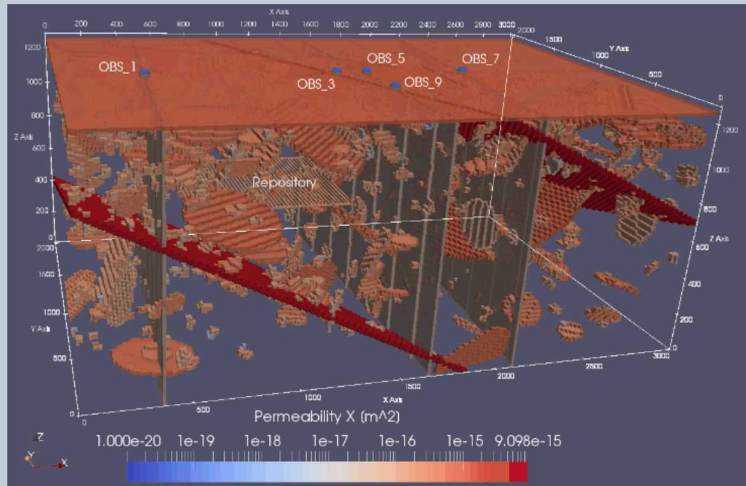
SAPONITE AS NEW GENERATION ENGINEERED BUFFER MATERIALS FOR HARSH ENVIRONMENTS

Yongliang Xiong, Yifeng Wang

Sandia National Laboratories

SAND2019-xxxx



SFWD

SPENT FUEL & WASTE DISPOSITION

Annual Working Group Meeting

UNLV-SEB – *Las Vegas, Nevada*

May 21-23, 2019

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Experimental Set-up
- Experimental Results
- Summary and Future Work

INTRODUCTION

- Montmorillonite, $Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$, di-octahedral smectite
- Montmorillonite-rich bentonite is a primary buffer candidate for high level nuclear waste (HLW) and used nuclear fuel to be disposed in mild environments:
  - Temperature: $\leq 90^{o}$C
    - Higher T may promote Illitization of di-octahedral smectite
  - Groundwaters: low ionic strengths
    - Salinity: < 70 g/L; Seawater: 35 g/L
    - Higher salinity leads to mineral transformation and decrease in swelling pressure
  - pH: close to neutrality
    - Higher pH: Smectite dissolution
    - silica release → Cementation; zeolite formation
    - Swelling pressures decrease significantly at pH ≥ 13

INTRODUCTION (CONT.), SAPONITE

- Saponite, $Mg_3(Si, Al)_4O_{10}(OH)_2 \cdot 4H_2O$ (saponite-15A), tri-octahedral smectite:
  - Pusch [1] identified saponite as a qualified candidate for buffer materials.
  - Saponite is less susceptible to alteration under harsh conditions [2-3].
  - Mg-bearing saponite has been favorably considered as a preferable engineered buffer material for the Swedish very deep holes (VDH) disposal concept in crystalline rock formations [4].

---

[1] Pusch, R. 1999a. Is the montmorillonite-rich clay of MX-80 type the ideal buffer for isolation of HLV. SKB Technical Report TR-99-33. Swedish Nuclear Fuel and Waste. Management Co. (SKB), Stockholm, Sweden.

[2] D.D. EBERL, G. WHITNEY AND H. KHOURY, "Hydrothermal reactivity of smectite," American Mineralogist, 63(3-4), 401-409 (1978).

[3] N. GÜVEN, "Longevity of bentonite as buffer material in a nuclear-waste repository," Engineering Geology, 28(3-4), 233-247 (1990).

[4] T. YANG, R. PUSCH, S. KNUTSSON, AND X.-D. LIU, "The assessment of clay buffers for isolating highly radioactive waste," WIT Transactions on Ecology and The Environment, 180, 403-413 (2014).

INTRODUCTION (CONT.)

Table 3: Hydraulic conductivity and swelling pressure of MX-80, GMZ, saponite and mixed-layer clays for typical densities at saturation and percolation with 3.5% $CaCl_2$ solution water saturation density [7, 9].

Samples	Density kg/m^3	Dry density kg/m^3	Hydraulic conductivity (K), m/s	Swelling pressure (p_s), kPa
MX-80	1800	1310	E-10	200
MX-80	2000	1175	2E-13	4700
GMZ	1788	1233	E-11	530
Saponite	1800	1175	4E-12	1300
Mixed-layer FIM	1800	1392	4E-11	280
Mixed-layer FIM	2000	1175	2E-11	1000
Mixed-layer Holmehus	1800	1310	2E-11	600
Mixed-layer Holmehus	2000	1175	8E-12	2000

From [4] T. YANG, R. PUSCH, S. KNUTSSON, AND X.-D. LIU, "The assessment of clay buffers for isolating highly radioactive waste," WIT Transactions on Ecology and The Environment, 180, 403-413 (2014).

INTRODUCTION (CONT.)

- However, the chemical stability of saponite is not well studied, nor well understood:
  - How its performance in high pH environments?
    - High pH are introduced by the repository designs in which concretes and cements are used as plugs and buffers.
  - How its performance in high ionic strength environments?
    - Repository designs in salt formations and sedimentary basins
      - Waste Isolation Pilot Plant (WIPP), USA: GWB, 8.26 mol•kg^{-1}; ERDA-6, 5.82 mol•kg^{-1}
      - Asse, Germany: Q-brine: ~13 mol•kg^{-1}
  - How its performance in higher temperature environments?
    - Repository designs in crystalline rocks including granite, salt formations, etc., temperatures may be significantly higher than 100^{o}C.

OBJECTIVE OF THIS STUDY

- We are to systematically assess the chemical stability of saponite in harsh environments.
- As concretes and cements are used as plugs and buffers in repository designs, the chemical stability of saponite in the presence of saturated cement was
  - Is important to the performance of saponite
  - Is the focus of this presentation
- In the near future, we are to investigate the chemical stability of saponite in high ionic strength solutions, and in high temperature environments.

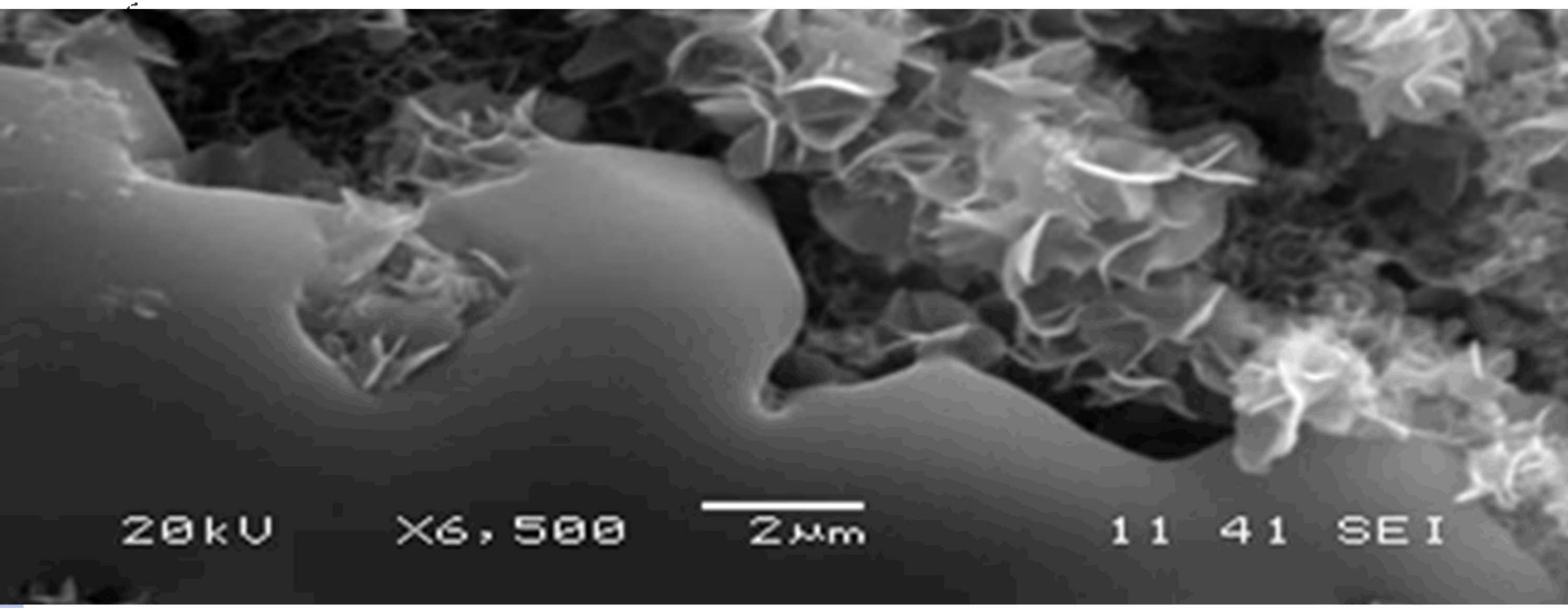
EXPERIMENTAL

- Investigation: Interaction of saponite with saturated $Ca(OH)_2$
- Saturated $Ca(OH)_2$ solution prepared at room temperature: 0.017 m
  - As portlandite [$Ca(OH)_2$(cr)] has retrograde solubility, usage of this solution ensures that the solution is in equilibrium with portlandite at elevated temperatures.
- Temperatures that have been studied: 60°C, 150°C
- Starting materials:
  - Synthetic saponite
  - Natural saponite from King Island, Tasmania, Australia
- Instrumental Analyses:
  - XRD
  - SEM-EDS
  - Electron Microprobe Analysis (EMPA)
  - XRF: to be performed on natural saponite
  - ICP-AES: to be performed on solution samples

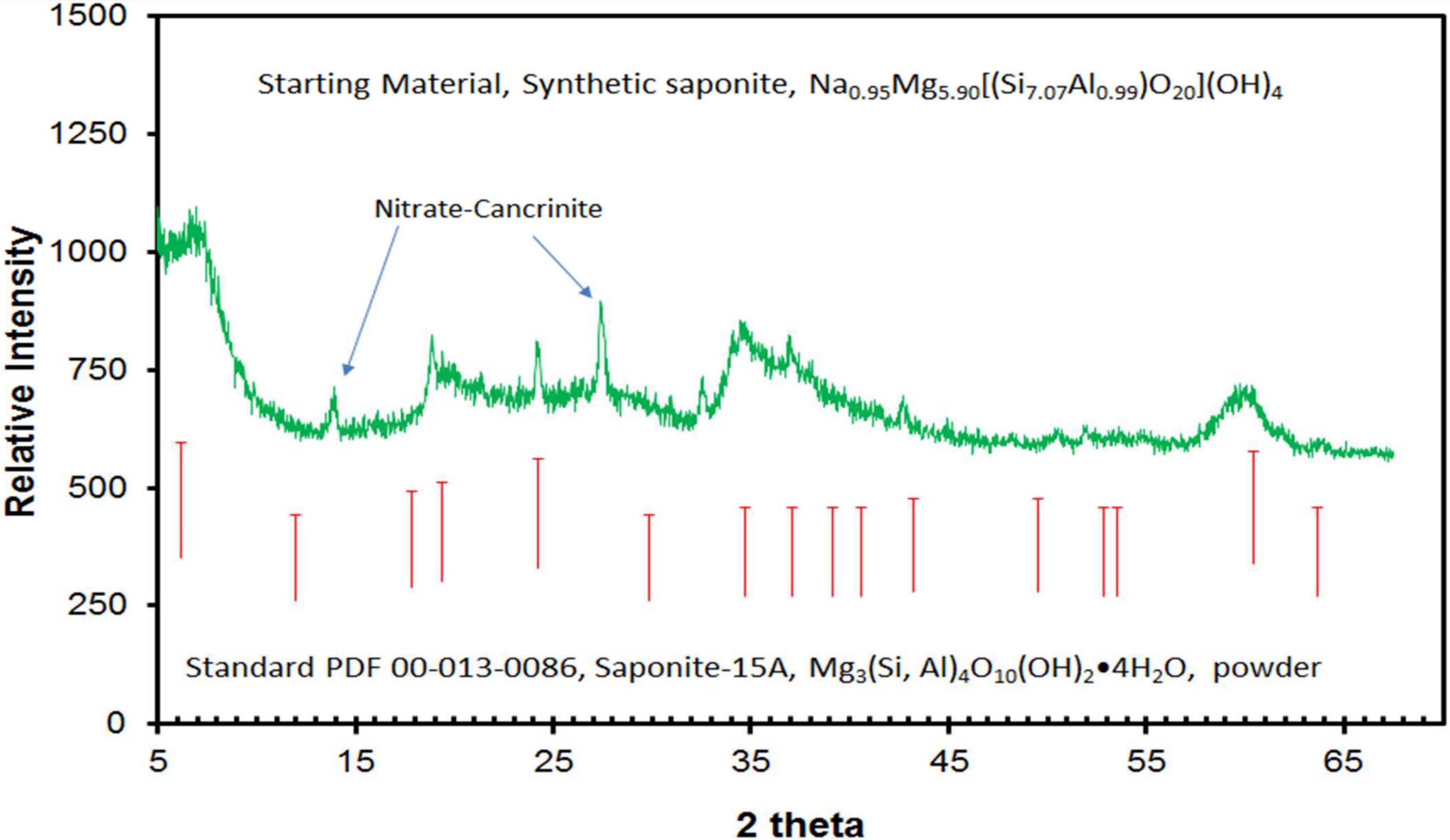
EXPERIMENTAL (CONT'D)

- For comparison, we also investigate interaction of natural montmorillonite (Swy-2) with saturated $Ca(OH)_2$
- Solid to solution mass ratios used in this work
  - Natural saponite experiments: 1:5
  - Synthetic saponite experiments: 1:17
  - Natural montmorillonite experiments: 1:5

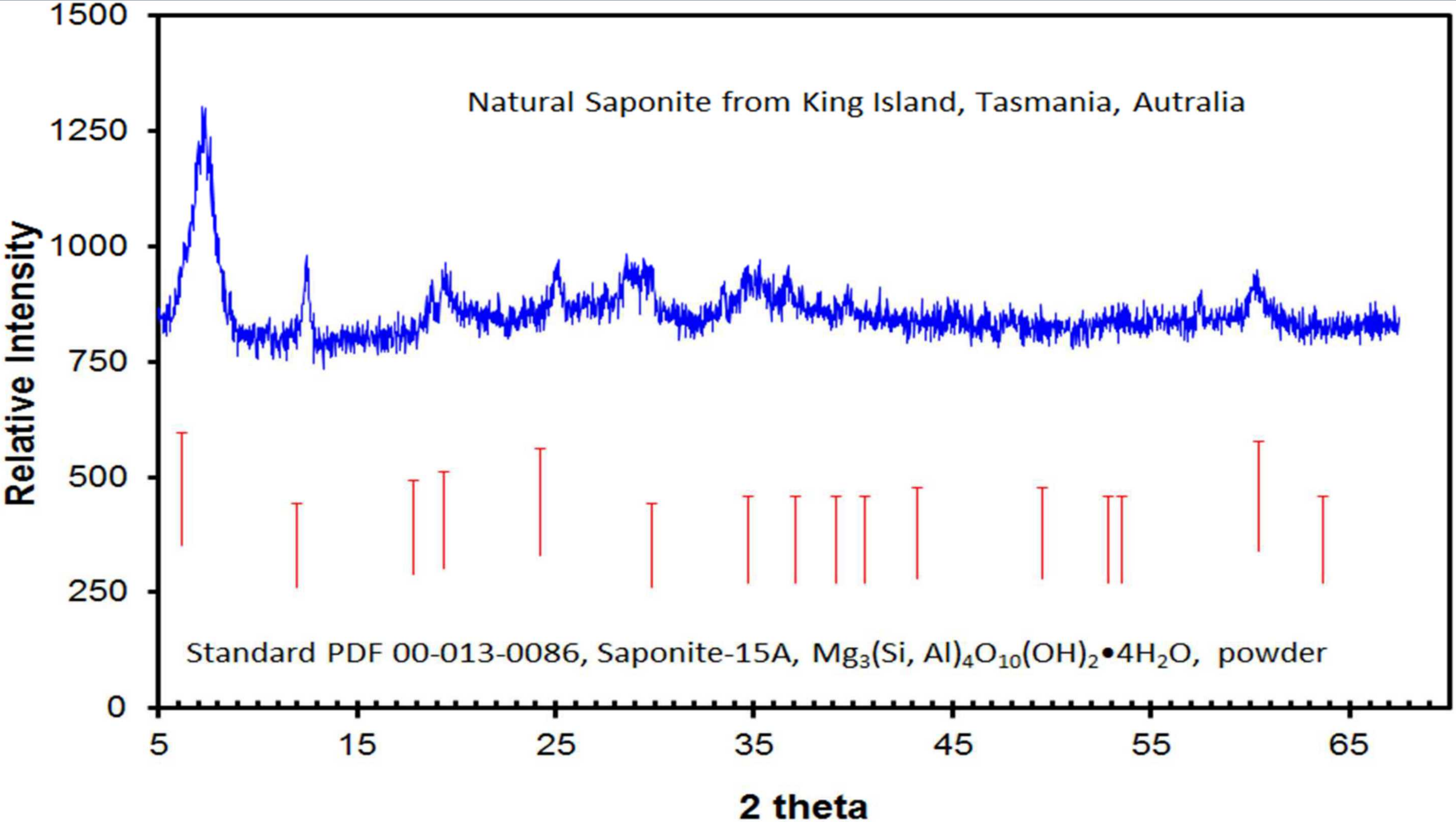
Experimental Results: Starting Material—Synthetic Saponite



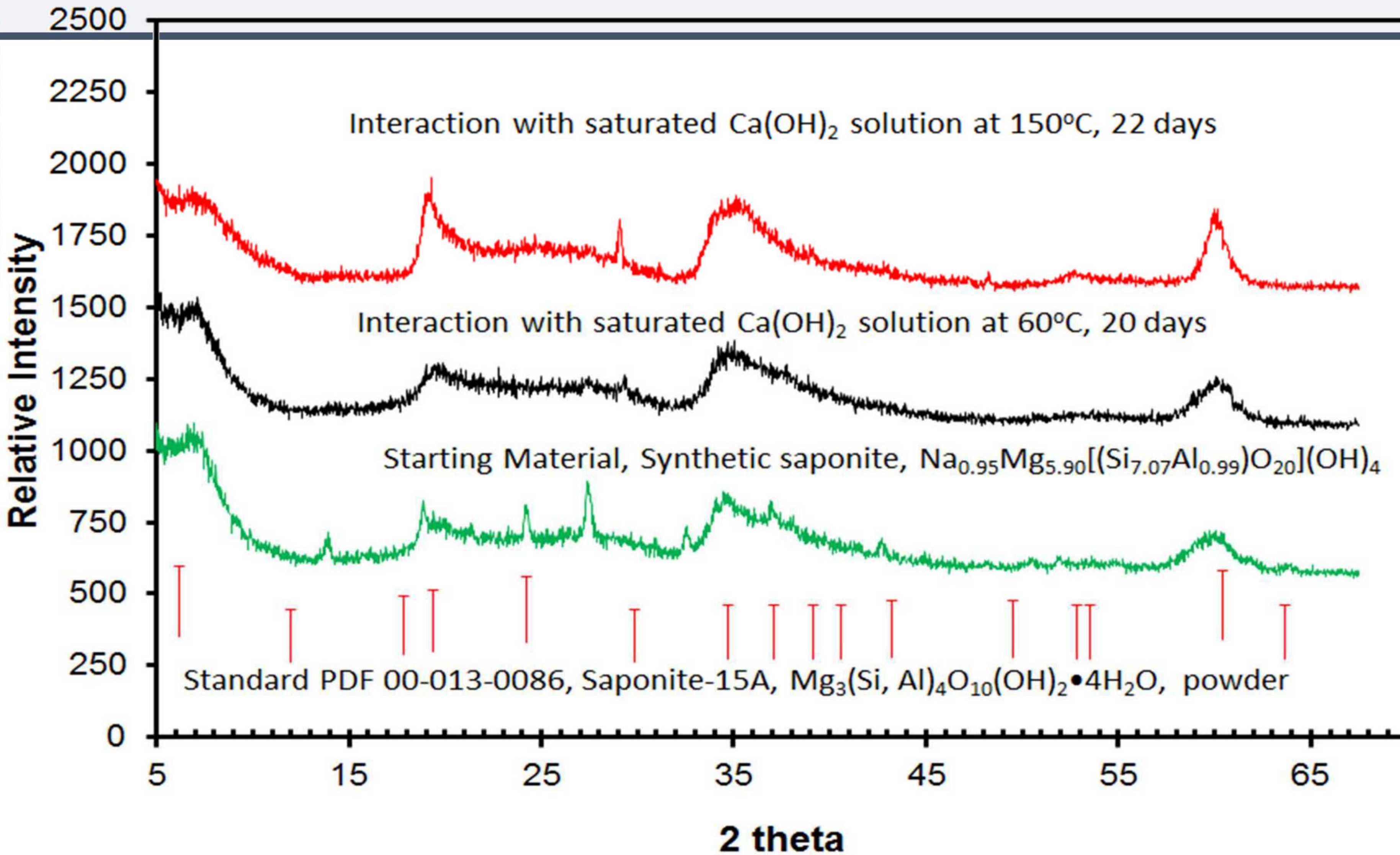
EXPERIMENTAL RESULTS: STARTING MATERIAL—SYNTHETIC SAPONITE



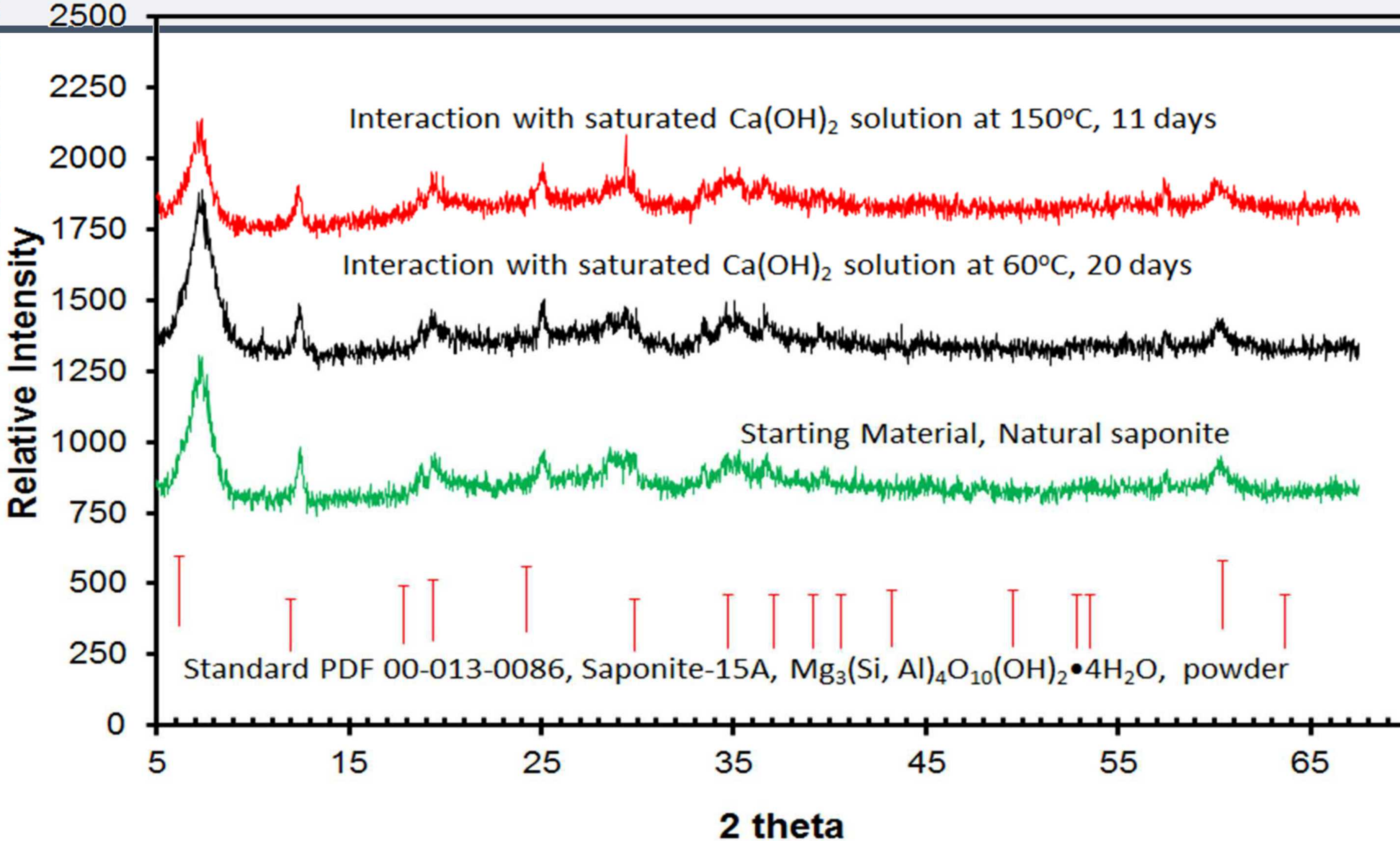
EXPERIMENTAL RESULTS: STARTING MATERIAL—NATURAL SAPONITE



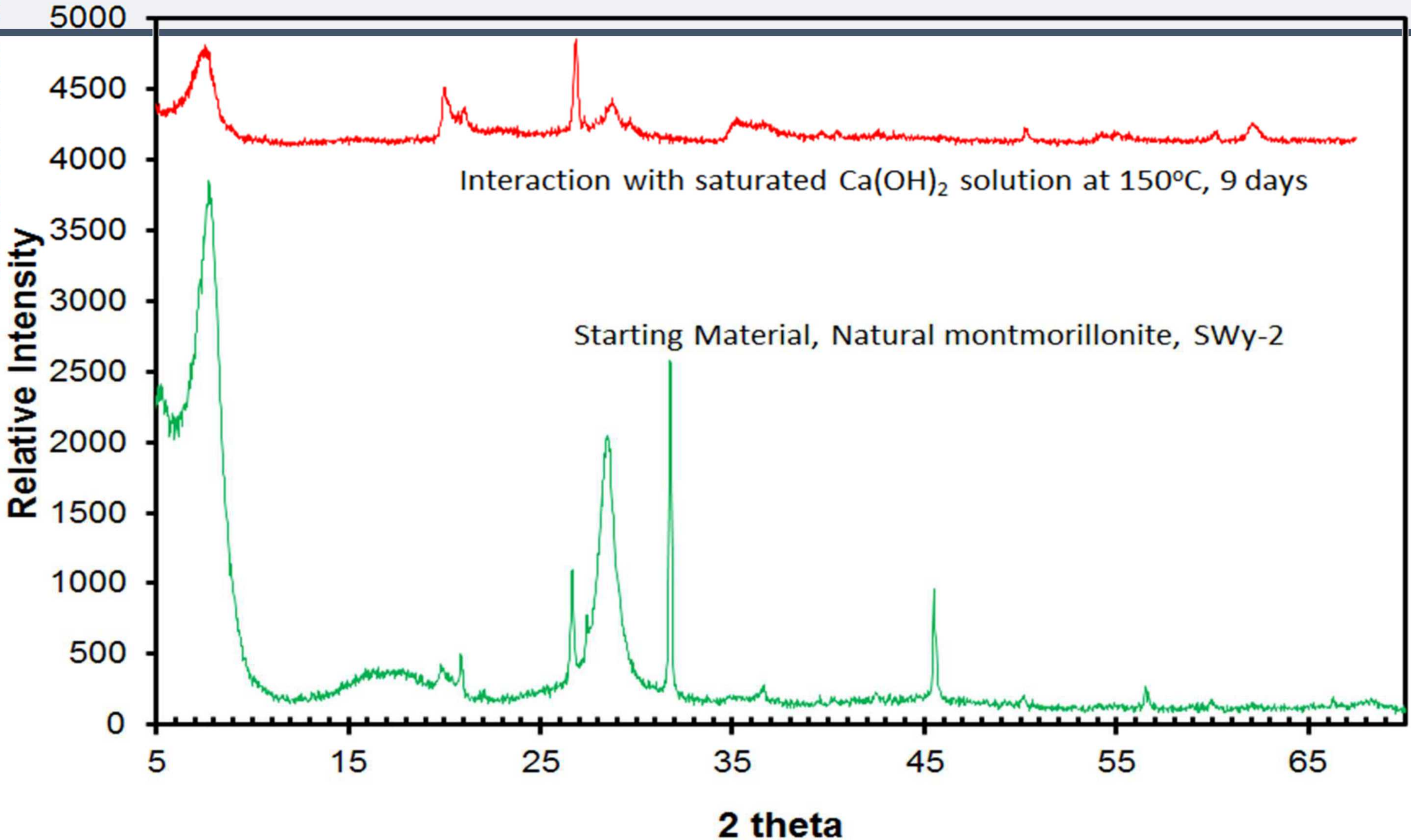
Experimental Results: Synthetic Saponite



Experimental Results: Natural Saponite



EXPERIMENTAL RESULTS: NATURAL MONTMORILLONITE



Summary and Future Work

- In this work, we have experimentally investigated the stability of both natural and synthetic saponite in the presence of saturated $Ca(OH)_2$ solutions,
  - Relevant to the repository designs using cements and concretes as plugs and buffers
  - Both natural and synthetic saponite is stable in saturated $Ca(OH)_2$ solutions at 60^{o}C and 150^{o}C
- For comparison, natural montmorillonite is unstable in saturated $Ca(OH)_2$ solutions at 150^{o}C.
- In the future, we are to assess the stability of saponite in high ionic strength solutions.

Questions?

SFWD

Spent Fuel &
Waste Disposition

Annual Working Group Meeting
May 21-23, 2019

UNLV-SEV – *Las Vegas, Nevada*