Generating Thermodynamic Data for Geochemical and SNF Degradation Models: A First-Principles Approach

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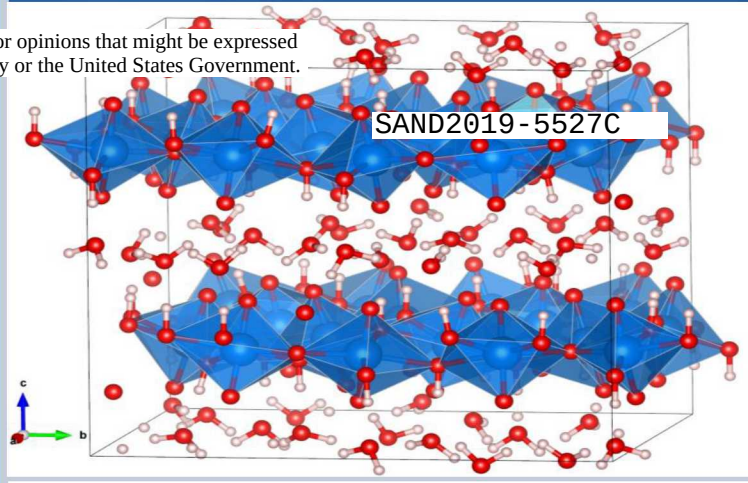

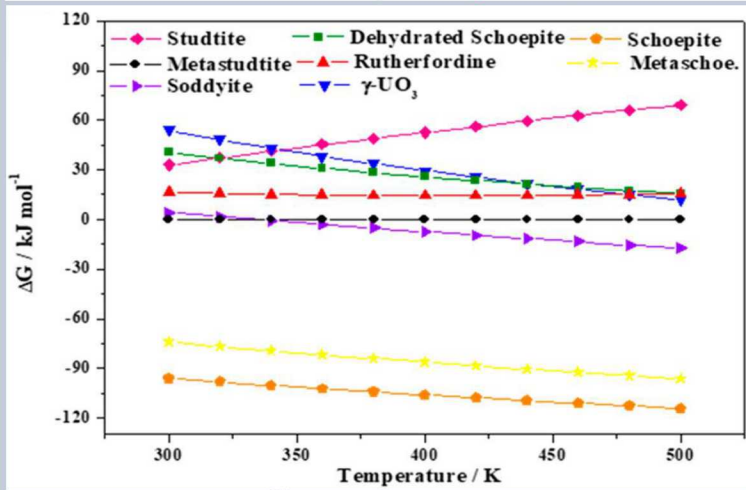

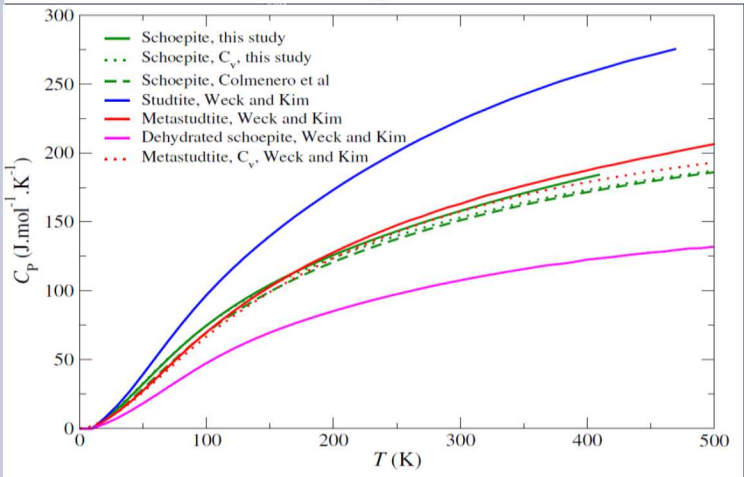

SFWD

Spent Fuel & Waste Disposition

Annual Working Group Meeting
UNLV-SEB – *Las Vegas, Nevada*
May 21-23, 2019

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INTRODUCTION

- **Background:**
  - **Oxidative dissolution of spend nuclear fuel (SNF) leads to the formation of uranyl-based phases**
  - **Likely Uranyl phases**
    - Primarily oxide hydrates
    - Others -- silicates, phosphates, carbonates
    - over 50 uranyl minerals occur in nature and as corrosion products of SNF
  - **Natural system minerals and engineered materials behavior in post-closure**
- **Thermodynamic parameters for corrosion phases of SNF and engineered barrier systems (EBS) materials and natural system (NS) minerals are critical to assess their stability and behavior in geologic disposal environments for safety assessments**
- **Thermodynamic Data Gaps and Research Needs:**
  - Uranyl corrosion products formed (e.g., schoepite, metaschoepite, dehydrated schoepite polymorphs, studtite, metastudtite…)
  - NS minerals surrounding the waste package (e.g. complex salts, clays, granite…)

Objectives and Approach

- **Objectives:**

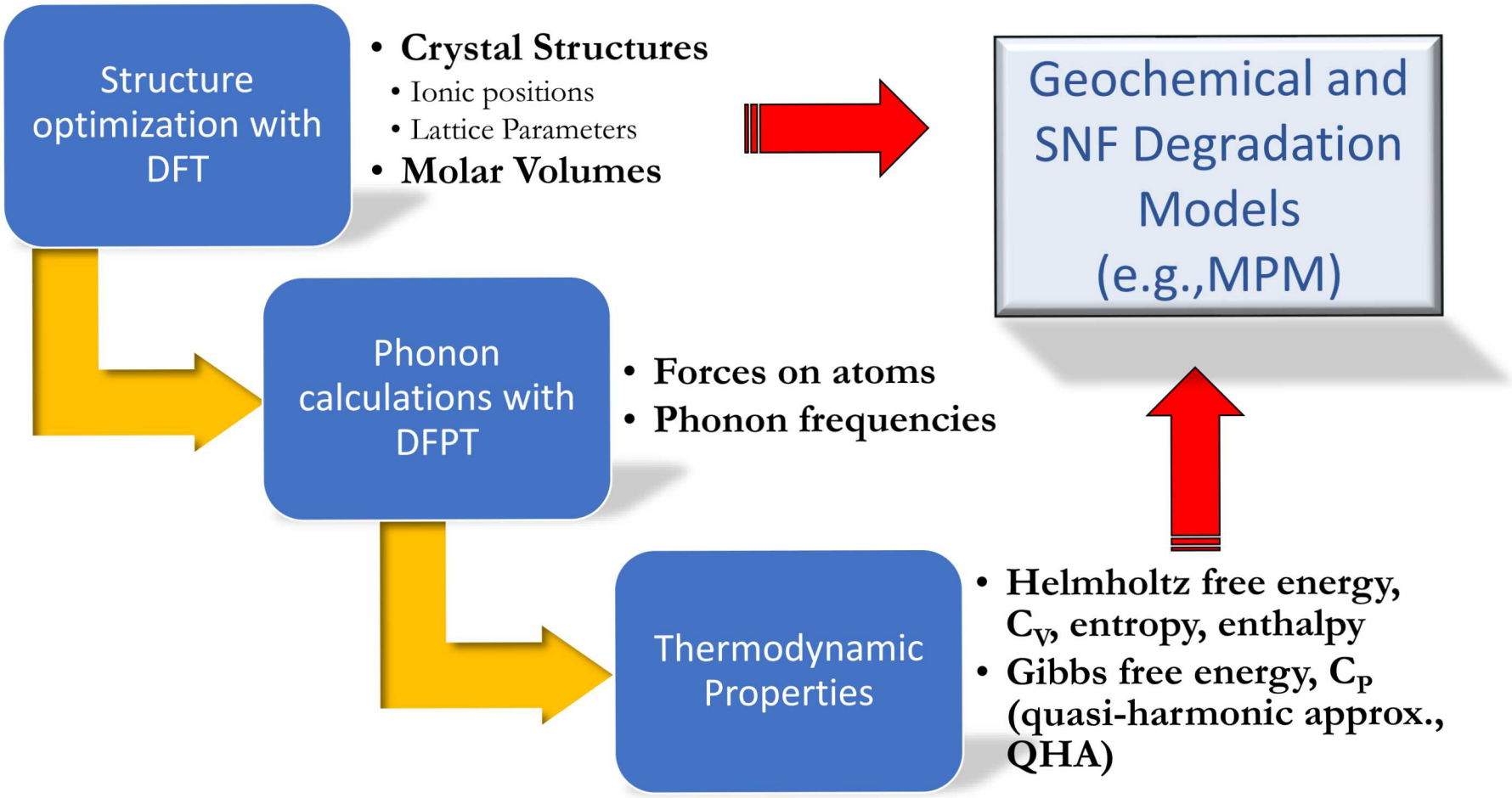
  Use first-principles methods to:

  - Calculate missing thermodynamic data needed for SNF degradation models, as a **fast, systematic, and early way to avoid using expensive UO_2-bearing real materials, which are difficult to handle by conventional laboratory methods,** and **to complement experiments**.
  - Provide an **independent assessment** of existing experimental thermodynamic data and resolve contradictions in existing calorimetric data.
  - Validate our computational approach using high-quality calorimetric data.

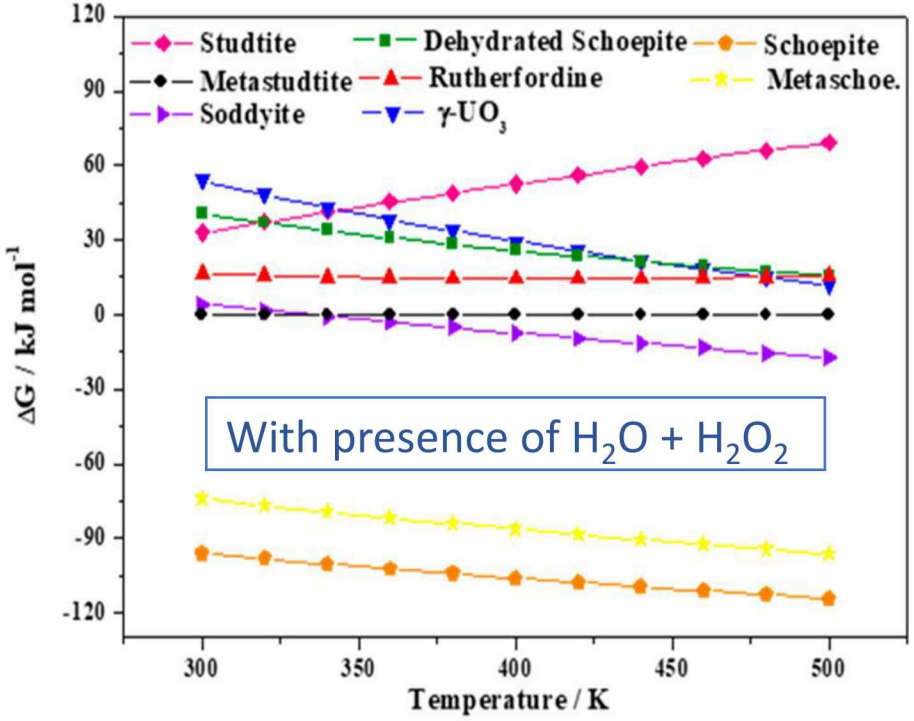
- **Approach:**

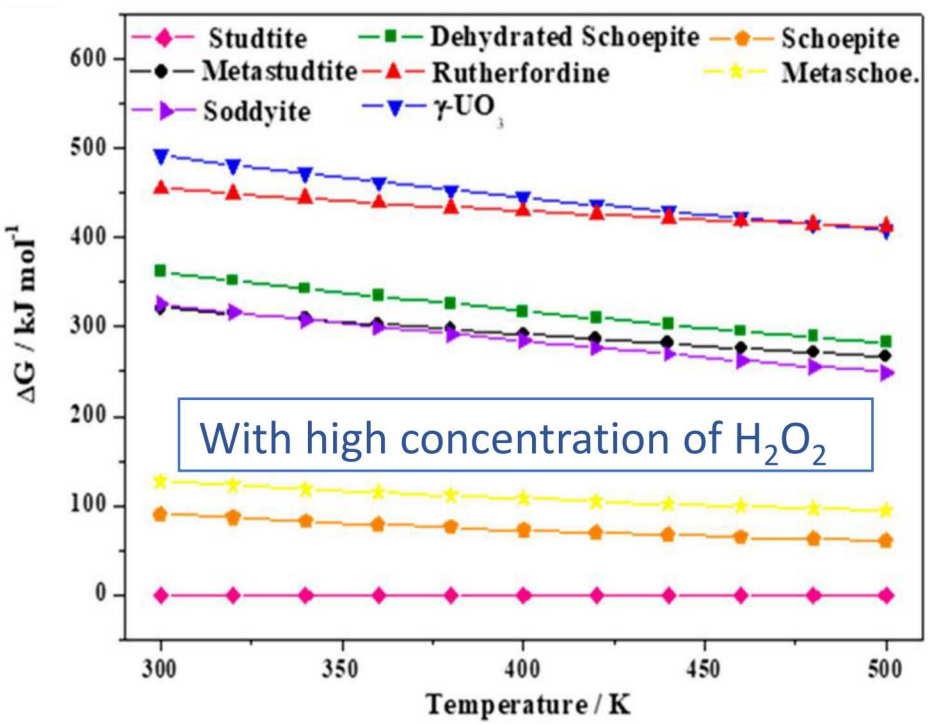
  - Structural optimization/materials discovery using density functional theory (DFT) [Vienna Ab initio Software Package (VASP)].
  - Use density functional perturbation theory (DFPT) to calculate the phonon properties of materials relaxed with DFT and derive their thermal properties.

Computational Methods



Relative Thermodynamic Stability of Corrosion Phases of SNF



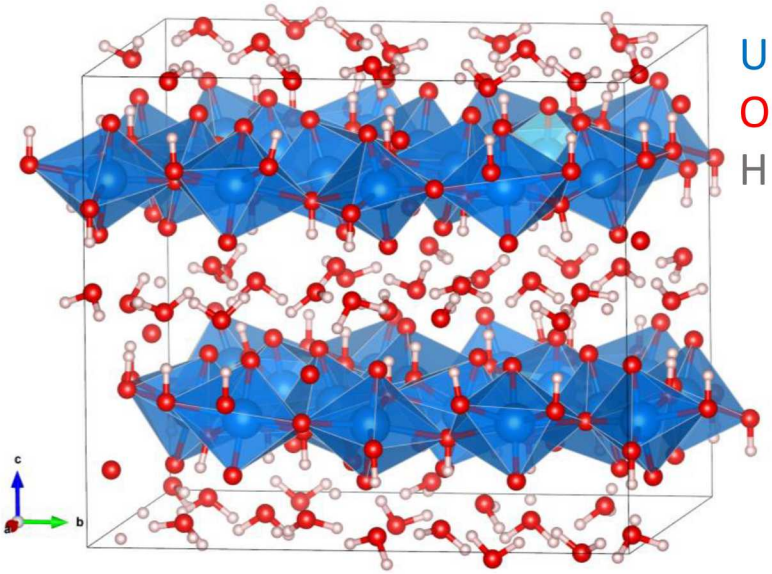


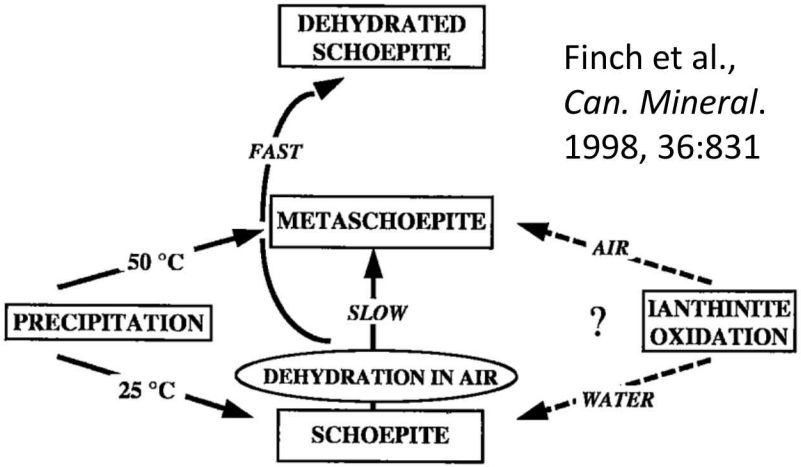
With $H_2O + H_2O_2$ → schoepite, metaschoepite, metastudtite and soddyite are predicted to be the most stable phases

With high concentration of H_2O_2 → studtite, schoepite, metaschoepite, soddyite and metastudtite are predicted to be the most stable phases

No thermodynamic data (e.g., C_P, S, etc.) for studtite and schoepite, with limited data for metaschoepite → Importance of DFT predictions (studtite & metastudtite : Weck & Kim, *J. Phys. Chem. C* 2016, 120:16553; schoepite & metaschoepite: Colmenero et al., *ACS Earth Space Chem.* 2019, 3:17)

Structure of Schoepite





Finch et al., *Can. Mineral.* 1998, 36:831

- **Schoepite: $[(UO_2)_8O_2(OH)_{12}]\cdot 12\ H_2O$** (or $UO_3\cdot 2.25\ H_2O$)
- Schoepite often mistaken in the literature for metaschoepite: $[(UO_2)_8O_2(OH)_{12}]\cdot 10\ H_2O$ (or $UO_3\cdot 2\ H_2O$))
- 433 atoms in the orthorhombic crystallographic unit cell (space group $P2_1ca$, IT No. 29, Z=4) → very challenging DFT calculations for such large size 5*f* electron systems that need special resource allocation of SNL high-performance computing (HPC).
- All U atoms coordinated by seven anions in pentagonal bipyramidal arrangements. U atoms with coordination $UO_2(OH)_5$ or $UO_2O(OH)_4$.
- XRD studies: H-atom position unknown and O-atom disorder (Finch et al., *Can. Mineral.* 1996, 34, 1071; *Powder Diffr.* 1997, 12:230; *Can. Mineral.* 1998, 36:831).
- Fully-solved structure of schoepite recently proposed from DFT calculations (CASTEP code) by Colmenero et al., *Inorg. Chem.*, 2018, 57:4470.

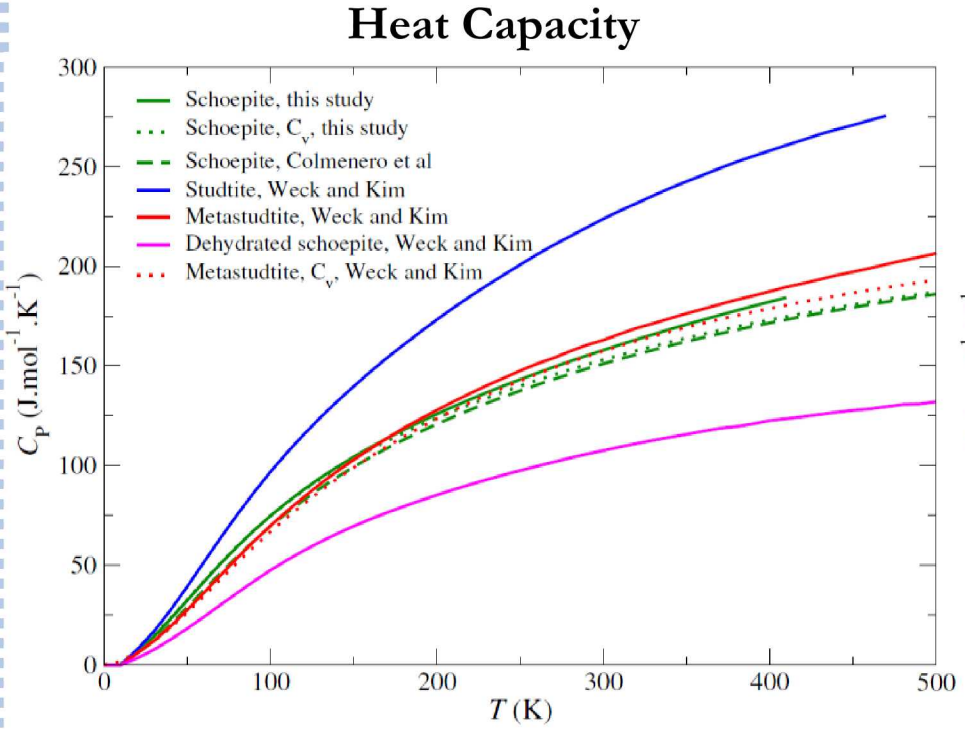
STRUCTURE OF SCHOEPITE (*CONT.*)

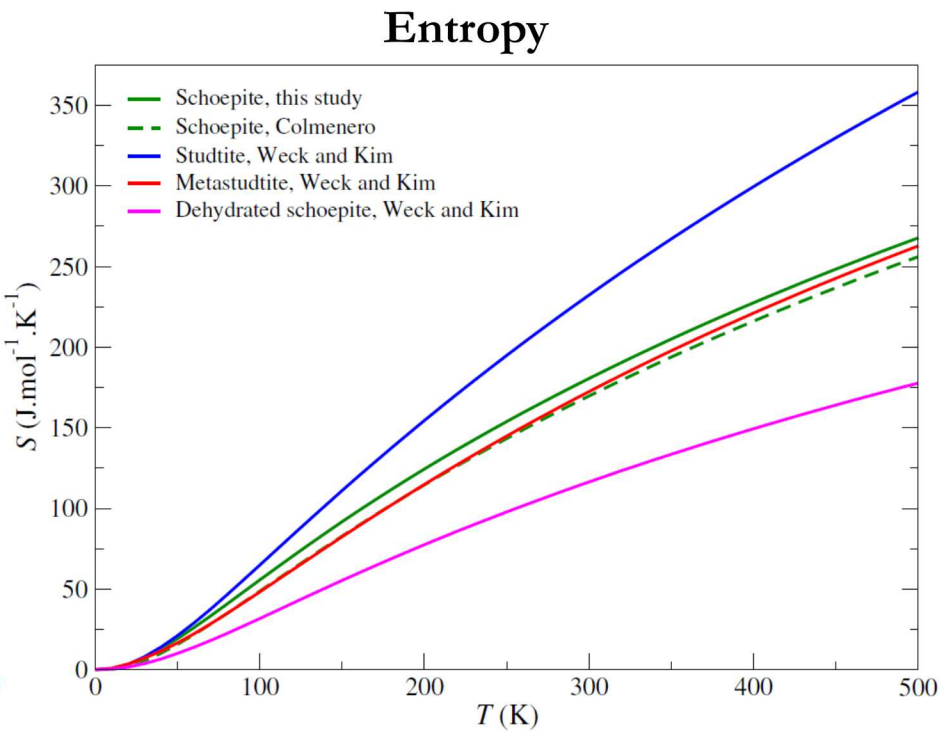
Experimental and DFT unit-cell lattice parameters

	a(Å)	*b*(Å)	*c* (Å)	*c*/*a*	*b*/*a*	*V*(Å^3)	ϱ (g/cm^3)
DFT, this study	**14.389** (+0.36%)	**16.870** (+0.34%)	**14.726** (-0.03%)	**1.023**	**1.172**	**3574.90** (+0.67%)	**4.854**
DFT, Colmenero 2018	**14.274** (-0.44%)	**16.808** (-0.03%)	**14.484** (-1.68%)	**1.015**	**1.177**	**3474.91** (-2.14%)	**4.993**
Powder XRD, Finch 1998	**14.337** (0%)	**16.813** (0%)	**14.731** (0%)	**1.027**	**1.173**	**3550.88** (0%)	**4.886**

- Better agreement between XRD lattice parameters and the present VASP DFT results than with CASTEP DFT results from Colmenero et al., 2018.
- CASTEP DFT calculations underestimate interlayer distance (-1.68%) as a results of the use of a van der Waals correction (DFT-D).
- Previous DFT calculations for dehydrated schoepite, studtite and metastudtite (Weck & Kim, Dalton Trans. 2014, 43:17191; *J. Phys. Chem. C* 2016, 120:16553) demonstrated that standard DFT is accurate to describe layered uranium(VI) hydroxides/peroxide hydrates.
- High-accuracy structural information needed to calculate reliable thermodynamic properties.

THERMODYNAMIC PROPERTIES OF SCHOEPITE

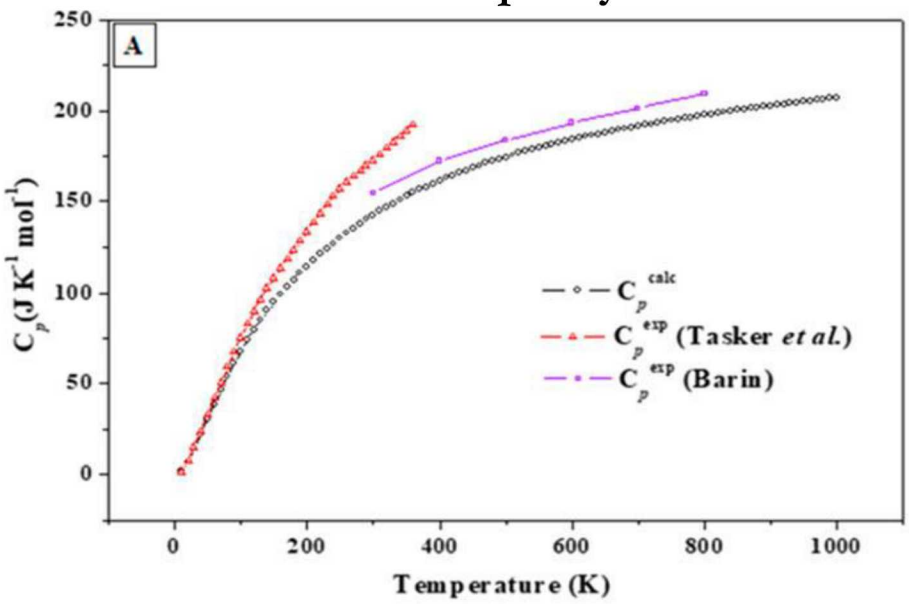




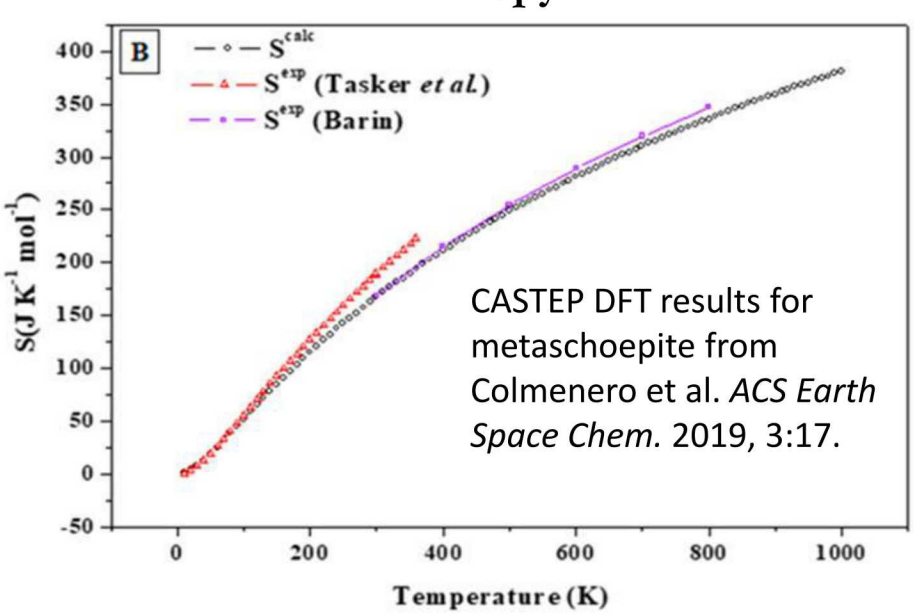
- The present heat capacity and entropy calculated at 298 K with VASP DFT are C_P= 157 J mol K^{-1} and S= 179 J mol K^{-1}, i.e., ~5% and ~7% larger than CASTEP DFT results from Colmenero et al. *ACS Earth Space Chem.* 2019, 3:17.
- C_P as a function of *T* is the thermodynamic parameter needed for temperature extrapolation of thermodynamic properties and hence solubilities. **Radionuclides solubility with temperature is a key knowledge gap** (see "RDOE SFWST Campaign R&D Roadmap Update", April 2019, ID (gap) activities: A-06, A-08, C-07, C-09, C-12, E-01, E-03, E-09, E-14, E-19, I-01, I-07, I-10, O-04, P-06, P-11, P-13, P-16,…).

Future Work: Structure and Thermodynamic Properties of Metaschoepite

Heat Capacity



Entropy



- C_P results from Colmenero et al. tend to systematically underestimate existing heat capacity data (i.e., similar trend as between their and our calculated predictions for schoepite).
- We will extend structural and thermal calculations carried out within the framework of DFT/DFPT to metaschoepite and other phases involved in the corrosion of SNF (polymorphs of dehydrated schoepite, …), as well as other NS minerals/EBS materials.
- C_P and other parameters will be generated and compared for the U(VI) hydroxy-peroxy solid assemblage to ensure internal consistency with calculations and evaluations against other data.

1. Introduction, Purpose, and Context

2. Safety Strategy

2.1 Management Strategy

a. Organizational/mgmt. structure
b. Safety culture & QA
c. Planning and Work Control
d. Knowledge management
e. Oversight groups

2.2 Siting & Design Strategy

a. National laws
b. Site selection basis & robustness
c. Design requirements
d. Disposal concepts
e. Intergenerational equity

2.3 Assessment Strategy

a. Regulations and rules
b. Performance goals/safety criteria
c. Safety functions/multiple barriers
d. Uncertainty characterization
e. RD&D prioritization guidance

3. Technical Bases

3.1 Site Selection

a. Siting methodology
b. Repository concept selection
c. FEPs Identification
d. Technology development
e. Transportation considerations
f. Integration with storage facilities

3.2 Pre-closure Basis

a. Repository design & layout
b. Waste package design
c. Construction requirements & schedule
d. Operations & surface facility
e. Waste acceptance criteria
f. Impact of pre-closure activities on post-closure

3.3 Post-closure Bases (FEPs)

3.3.1 Waste & Engineered Barriers Technical Basis

a. Inventory characterization
b. WF/WP technical basis
c. Buffer/backfill technical basis
d. Shafts/seals technical basis
e. UQ (aleatory, epistemic)

3.3.2 Geosphere/ Natural Barriers Technical Basis

a. Site characterization
b. Host rock/DRZ technical basis
c. Aquifer/other geologic units technical basis
d. UQ (aleatory, epistemic)

3.3.3 Biosphere Technical Basis

a. Biosphere & surface environment:
   - Surface environment
   - Flora & fauna
   - Human behavior

4. Disposal System Safety Evaluation

4.1 Pre-closure Safety Analysis

a. Surface facilities and packaging
b. Mining and drilling
c. Underground transfer and handling
d. Emplacement operations
e. Design basis events & probabilities
f. Pre-closure model/software validation
g. Criticality analyses
h. Dose/consequence analyses

4.2 Post-closure Safety Assessment

a. FEPs analysis/screening
b. Scenario construction/screening
c. PA model/software validation
d. Barrier/safety function analyses and subsystem analyses
e. PA and Process Model Analyses/Results
f. Uncertainty characterization and analysis
g. Sensitivity analyses

4.3 Confidence Enhancement

a. R&D prioritization
b. Natural/anthropogenic analogues
c. URL & large-scale demonstrations
d. Monitoring and performance confirmation
e. International consensus & peer review
f. Verification, validation, transparency
g. Qualitative and robustness arguments

5. Synthesis & Conclusions

a. Key findings and statement(s) of confidence
b. Discussion/disposition of remaining uncertainties
c. Path forward

Roadmap Mapping

High Impact R&D Topics	High-Priority R&D Activities	Medium-High-Priority R&D Activities
High temperature impacts	D-1, D-4, I-4, I-6, I-16, E-11, S-5	I-2, I-3, I-7, E-10
Buffer and seal studies	I-4, E-9, E-17, A-8, C-15	I-2, I-3, I-7, A-4, C-6, C-8, C-11
Generic PA Models	P-1, P-2, P-3, P-4	P-11, P-13, P-14
Coupled processes (Salt)	S-1, S-3, S-4, I-12, I-13	I-14, S-2, S-7, S-8, S-11
Gas flow in the EBS	I-6, I-8, I-18	I-9, P-17
Criticality	D-1, D-4, D-5	
Waste Package degradation	C-16, P-12	E-4, E-6
Radionuclide Transport	P-6	C-11, C-13, C-14. P-15, P-16
In-Package Chemistry	E-14	E-2, E-20, P-15, P-16
DFN issues		I-21, C-1, C-17
GDSA Geologic Modeling		O-2, O-3
THC Processes in EBS		E-3

QUESTIONS?

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