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Experimental Studies of Pr(III)- and Nd(III)-Oxalates to High Ionic Strengths: Applications to Nuclear Waste Management

PRESENTED BY

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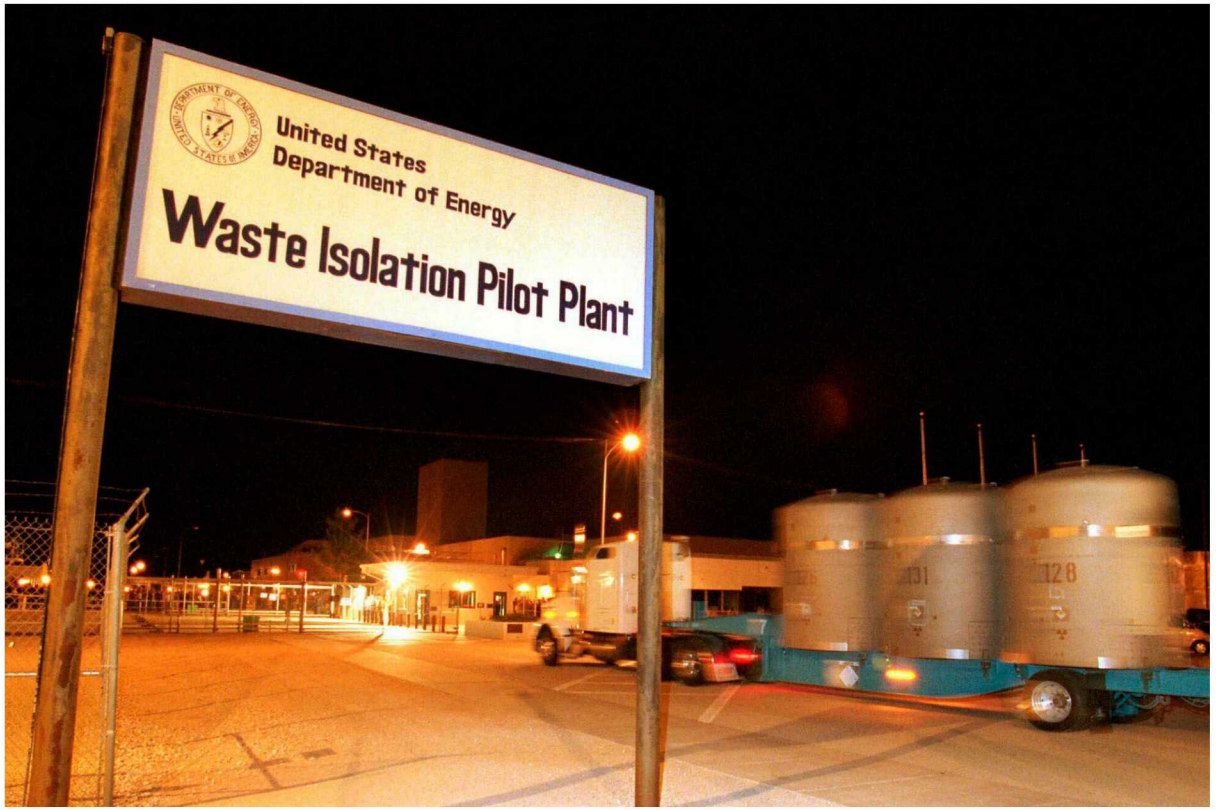
Outline



Introduction → Objective → Methodology → Preliminary results → Conclusion

Introduction

- Actinides and oxalates are both present in nuclear waste streams in geological repositories.
- As an example, 1.18×10^{-2} M of oxalate was present in 2014 performance assessment for the Waste Isolation Pilot Plant[3].
- Significant inventories of actinides are also present in the WIPP.
- As actinide oxalates have very low solubilities, they could become solubility-controlling phases and prevents the mobility of actinides.
- REE are ideal for this investigation because they are good analogs to actinides and do not have radiotoxicity.
- Solubility of Pr- and Nd-oxalates is determined as a function on ionic strength

Objective

- In combination of the literature data, the validation of the Pitzer model with current experimental data.
- Solubility of Pr- and Nd-oxalates is determined as a function on ionic strength.
- The Pitzer model can describe the solubilities of actinide oxalates in various disposal concepts, specially in high ionic strength environments.

Description of the methodology

- Synthesis of Pr- and Nd-oxalates

- $Pr_2(C_2O_4)_3 \cdot 10H_2O$ was synthesized
- Dropwise addition of 0.67 M $PrCl_3$ into 0.18 M $H_2C_2O_4$
- $Pr_2(C_2O_4)_3 \cdot 10H_2O$ has an identical stoichiometry with the plutonium analog, $Pu_2(C_2O_4)_3 \cdot 10H_2O$
- $Pr_2(C_2O_4)_3 \cdot 10H_2O$ has the characteristic light green color

Description of the methodology

- Synthesis of Pr- and Nd-oxalates

- We synthesized $Nd_2(C_2O_4)_3 \cdot 10H_2O$
- Dropwise addition of 0.70 M $NdCl_3$ into 0.18 M $H_2C_2O_4$
- $Nd_2(C_2O_4)_3 \cdot 10H_2O$ has an identical stoichiometry with the americium analog, $Am_2(C_2O_4)_3 \cdot 10H_2O$
- $Nd_2(C_2O_4)_3 \cdot 10H_2O$ has the characteristic light purple color

Description of the methodology

- Set-up solubility experiments

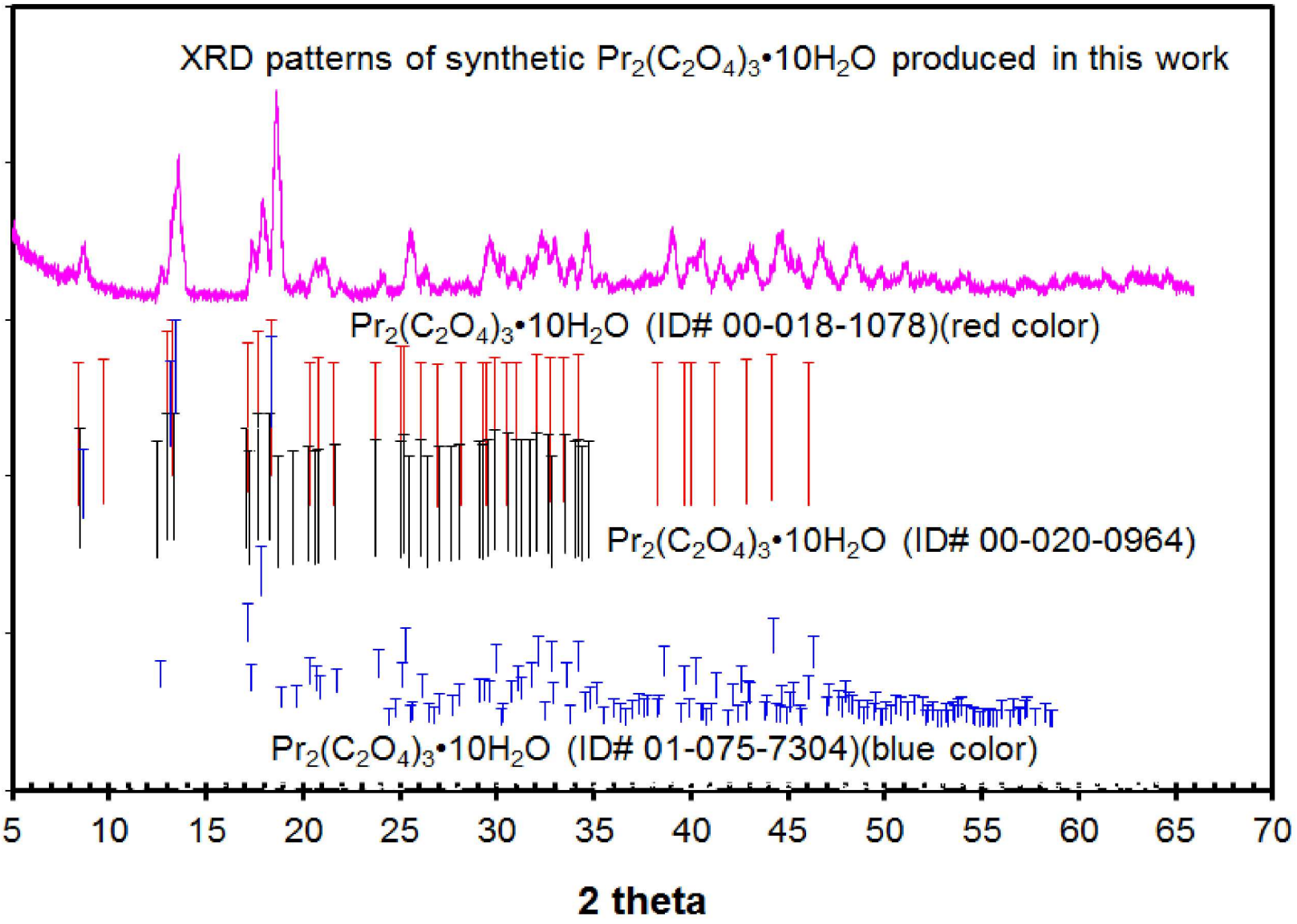
- Supporting solutions: 0.1 M, 0.5 M, 1.0 M HNO_3, 0.016 M $H_2C_2O_4$ + 1.82 M HNO_3, 0.030 M $H_2C_2O_4$ + 2.50 M HNO_3, and 0.051 M $H_2C_2O_4$ + 2.9 M HNO_3
- Mass of solubility-controlling phases in our experiments: ~0.5 g to ~1.25 g
- Volume of supporting solutions in our experiments: 100 mL to 140 mL.

Description of the methodology

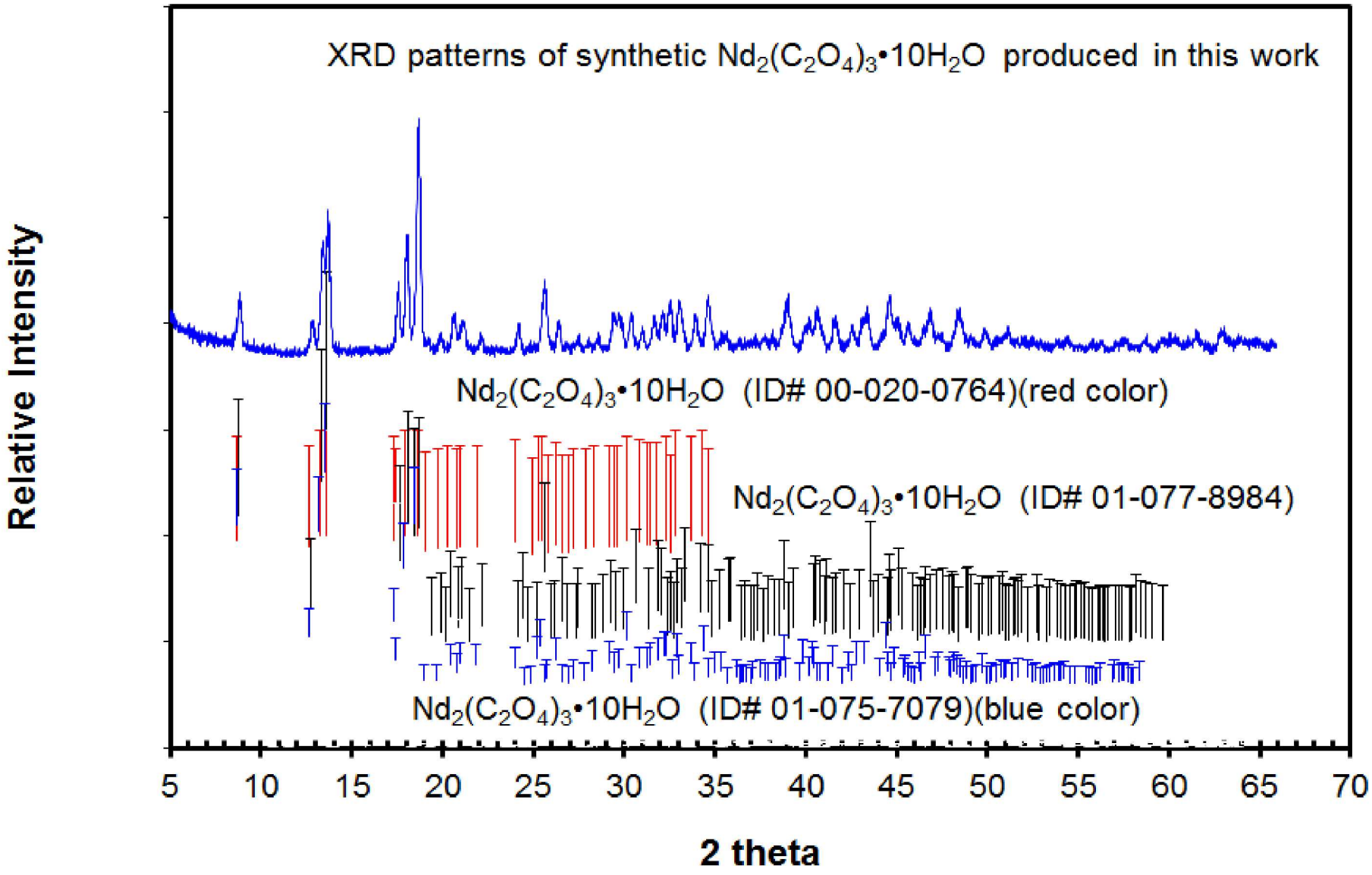
- **Instrumental Analyses**

- **Solid phases are analyzed with XRD**
- **Solution samples were analyzed with ICP-OES**

Experimental Results: XRD



Experimental Results: XRD



References

1. Abraham, F., et al, 2014. Actinide oxalates, solid state structures and applications. *Coordination Chemistry Reviews* 266-267 (2014) 28-68.
2. Brush, L.H. and Domski, P.S., 2013. Calculation of Organic Ligand Concentrations for the WIPP CRA-2014 PA. *Analysis report, January*, *14*, p.2013.
3. Chung, D.Y., et al, 1998. Solubility of Rare Earth Oxalate in Oxalic and Nitric Acid Media. *Journal of Industrial and Engineering Chemistry*. Vol 4, No 4.
4. Crouthamel, C. and Martin, D.S., 1951. Solubility of the Rare Earth Oxalates and Complex Ion Formation in Oxalate Solution. II. Neodymium and Cerium (III). Institute for Atomic Research and the Department of Chemistry, Iowa State College.
5. Feibush, A.M., 1958. Solubility of Yttrium Oxalate. *Analytical Chemistry*. Vol. 30, No., 10 October 1958.
6. Johansson, L., 1968. Solubility measurements and complex formation in solution. *Coordination Chemistry Reviews* 3 (1968) 293-318.
7. Laine, H. and Karttunen, P., 2010. Long-Term Stability of Bentonite: A Literature Review. *Posiva Oy*.
8. Thakur, P., et al, 2015. An improved thermodynamic model for the complexation od trivalent actinides and lanthanide with oxalic acid valid to high ionic strength. *Chemical geology* 413 (2015) 7-17.
9. Xiong, Y., 2011. Organic species of lanthanum in natural environments: Implications to mobility of rare earth elements in low temperature environments. *Applied Geochemistry*.
10. Xiong, Y., et al, 2013. Experimental determination of solubilities of lead oxalate in a NACL medium to high ionic strengths, and the importance of lead oxalate in low temperature environments. *Chemical Geology* 342 (2013) 128-137.
11. Xiong, X., et al, 2017. Long-Term Experimetnal Determination of Solubilities of Micro-Crystalline Nd(III) Hydroxide in High Ionic Strength Solutions: Applications to Nuclear Waste Management. *Aquat Geochem* 23:359-375.