

# SOLUBILITY OF PU(III)- AND AM(III)-OXALATES TO HIGH IONIC STRENGTHS: INSIGHT FROM EXPERIMENTAL STUDIES ON PR(III)- AND ND(III)-OXALATES

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# OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Experimental
  - Synthesis of Pr- and Nd-Oxalates
  - Solubility Experiment Set-up
- Results
  - Comparison with literature data for Am(III)-oxalate
- Summary and Future Work

# INTRODUCTION

- Actinide oxalates are important to nuclear industry and other fields:
  - Precipitation of actinide(III) and actinide(IV) is widely used as technological method for isolation and purification of actinides
  - Such oxalates are the precursors of oxide fuels.
- Actinide Oxalate to Nuclear Waste Management:
  - Oxalate is one of the most important degradation products of humic and fulvic acids (Ferri et al., 2000).
    - Such natural oxalate can impact the mobility of radionuclides.
  - Oxalate is present in waste stream for geological repositories.
    - For instance, liquid oxalate waste from the reprocessing process in France will be conditioned and then be disposed of in the repository.
  - As actinides and oxalates are both present in nuclear waste streams in geological repositories,
    - Actinide oxalates could become solubility-controlling phases and prevents the mobility of actinides, as actinide oxalates have very low solubilities.

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Ferri, D., Iuliano, M., Manfredi, C., Vasca, E., Caruso, T., Clemente, M. and Fontanella, C., 2000. Dioxouranium (VI) oxalate complexes. *Journal of the Chemical Society, Dalton Transactions*, (19), pp.3460-3466.

# INTRODUCTION (cont'd)

- Rare earth elements (REE) oxalates are ideal analogs to actinide(III) oxalates:
  - Their effective ionic radii are almost identical:
    - The effective radius of Pu(III) at coordination number of six: 1.00 Å
    - The effective radius of Pr(III) at coordination number of six: 0.99 Å
    - The effective radius of Am(III) at coordination number of six: 0.975 Å
    - The effective radius of Nd(III) at coordination number of six: 0.983 Å
  - They have identical stoichiometry:
    - $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  vs  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$
    - $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  vs  $\text{Am}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$
  - REE do not have radioactivity.

# OBJECTIVE OF THIS STUDY

- Experimentally determine solubilities of Pr- and Nd-oxalates as a function of ionic strength.
- In combination of the literature data, the goal is to develop a Pitzer model that
  - can describe the solubility of actinide oxalates in various disposal concepts, specially in high ionic strength environments.

# Experimental

## Synthesis of Pr- and Nd-oxalates

- $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  was synthesized
- Dropwise addition of 0.67 M  $\text{PrCl}_3$  into 0.18 M  $\text{H}_2\text{C}_2\text{O}_4$
- $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  has an identical stoichiometry with the plutonium analog,  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$
- $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  has the characteristic light green color

# Experimental

## Synthesis of Pr- and Nd-oxalates

- We synthesized  $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$
- Dropwise addition of 0.70 M  $\text{NdCl}_3$  into 0.18 M  $\text{H}_2\text{C}_2\text{O}_4$
- $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  has an identical stoichiometry with the americium analog,  $\text{Am}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$
- $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  has the characteristic light purple color

# Experimental

## Set-up solubility experiments

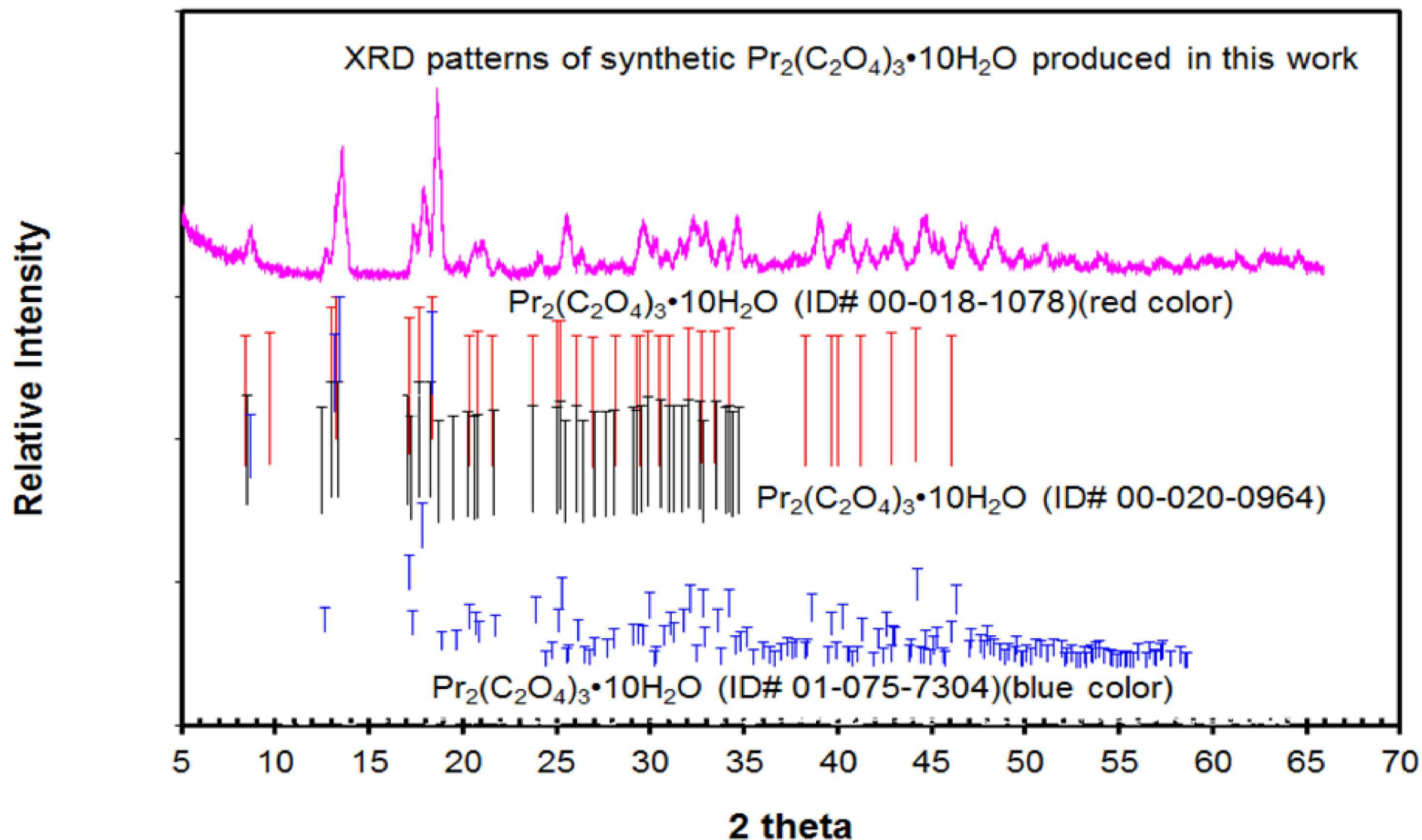
- Supporting solutions: 0.1 M, 0.5 M, 1.0 M  $\text{HNO}_3$ , 0.016 M  $\text{H}_2\text{C}_2\text{O}_4$  + 1.82 M  $\text{HNO}_3$ , 0.030 M  $\text{H}_2\text{C}_2\text{O}_4$  + 2.50 M  $\text{HNO}_3$ , and 0.051 M  $\text{H}_2\text{C}_2\text{O}_4$  + 2.9 M  $\text{HNO}_3$
- Mass of solubility-controlling phases in our experiments: ~0.5 g to ~1.25 g
- Volume of supporting solutions in our experiments: 100 mL to 140 mL
- Temperature at 25°C.

# Experimental

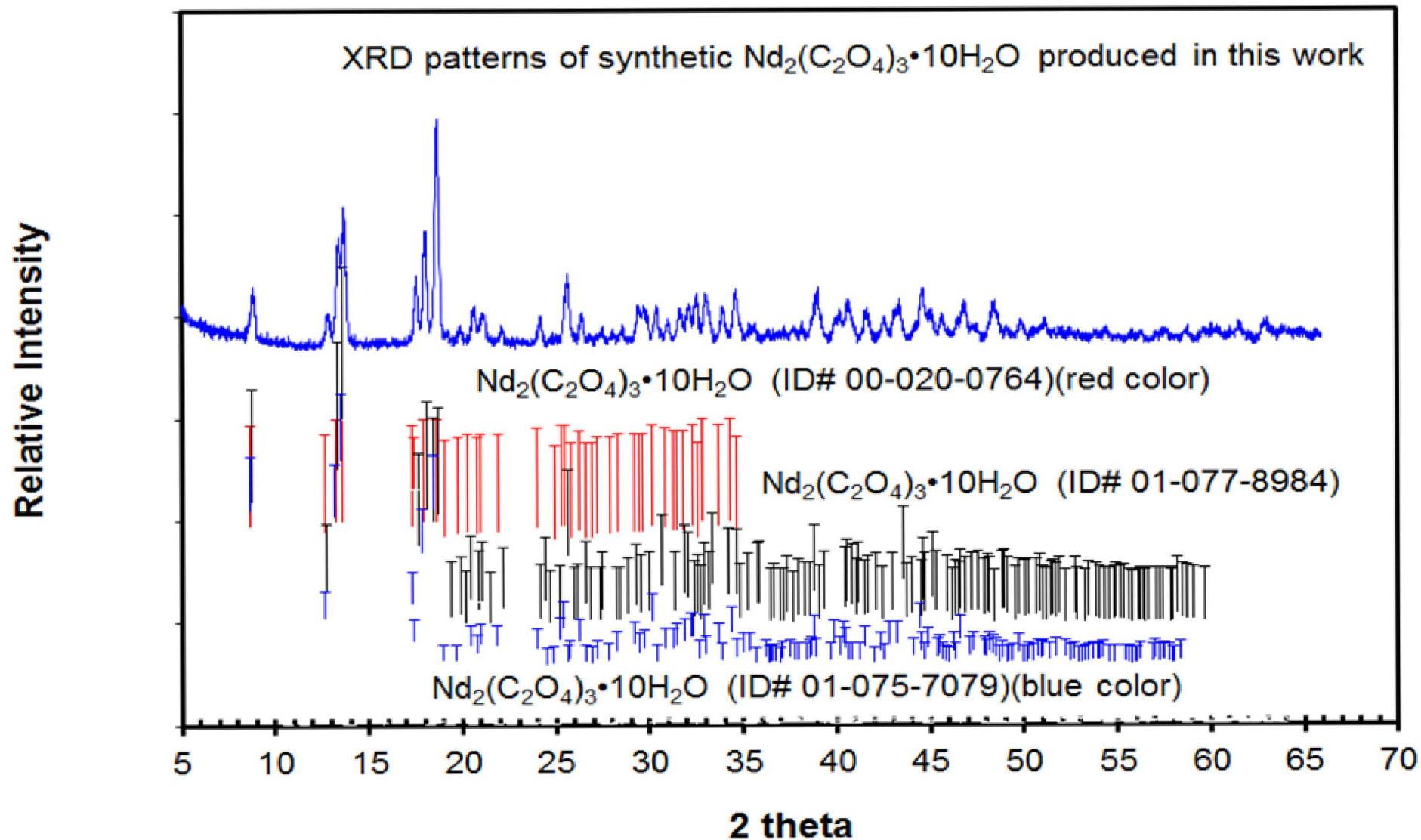
## Instrumental Analyses

- Solid phases are analyzed with XRD
- Solution samples were analyzed with ICP-AES

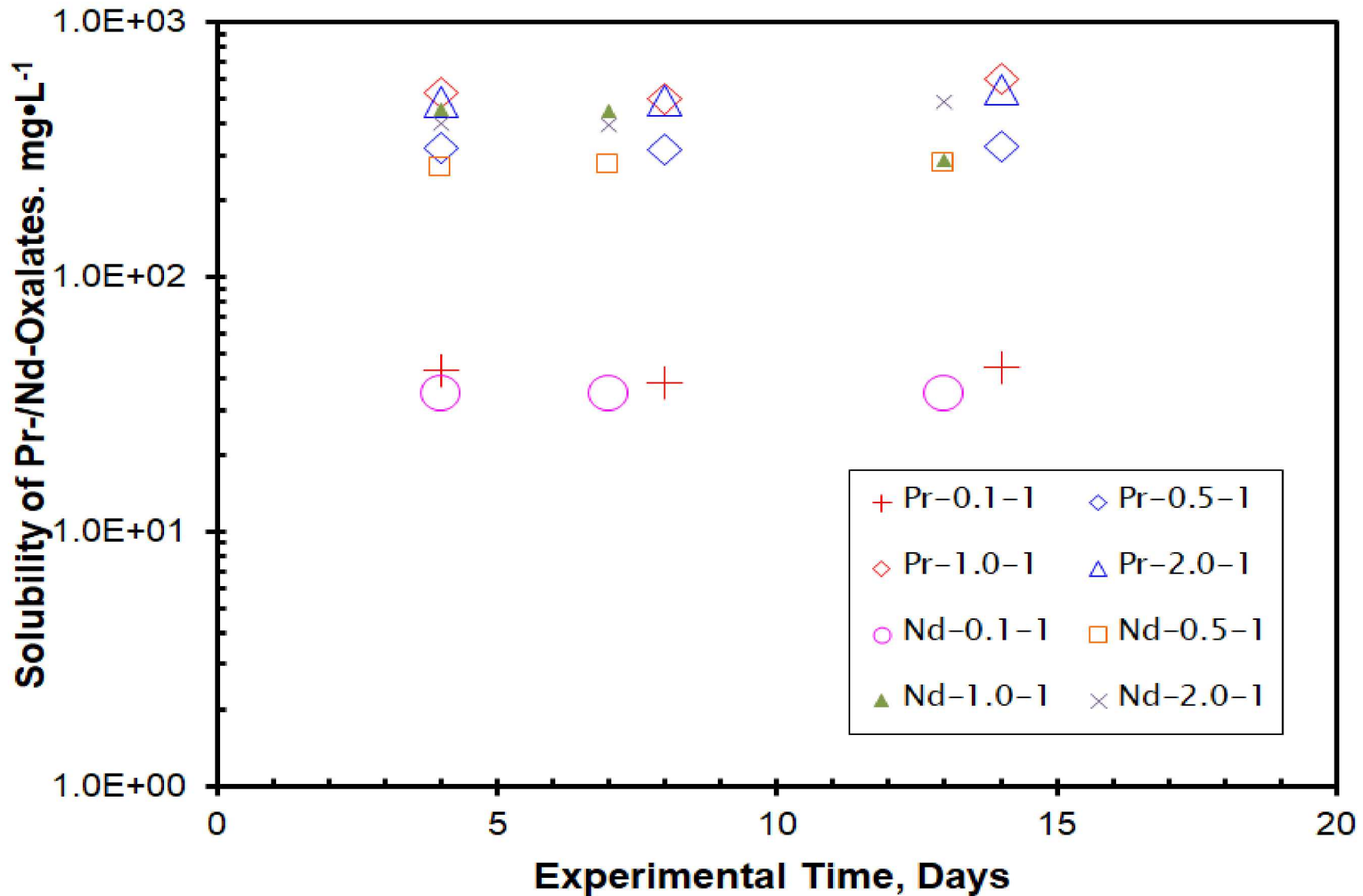
# Experimental Results: XRD



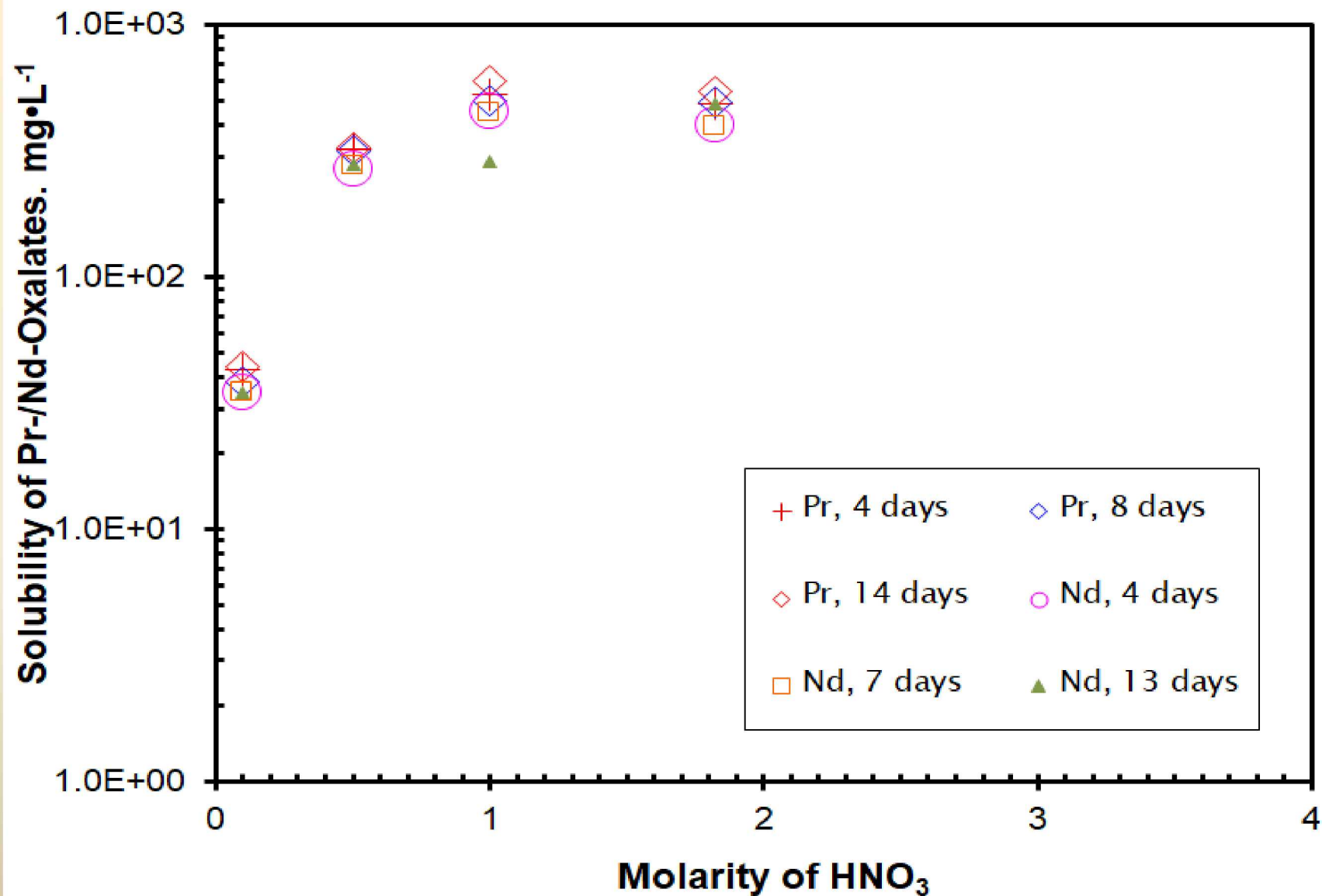
# Experimental Results: XRD



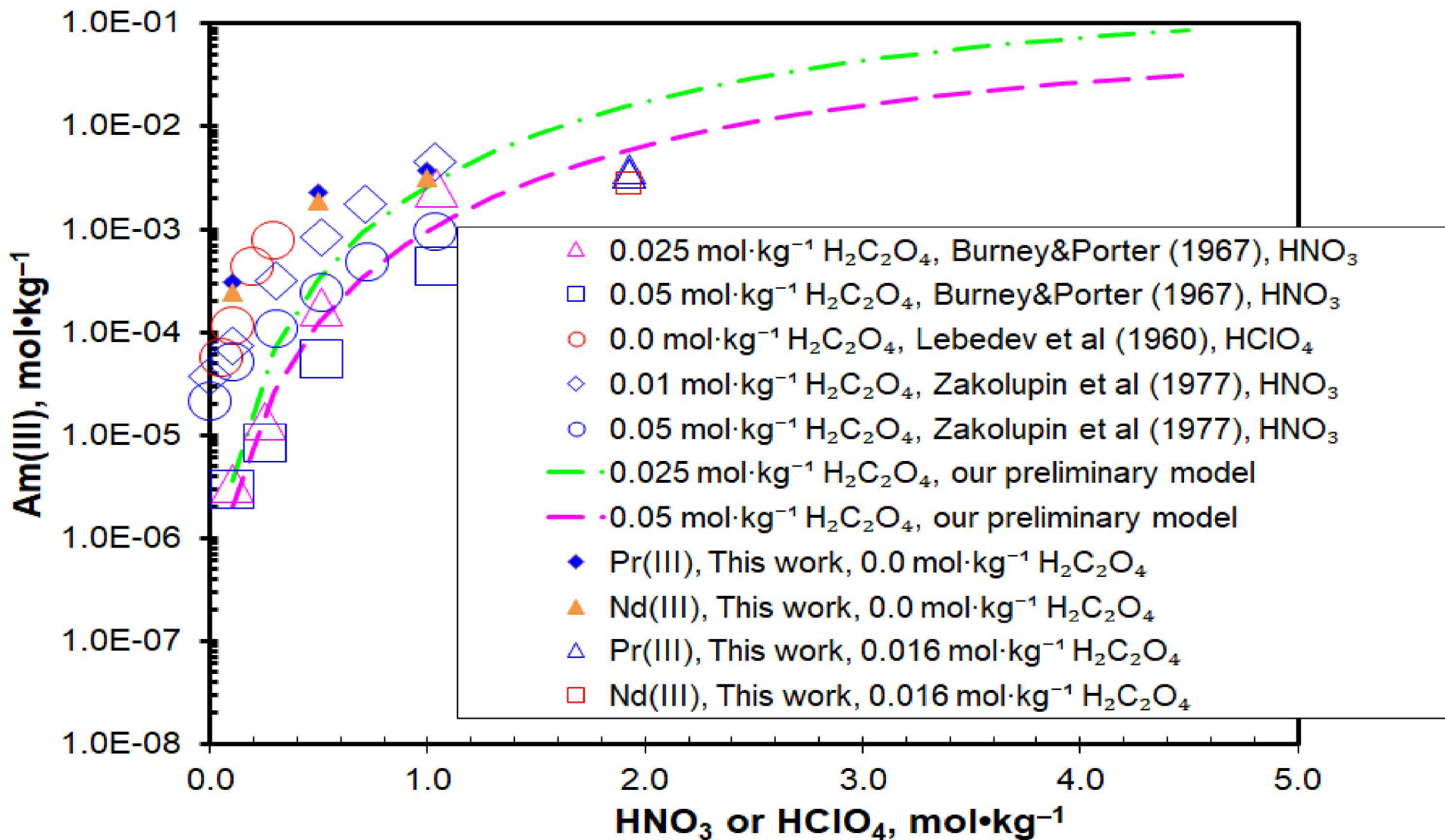
# Experimental Results: Solubility



# Experimental Results: Solubility



# Experimental Results: Comparison



# Summary and Future Work

- We have determined solubilities of Pr- and Nd-oxalates in nitric acid and in the mixtures of nitric and oxalic acids.
  - Equilibrium was attained in a few days
  - The solubility of Pr- and Nd-oxalates has a strong dependence on molarity of  $\text{HNO}_3$
- In combination with the literature data, we are in the process of developing a Pitzer model applicable
  - to describe the solubility of actinide(III) oxalates in various disposal concepts.