.5 approved for non-actinide WIPP work in 2007

EQ3/6 and PHREEQC Capabilities

Capability	EQ3/6	PHREEQC
Speciation/Saturation	⚑	⚑
Phase Equilibrium	⚑	⚑
Temperature/Pressure	⚑	⚑
Oxidation/Reduction	⚑	⚑
Pitzer Aqueous Model	⚑	⚑
Reaction Path Calculations	⚑	Limited
Surface Chemistry	No	⚑
Transport	No	⚑
Many other capabilities	No	⚑

Roles of Geochemical Codes

- EQ3/6 has Superior Reaction-Path Capabilities
  - Because of its robust reaction-path capabilities EQ3/6 has been used on WIPP since at least 1990 (Brush, 1990). Reaction path calculations provide a detailed examination of complex systems that allow for complete forensic analysis of the causes of chemical changes in a system that a one-step equilibrium calculation does not. The 2008 SCA, “Verification of the Waste Isolation Pilot Plant Chemistry Conceptual Models, Final Report.”, provides many examples of this type of forensic analysis.
  - PHREEQC, using the REACTION key word, can simulate reaction paths but are limited in that its reaction steps are static whereas EQ6 uses dynamic stepping which allows phase boundaries to be clearly defined. Additionally, in PHREEQC the user must specify *a priori* which phases are allowed to form, while EQ6 tracks the saturation of all phases in the system that is being simulated and precipitates phases as they become saturated.
- What role can PHREEQC play?
  - There are many modeling tasks that do not require reaction-path calculations that would be greatly streamlined by having the ability to use PHREEQC, for example, the actinide uncertainty analysis.
  - PHREEQC would allow for examination of complex processes that EQ3/6 lacks capability. For example, surface complexation of actinides with ferrous mineral phases.

Questions?

References

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