SAND2021-7420C

Exceptional service in the national interest

Sandia
National
Laboratories

Experimental and Modeling Study of Interactions of Rare Earth Elements (REE) Pr(III) and Nd(III) with Citrate and Oxalate: Implications to the Mobility of Actinides and REE and Their Extractions (Invited)

Goldschmidt Conference

July 5-9, 2021, Virtual Meeting

Yongliang Xiong, Yifeng Wang, Guanping Xu, Sara Russo

U.S. DEPARTMENT OF ENERGY

NNSA
National Nuclear Security Administration

Sandia National Laboratories (SNL) is a multimission laboratory managed and operated by National Technology and 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-NA-0003525..
This research is funded by the LDRD from SNL and Spent Fuel & Waste Science and Technology (SFWST) programs administered by the Office of Nuclear Energy (NE) of the U.S Department of Energy. SAND2021-xxxxC

OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Experimental Method
- Experimental Results
- Preliminary Interpretations of Experimental Results
- Work in Progress

INTRODUCTION

- The knowledge of the interactions of rare earth elements (REE) and actinides with both oxalate and citrate at the same time is important to many fields.
- The accurate knowledge of actinide solubilities that could be dissolved in natural groundwaters is required for safe disposal of nuclear waste.
- The interactions of actinides with both oxalate and citrate are important for prediction of actinide solubilities in geological repositories:
  - In the waste streams in some geological repositories for nuclear waste disposal, for instance, at the Waste Isolation Pilot Plant (WIPP), both oxalate and citrate are present at significant concentrations.
  - The ternary interactions of actinides with oxalate and citrate are unknown.
  - Such ternary interactions are expected to be significant, as similar ternary interactions such as Am(III)-EDTA-Oxalate have been documented [1].

---

[1] Thakur, P., Mathur, J.N., Dodge, C.J., Francis, A.J. and Choppin, G.R., 2006. Thermodynamics and the structural aspects of the ternary complexes of Am (III), Cm (III) and Eu (III) with Ox and EDTA+ Ox. *Dalton transactions*, (40), pp.4829-4837.

INTRODUCTION (Cont.)

- In the surface environments of the Earth, both oxalate and citrate are naturally present along with REE.
  - The ternary interactions of REE with oxalate and citrate impact,
    - Mobility and enrichment of REE in weathering and sedimentary environments.
- In REE extraction industries,
  - REE are usually precipitated as REE oxalates.
  - REE oxalates as feeds along with citric acid are subject to further purification/separation in the environmentally friendly processes.
  - Therefore, the knowledge of ternary interactions of REE with oxalate and citrate is beneficial to REE extraction industries.
- In nuclear waste management, actinides are also precipitated as actinide oxalates:
  - Actinide oxalates are purified/separated with citric acid as feeds for manufacturing new nuclear fuel

OBJECTIVE OF THIS STUDY

- To measure solubility of $Pr_2(C_2O_4)_3\bullet10H_2O$ and $Nd_2(C_2O_4)_3\bullet10H_2O$ in citric acid at 25^oC
- The above Pr(III)- and Nd(III)-oxalates provide the sources for both REE and oxalate.
- Pr(III) as an excellent analog to Pu(III) [2]
- Nd(III) as a good analog to Am(III) and Cm(III) [3, 2]
- Based on the experimental data, we develop a thermodynamic model to describe the ternary interactions of REE with oxalate and citrate.

---

[2] Xiong, Y.-L., and Wang, Y.-F., 2021. Experimental and modeling studies of Pr and Nd oxalates to high ionic strengths: Insight into actinide(III) oxalates. Chemical Geology 573, p. 120200.

[3] Choppin, G.R., 1999. Utility of oxidation state analogs in the study of plutonium behavior. Radiochimica Acta 85 (3), 89–96.

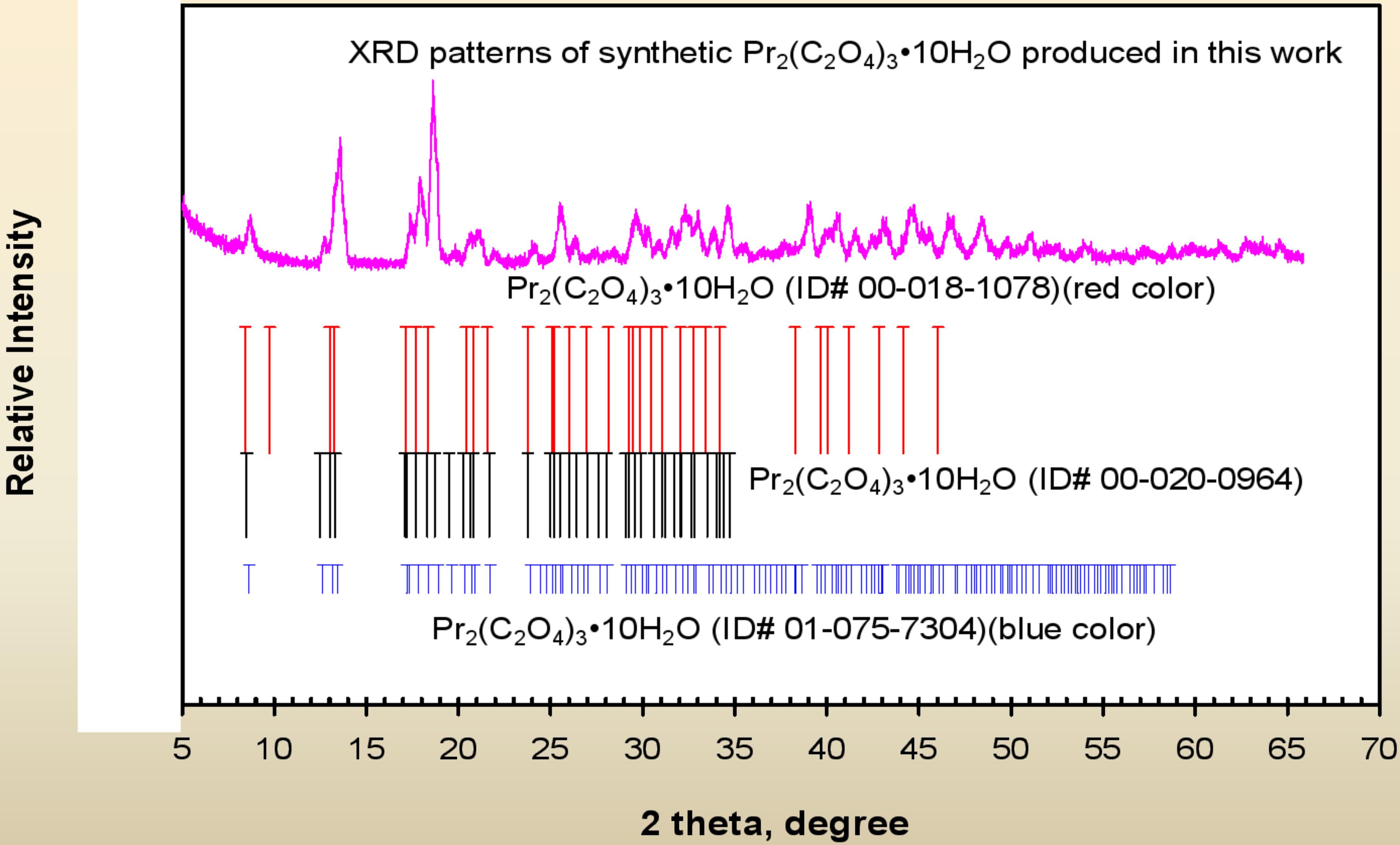
EXPERIMENTAL METHOD

- Synthesis of Pr-oxalate:
  - $Pr_2(C_2O_4)_3 \bullet 10H_2O$ was synthesized by dropwise addition of 0.67 $PrCl_3$ into 0.18 M $H_2C_2O_4$.
  - $Pr_2(C_2O_4)_3 \bullet 10H_2O$ has an identical stoichiometry with the plutonium analog, $Pu_2(C_2O_4)_3 \bullet 10H_2O$.
  - Pr(III) has effective radii almost identical to those of Pu(III).
    - For instance, for six coordination number, 0.99 Å for Pr(III) versus 1.00 Å for Pu(III).
  - $Pr_2(C_2O_4)_3 \bullet 10H_2O$ has a characteristic light green color, like the color of pistachio
- Synthesis of Nd-oxalate:
  - $Nd_2(C_2O_4)_3 \bullet 10H_2O$ was synthesized by dropwise addition of 0.70 $NdCl_3$ into 0.18 M $H_2C_2O_4$.
  - $Nd_2(C_2O_4)_3 \bullet 10H_2O$ has an identical stoichiometry with the americium and curium analogs, $Am_2(C_2O_4)_3 \bullet 10H_2O$ and $Cm_2(C_2O_4)_3 \bullet 10H_2O$.
  - Nd(III) has effective radii almost identical to those of Am(III) and Cm(III).
    - For instance, for six coordination number, 0.983 Å for Nd(III) versus 0.975 Å for Am(III) or 0.97 Å for Cm(III).
  - $Nd_2(C_2O_4)_3 \bullet 10H_2O$ has a characteristic light purple color.

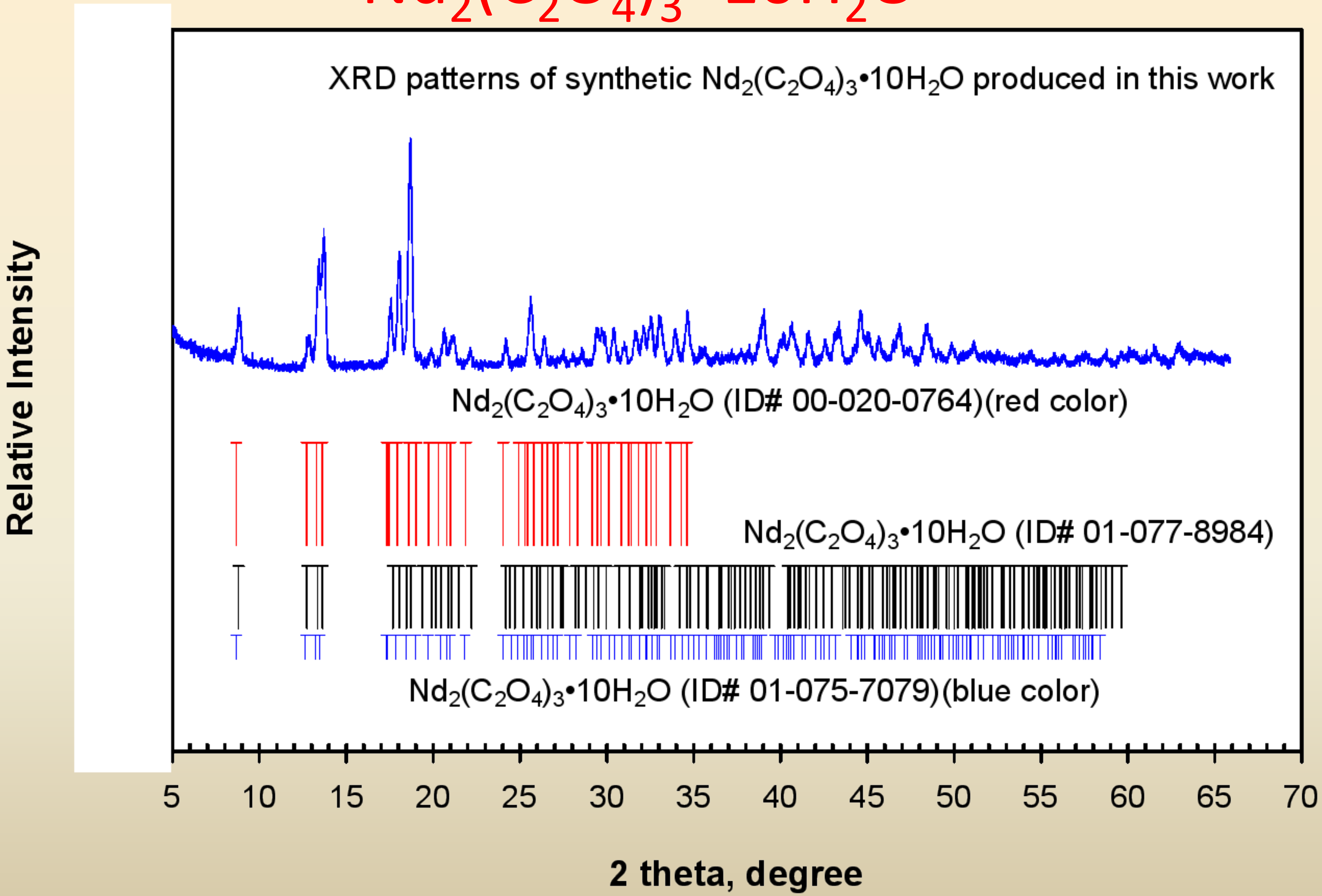
EXPERIMENTAL METHOD (Cont.)

- Experimental conditions: T = 23°C ±0.2°C
- Hydrogen ion concentrations (pH_m, molal scale) of the experimental systems are first controlled/buffered by solubility of $Pr_2(C_2O_4)_3 \bullet 10H_2O$ or $Nd_2(C_2O_4)_3 \bullet 10H_2O$, and then are adjusted with NaOH solutions.
- pH_m are determined by applying correction factors to pH readings obtained using a pH meter.
- Pr(III) and Nd(III) concentrations are analyzed using ICP-AES.
- Oxalate and citrate concentrations are analyzed using IC.
- Approaching equilibrium from undersaturation
- Supporting solutions:
  - A series of citric acid solutions: 0.001, 0.01, 0.1, and 0.5 $mol \bullet kg^{-1}$, with stoichiometric ionic strengths up to 3 $mol \bullet kg^{-1}$

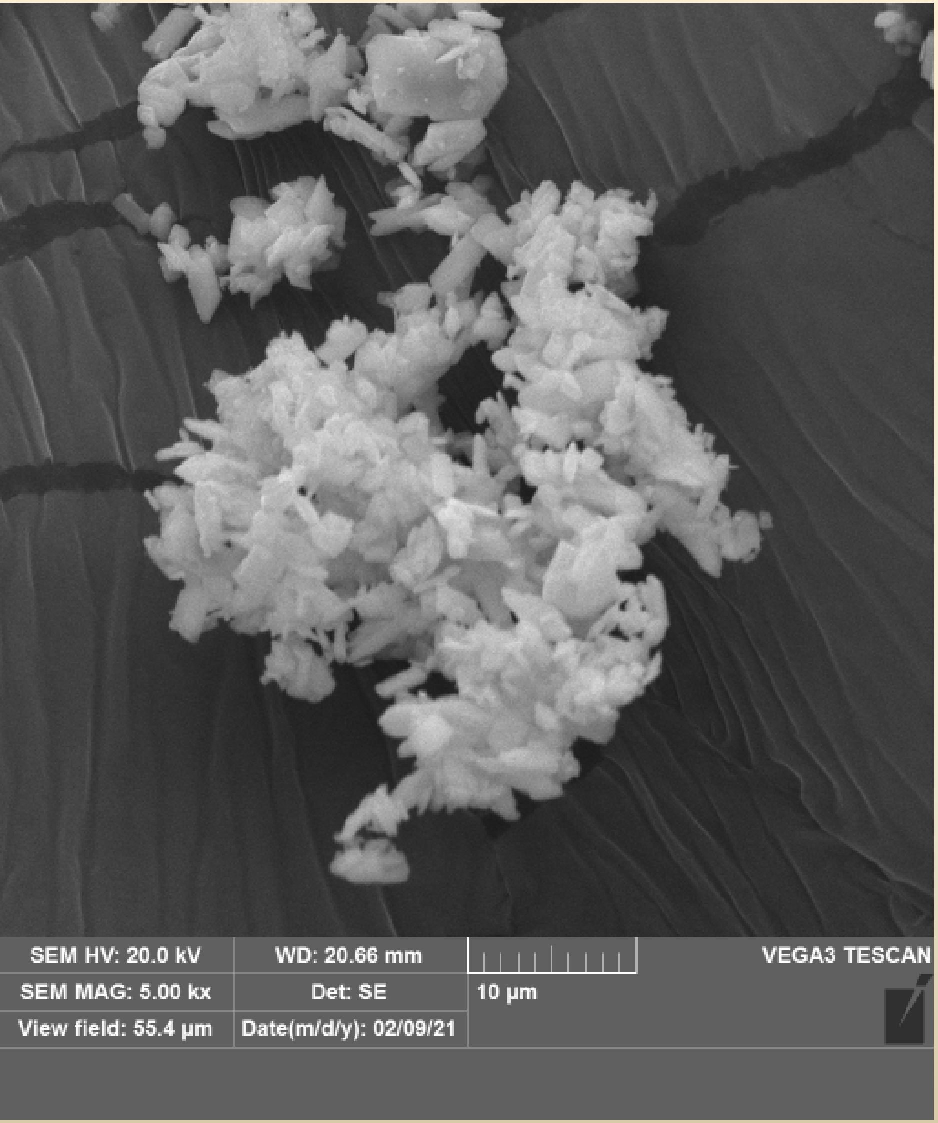
XRD Pattern of Starting Material: $Pr_2(C_2O_4)_3 \bullet 10H_2O$

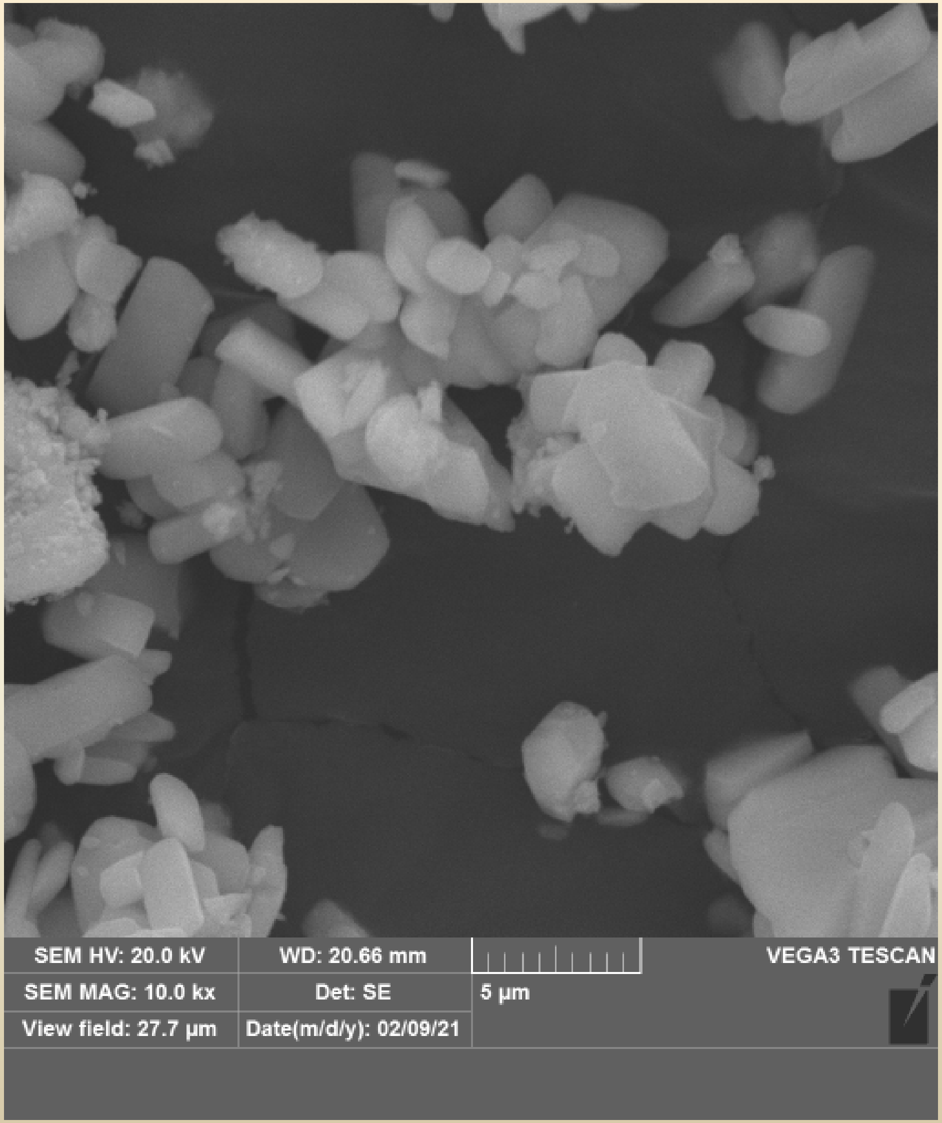


XRD Pattern of Starting Material: $Nd_2(C_2O_4)_3 \bullet 10H_2O$

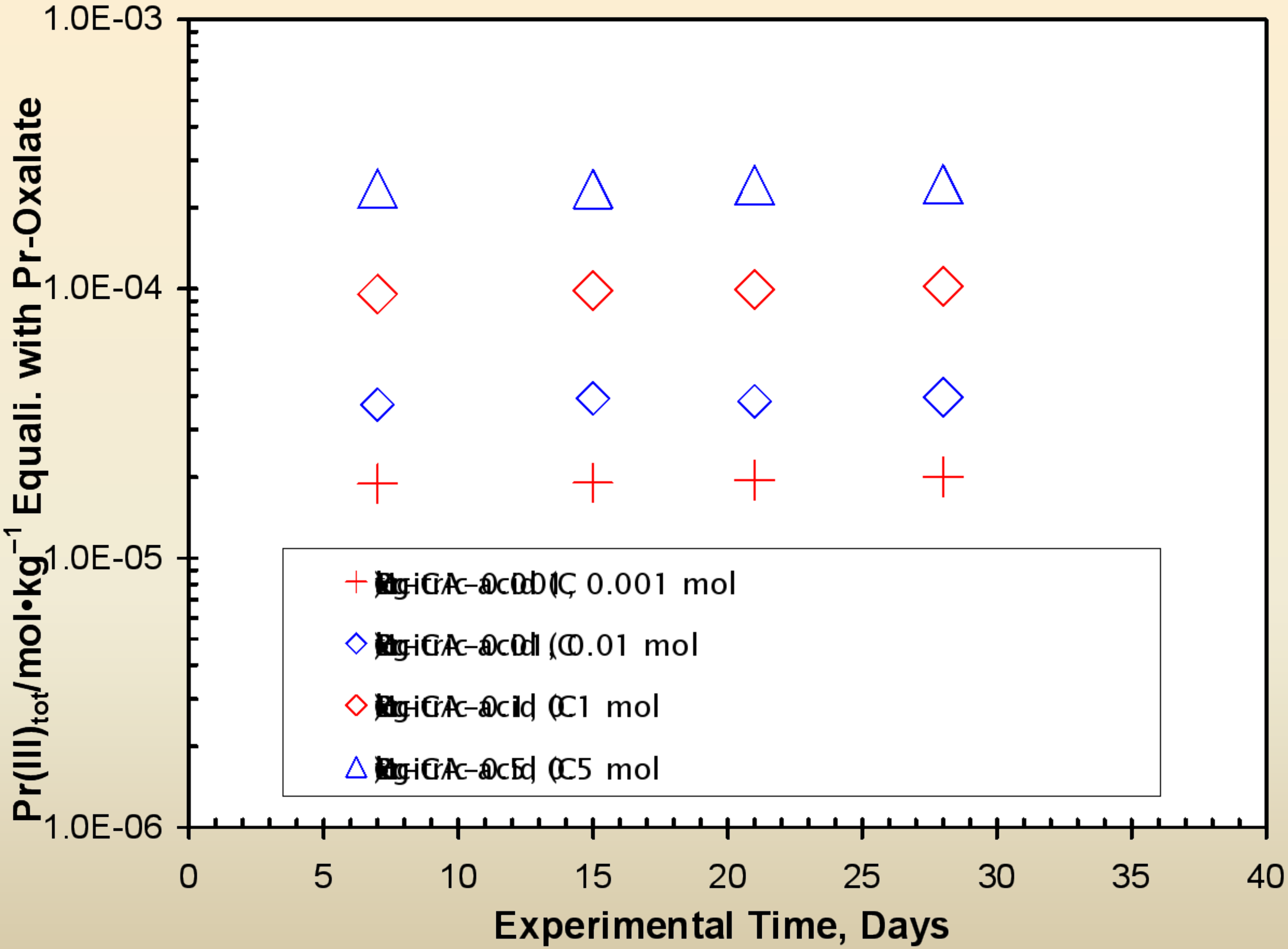


SEM Images of Starting Materials: $Pr_2(C_2O_4)_3 \bullet 10H_2O$ (left) and $Nd_2(C_2O_4)_3 \bullet 10H_2O$ (right)

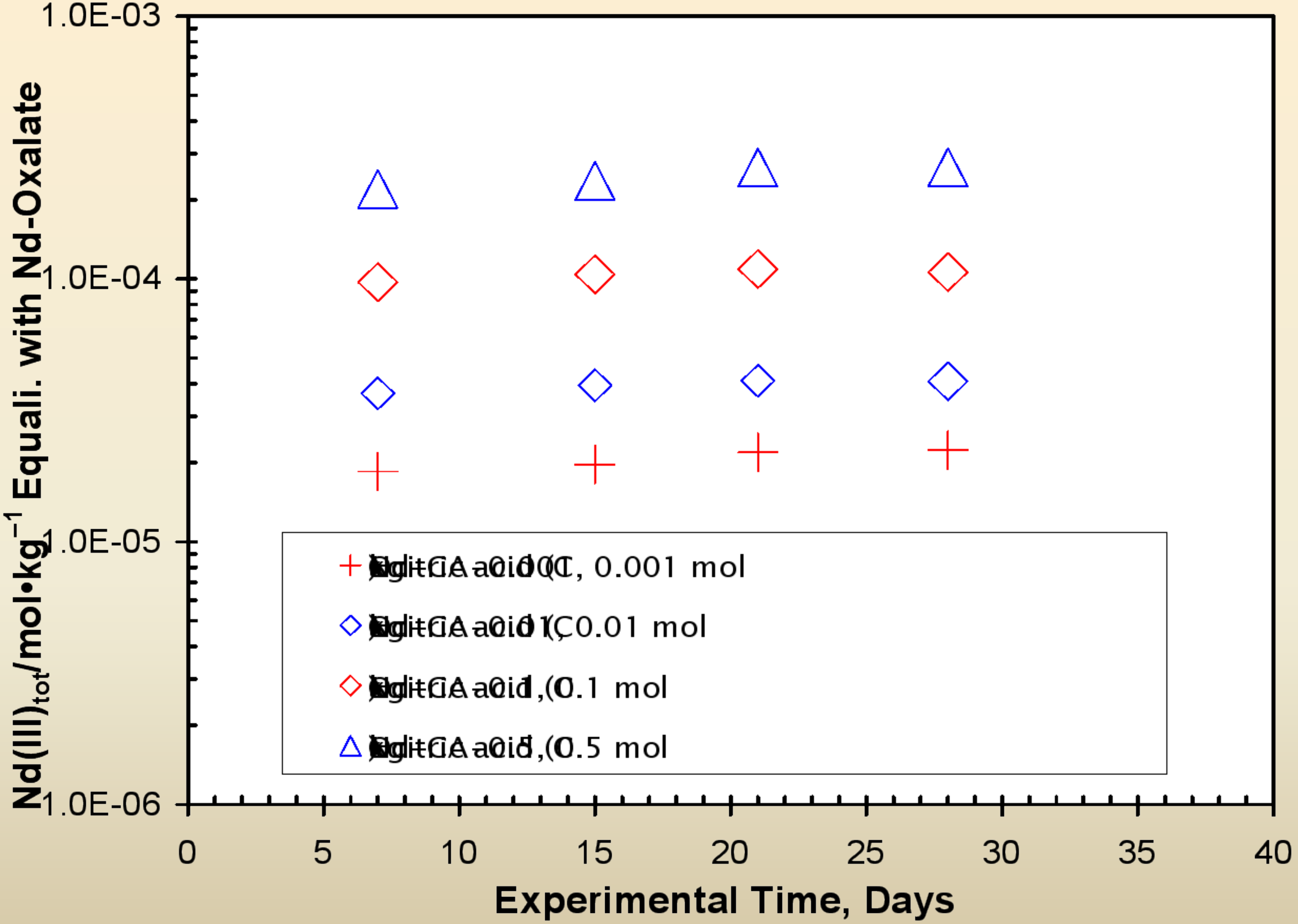




Solubility of $Pr_2(C_2O_4)_3 \cdot 10H_2O$



Solubility of $Nd_2(C_2O_4)_3 \cdot 10H_2O$



Preliminary Interpretations

- The equilibrium for the solubility measurements was attained at the first sampling (i.e., 7 days), indicating that
    - The systems with $Pr_2(C_2O_4)_3 \bullet 10H_2O$ and $Nd_2(C_2O_4)_3 \bullet 10H_2O$ as the solubility -controlling phases have the fast kinetics to reach equilibrium.
- Our results indicate that $Pr_2(C_2O_4)_3 \bullet 10H_2O$ has slight higher solubilities than $Nd_2(C_2O_4)_3 \bullet 10H_2O$ in citric acid solutions, consistent with the previous observations in $HNO_3 + H_2C_2O_4$ solutions [2].
- Our results indicate that the measured solubilities in citric acid solutions are at least several times higher than those predicted with all oxalate and citrate binary complexes with Pr(III) and Nd(III), implying
    - The ternary complex(es) of Pr(III)/Nd(III) with oxalate and citrate contributes to the higher solubility.

---

[2] Xiong, Y.-L., and Wang, Y.-F., 2021. Experimental and modeling studies of Pr and Nd oxalates to high ionic strengths: Insight into actinide(III) oxalates. Chemical Geology 573, p. 120200.

Work in Progress

- We are in the process of determining the stoichiometry of the ternary complex(es) of Pr(III)/Nd(III) with oxalate and citrate, via
  - Further experimental work
  - Modeling, including thermodynamic modeling and possibly DFT calculations