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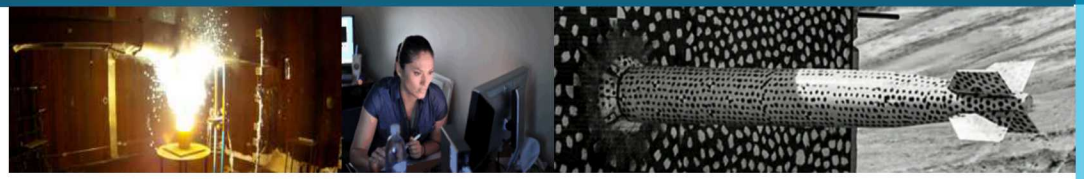
POTENTIAL USE OF NOVEL Zr-P-W WASTE-FORMS FOR RADIONUCLIDE WASTE STREAMS



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Background

- Characteristics of effective radionuclide waste-forms
- Benefits of a zoned waste-form with a radionuclide-loaded core.
  - Isolation
  - Effects of radiation-induced amorphization (metamictization)
- Proposed Zr-W-(P) waste-form materials and their special properties
- Overall characterization goals and approach
- Leaching behavior of ZrW_2O_8 and $Zr_2P_2WO_{12}$ (the focus of this talk)

Characteristics of Effective Waste-form Materials

Effective radionuclide waste-forms must meet several criteria

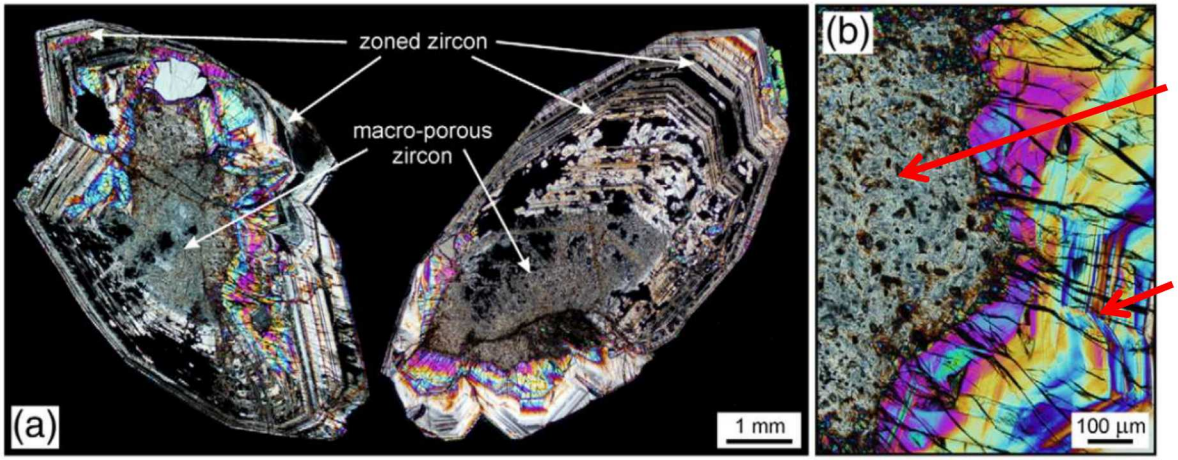
- Low solubility or leach rate
  - Slow release to the environment
- Structurally compatible with radionuclide(s) of interest:
  - Required to achieve effective radionuclide loading
- Resistant to radiation damage
  - Radiation-induced amorphization increases solubility
  - Related swelling and cracking can increase accessible surface area.

Possible Zoned Waste-forms

- **A zoned waste-form with a radionuclide-loaded core?**
  - Benefit: Radionuclide is (at least initially) isolated from the environment.
  - Disadvantage: For most materials, core metamictization will eventually result in expansion, shattering wasteform, allowing releases to the environment
- **Natural analog: zircon**
  - Zircon commonly incorporates uranium during crystallization, and is frequently zoned

Preferential dissolution of radiation-damaged zones in a natural zircon

Accumulation of radiation damage results in swelling and amorphization of U-rich core, and rim cracking, increased solubility and surface area, and more rapid radionuclide release.

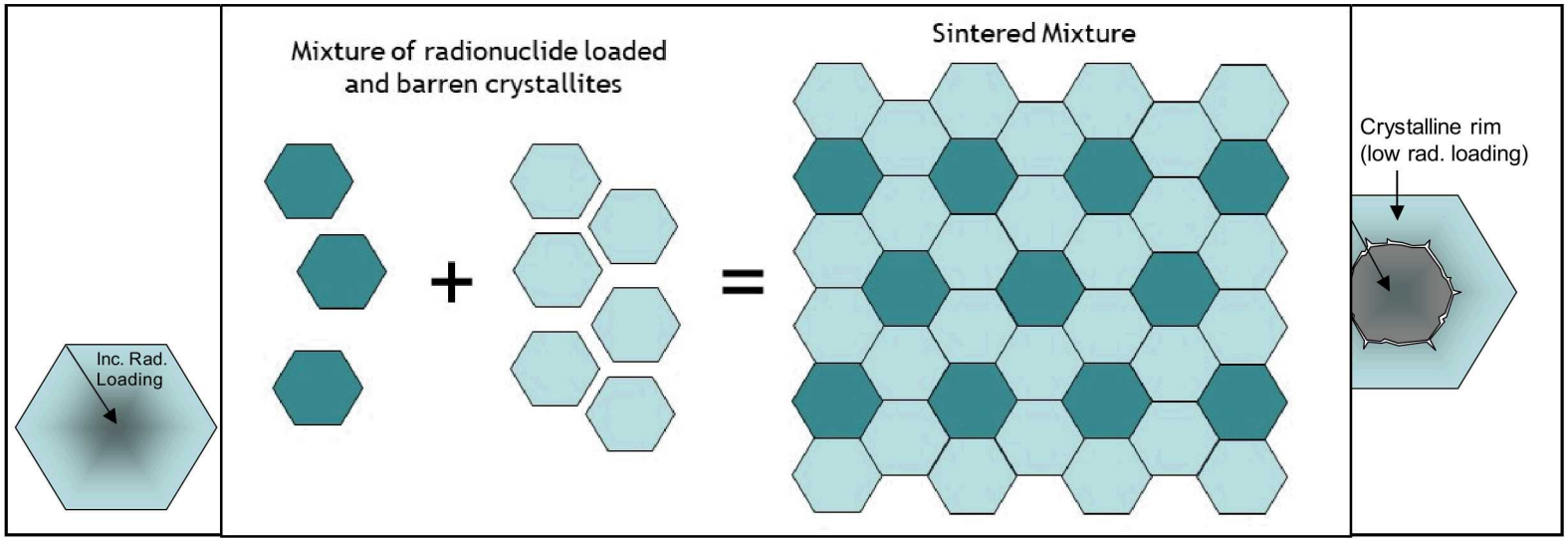


Heavily altered radiation-damaged core (high U)

Unaltered low-U rim (note cracking due to core swelling)

Proposed Zr-W-(P) Zoned Wasteforms

- **Some Zr-W-(P) phases have unusual and useful properties**
  - ZrW_2O_8 (cubic), $Zr_2P_2WO_{12}$ (orthorhombic)
  - Widely studied for negative thermal expansion (NTE) properties.
  - *Undergo pressure-induced amorphization (the materials shrink upon amorphization); radionuclide core would not expand upon amorphization and shatter encapsulating rim*



- **Potential radionuclide loading:**
  - IV actinides (U, Pu) are nearly identical in size and substitute freely for Zr^{+4} in many Zr phases.
  - Tc(IV) can also substitute for Zr^{+4}. Tc(VII)—coupled substitution for W(VI)?
  - Possible uses: waste-form for specific hard-to-handle radionuclide waste-streams (e.g., weapons-grade plutonium, Tc)

Evaluation of Zr-W NTE Phases as Waste-Forms

- Synthesis, characterization, and sintering of materials (companion talk Gordon et al.)
- Molecular modeling studies of the material:
  - Density Functional Theory (DFT) studies: Structure, radionuclide substitution and loading (companion talk Kim et al.; Weck et al., 2018a, 2018b, 2018c)
  - Molecular Dynamics (MD) studies: Stresses associated with radiation damage, amorphization (companion talk Greathouse et al.; Greathouse et al., 2019 (submitted))
- Ion Beam and TEM studies of waste-form amorphization
- Dissolution and leaching behavior of ZrW_2O_8, and $Zr_2P_2WO_{12}$ *(this talk)*

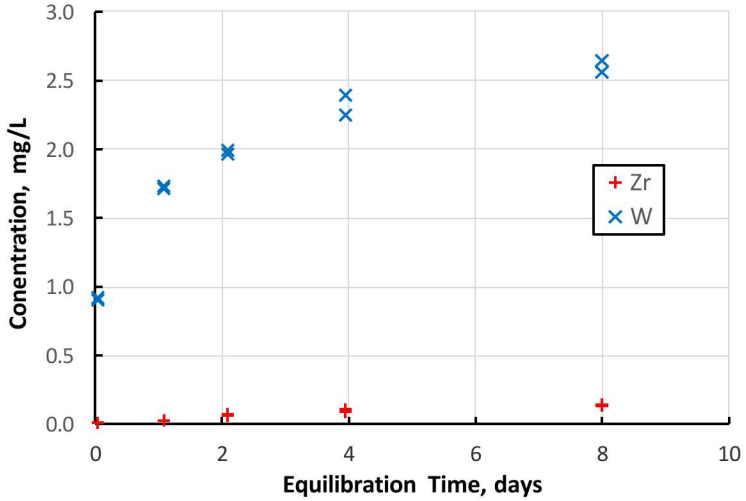
Dissolution rates of cubic ZrW_2O_8

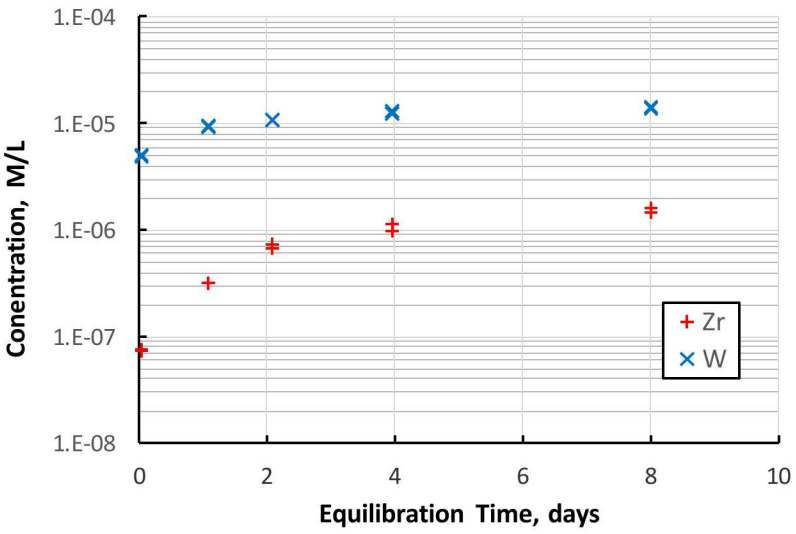
An effective wasteform must have a low dissolution/radionuclide release rate. Dissolution rates evaluated through geochemical modeling and dissolution/leaching experiments.

- Thermodynamic model for ZrW_2O_8 solubility:
  - Two measured calorimetric data sets available for cubic ZrW_2O_8
    - Data differ significantly, predict solubilities that differ by about 5 orders of magnitude
    - Both predict a minimum solubility around pH 5.5-6, with solubility increasing rapidly with increasing pH, due to increasing stability of polynuclear tungstate phases.
- Dissolution rate experiments using synthesized ZrW_2O_8. Two scoping experiments have been run:
  - Dissolution as a function of time (pH 5.3, 0-8 days)
  - Dissolution as a function of pH (pH 4-8, 18 days)

ZrW_2O_8 Dissolution at Constant pH

- **Conditions:**
  - Synthesized material 50 mg ZrW_2O_8/40 ml 0.001 M NaCl.
  - Surface area about 5 m^2/g
  - pH 5.3 (equil. pH)
  - Equilibration time 0-8 days
- Solution concentrations low, but continue to increase over 8 days.
- Release highly non-stoichiometric (W/Zr ratio >> 2).
  - Zr oxide/hydroxide is highly insoluble, while tungstate is relatively soluble, especially at high pH.
  - Does Zr-oxide/hydroxide form a leached layer on the surface? Is it protective?





Dissolution as a Function of pH

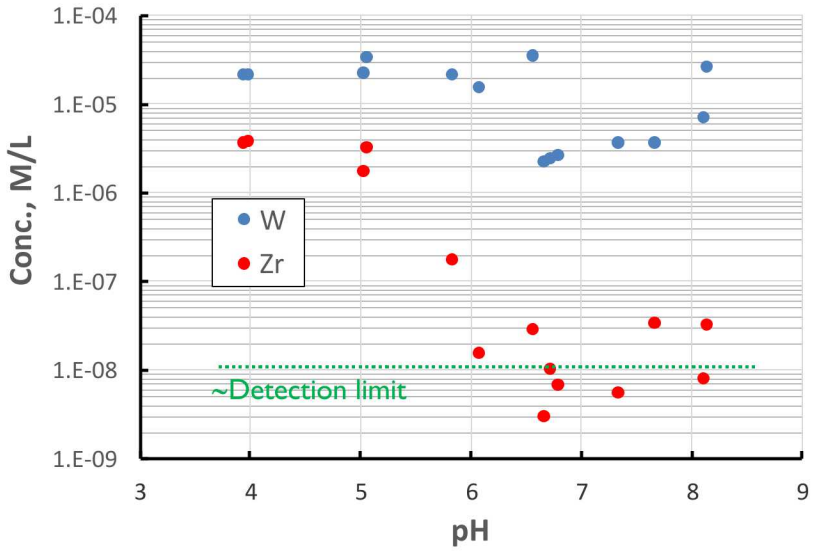
Conditions:

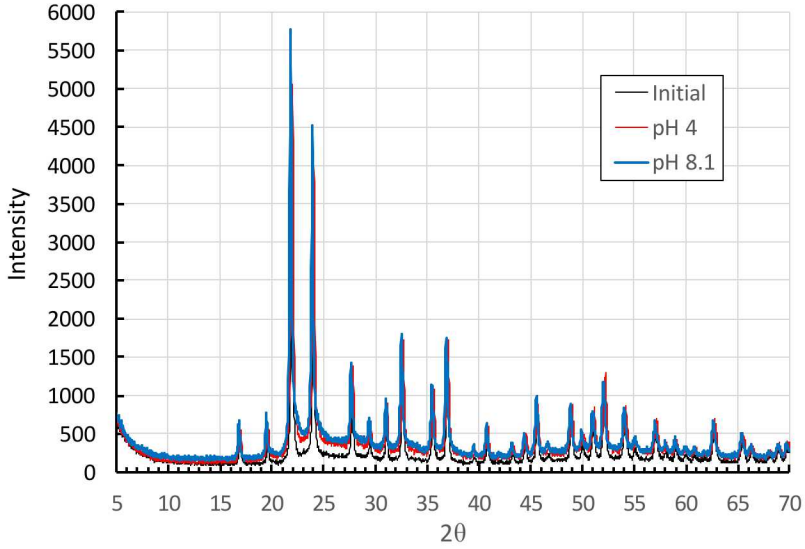
- Synthesized material 50 mg ZrW_2O_8/40 ml 0.001 M NaCl.
- Surface area about 5 m^2/g
- pH 4-8.2, readjusted as necessary
- Equilibration time 18 days

Again, incongruent dissolution—much higher W concentrations than Zr concentrations.

- W concentrations much higher than Zr concentrations. Suggests incongruent dissolution.
- Zr concentrations probably limited by ZrO_2 or $Zr(OH)_4$ (Solubilities $<10^{-8}$ M to 10^{-7} M over this pH range). Re-precipitation or leach layer?
- Measured solution concentrations limited by solubility of other phases, not a good measure of ZrW_2O_8 solubility.
- However, post-test XRD analysis of solids indicates no significant conversion.

Batch experiments not useful for determining dissolution rates, as solution concentrations potentially reflect incongruent dissolution and precipitation of other phases. Flow-through reactor experiments initiated.

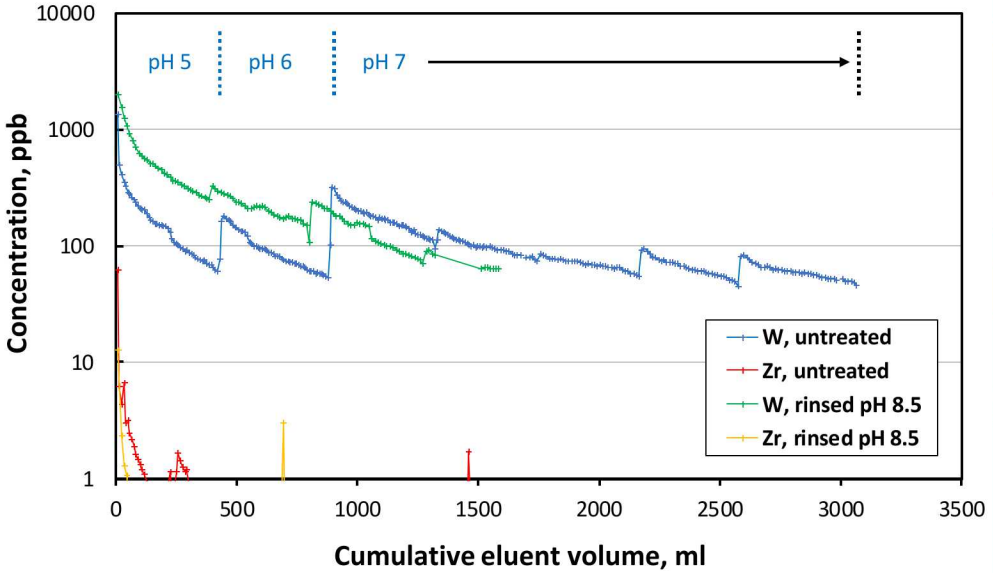


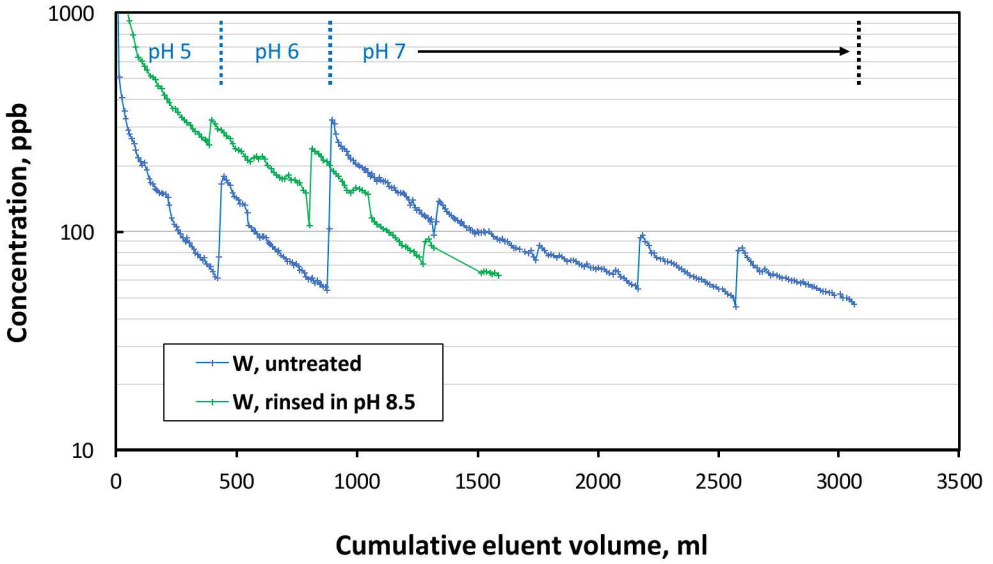


Measuring ZrW_2O_8 Leach Rates
Flow-Through Reactor

- Conditions:
  - 80 mg of ZrW_2O_8
  - 3 kD ultrafilter, solution pumped through under low pressure (~2.5 bar).
  - Eluent: 0.001 M NaCl, pH 5, 6, 7
  - W used as a tracer for waste-form dissolution (Zr release limited by Zr oxide/hydroxide solubility)
- Results:
  - Zr and W concentrations initially high, but both drop rapidly with time (Zr to below detection limit).
  - W drops more slowly, than Zr, consistent with formation of a leached layer that is inhibiting further dissolution.
  - *However,* concentration jumps during pump refills ($^1/_2$ hour), suggesting leach layer is not protective.
- Second experiment with ZrW_2O_8 rinsed with pH 8.5 water to eliminate possible WO_3 contamination yielded same results.

ZrW_2O_8 readily leaches, and may not form an effective wasteform.

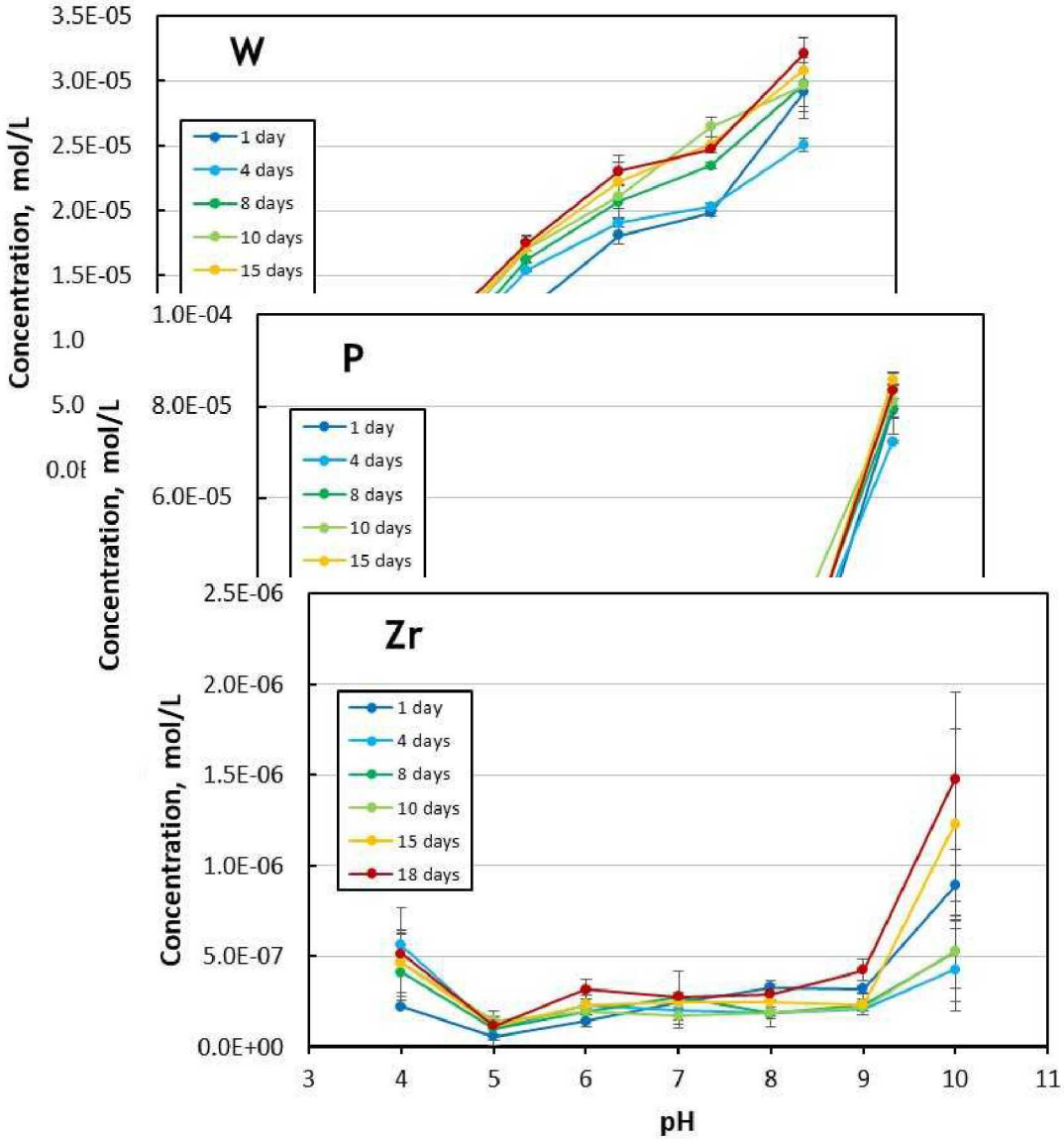




$Zr_2P_2WO_{12}$ Dissolution as a function of pH

- Conditions:
  - 50 mg of ZrW_2O_8 (SA = 17 m^2/g)
  - 40 ml electrolyte (0.001 M NaCl, pH 4-10, readjusted after each sampling).
  - Sampled periodically 1-18 days, filtered with 0.2 µm syringe filter.
  - Measured W, P, Zr by ICP-MS.

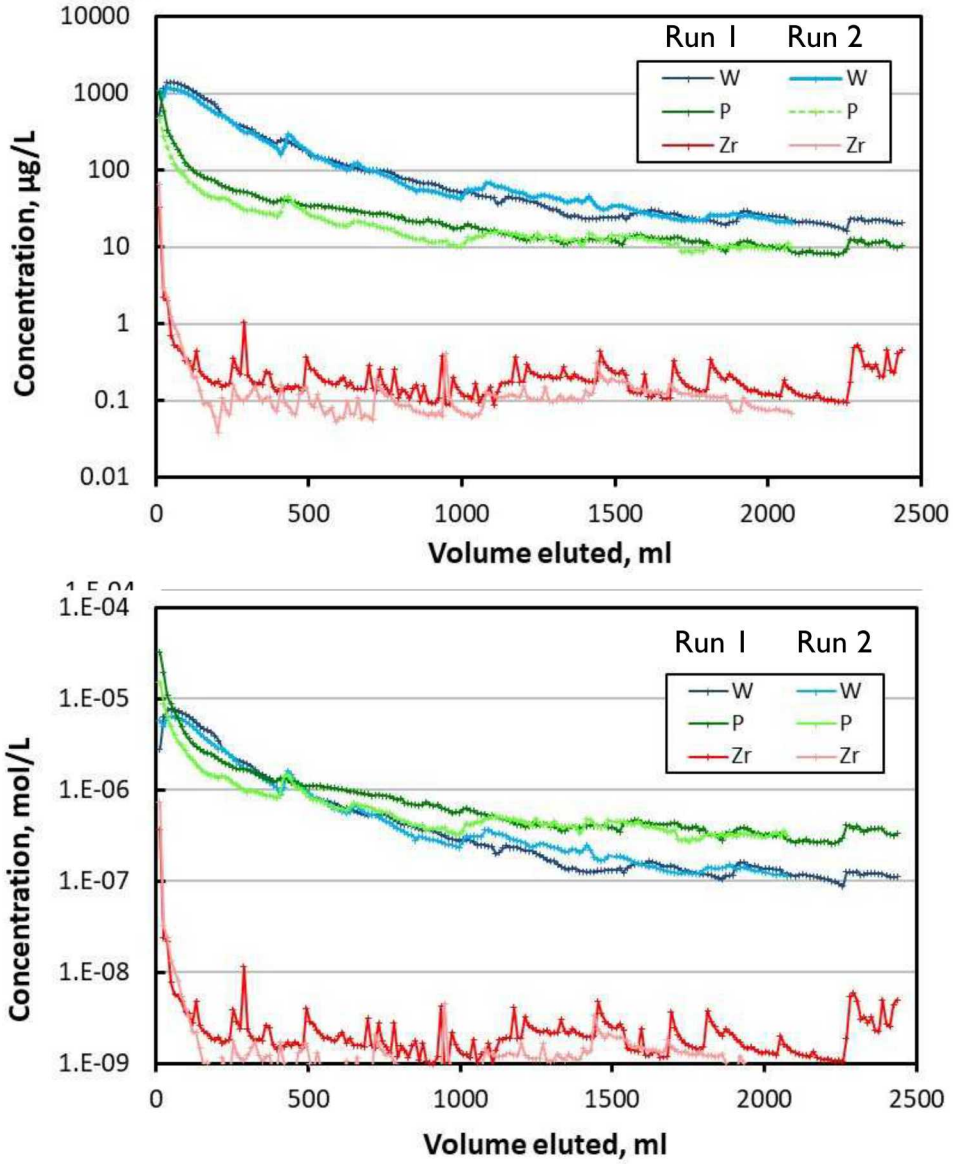
- Results: Each element exhibits different behavior.
  - W—large increase with pH, and consistent increase with time.
  - P—slight increase with pH, except at highest values. No time dependence.
  - Zr—increases at lowest and highest pH values. From pH 5-9, slightly above detection limit (colloidal material passing through the filter?). No time dependence except at highest pH.



Measuring $Zr_2P_2WO_{12}$ Leach Rates
Flow-Through Reactor

- Conditions:
  - 80 mg of $Zr_2P_2WO_{12}$
  - 3 kD ultrafilter, solution pumped through under low pressure (~2.5 bar).
  - Eluent: 0.001 M NaCl, pH 7
  - W and P used as tracers for waste-form dissolution (Zr release limited by Zr oxide/hydroxide solubility)
- Results for Run 2 (Partially sintered, surface area = 5.7 m^2/g)
  - Zr, P and W concentrations initially high, but all drop rapidly with time (Zr to near detection limit).
  - Similar behavior as Run 1.
  - W and P concentrations evolve to values close to stoichiometric with respect to the phase (W/P = 0.5 in phase, W/P = 0.4 in eluent).
  - *However*, pump refills not evident—residence time is less important than for ZrW_2O_8.
  - Lack of surface area dependence indicates leaching is not kinetically controlled
- Significance
  - Lack of dependence on surface area indicates leaching is not a steady state process (e.g., diffusion through a leached layer).

Simplest explanation: Release rate appears to be controlled by equilibrium dissolution. If so, solubility of $Zr_2P_2WO_{12}$ is about 10^{-7} mol/L



Summary

- Evaluating ZrW_2O_8 ad $Zr_2P_2WO_{12}$ as possible waste-forms for select radionuclide waste streams.
- Materials are structurally compatible with incorporation of IV actinides and possibly Tc.
- Materials lose volume upon amorphization, potentially allowing formation of a zoned waste-form highly tolerant of radiation damage.
- Leaching behavior:
  - Both phases dissolve incongruently due to low solubility of Zr oxides/hydroxides
  - ZrW_2O_8 leaches readily; solution concentrations are strongly a function of residence time Zr oxide/hydroxide leach layer or reprecipitate does not appear to limit further leaching of W
  - $Zr_2P_2WO_{12}$ appears leach via equilibrium dissolution. If so, solubility is about 10^{-7} mol/L
- Conclusion: On the basis of leaching behavior evaluated to date, $Zr_2P_2WO_{12}$ appears to be a good candidate for use as a zoned, radiation tolerant waste-form.