Sorption of Uranium (VI) to Graphite under Potential Repository Conditions

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Outline

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- Experimental Methodology
- Graphite Characterization
- Results
  - Effect of pH on Equilibrium Sorption
  - Carbonate and Ionic Strength
  - Sorption Kinetics and Desorption
  - Sorption Isotherms
- Conclusions & Future Work

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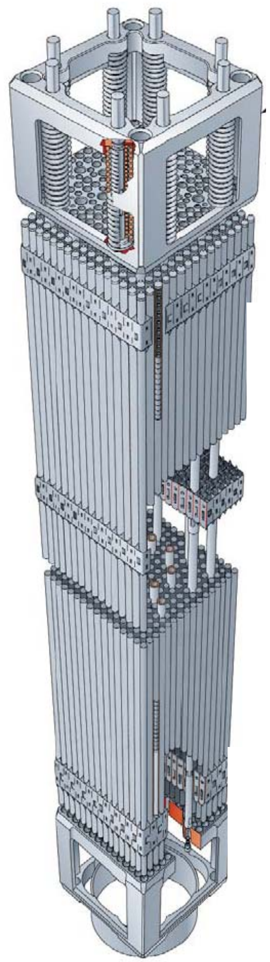
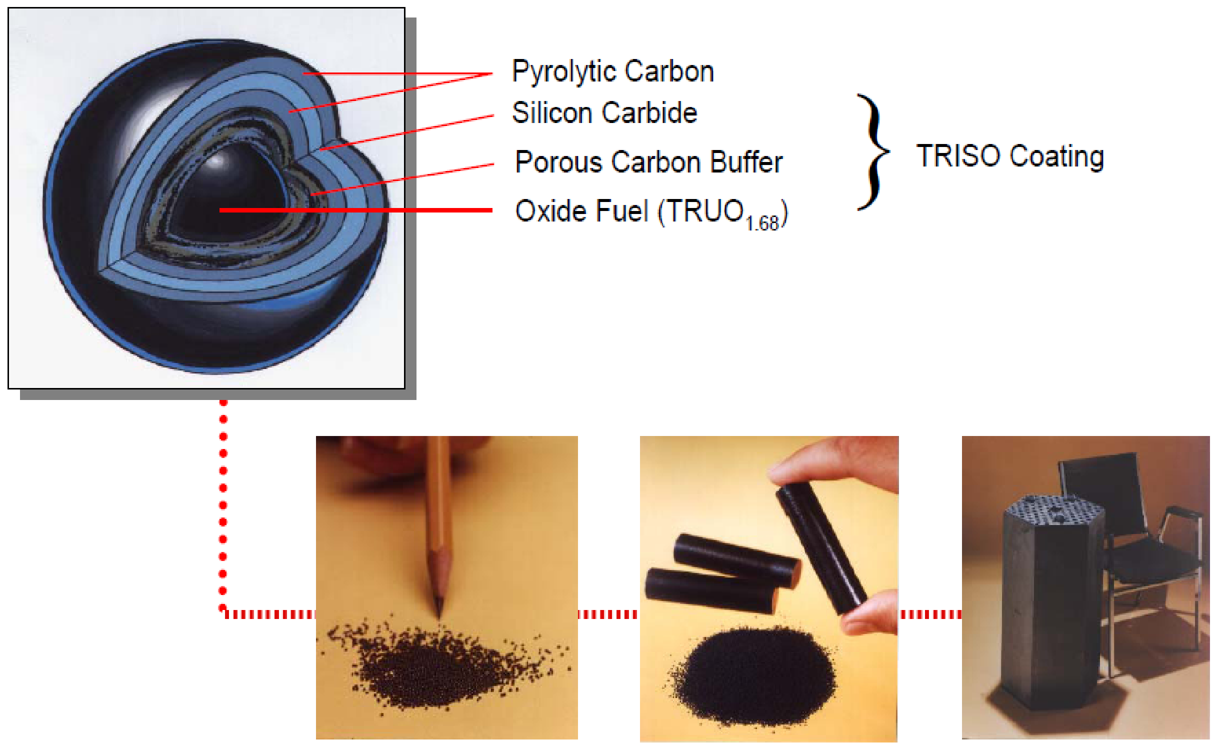
HTGR Fuel Disposal

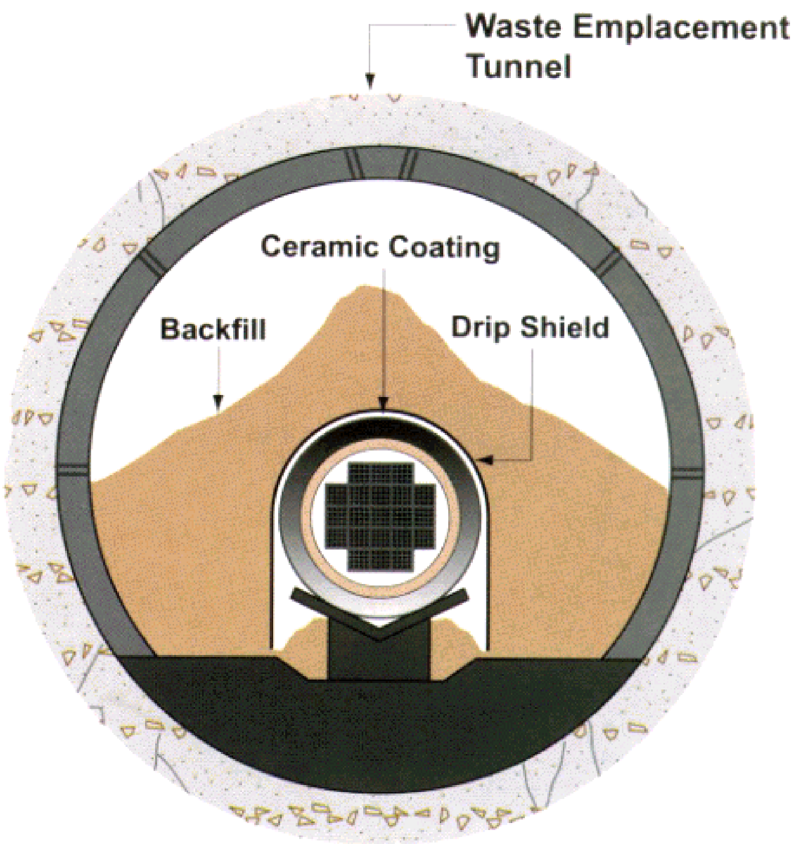
BWR Fuel[1]

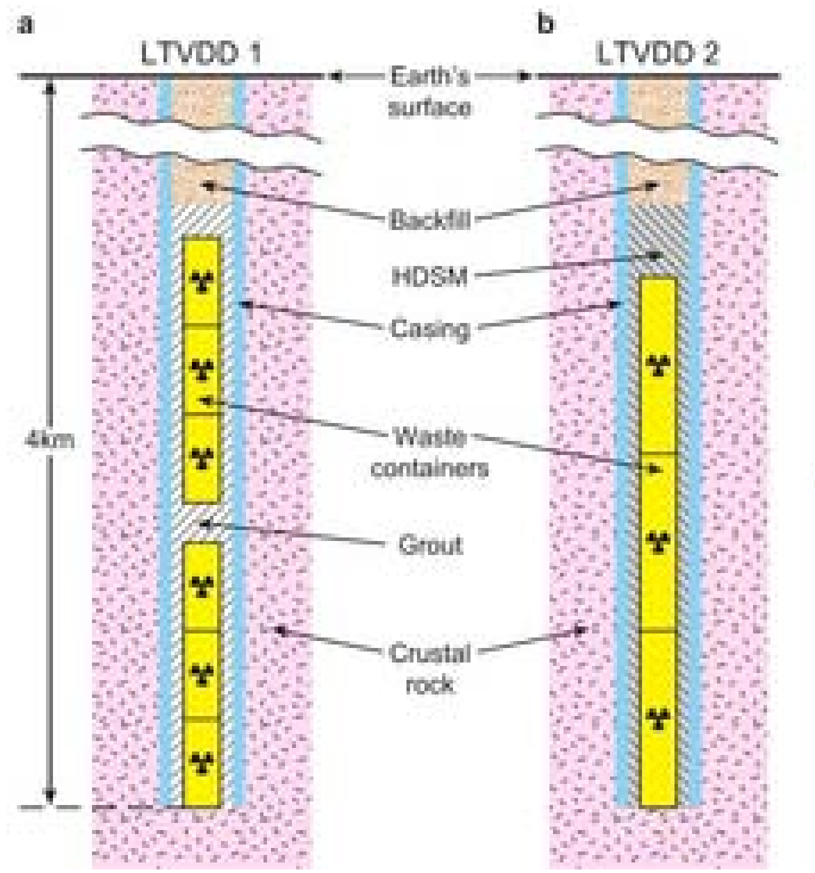


TRISO Fuel[2]



Backfill Applications





Drift Backfill

Borehole Casing/Backfill

http://www.tms.org/pubs/journals/JOM/0009/Yim-0009.html

http://www.neimagazine.com/story.asp?storyCode=2055862

Experimental Methodology

- Stock Solutions
  - Depleted uranium – $UO_2(NO_3)_2$ in 0.01 M HCl
  - Spiked with ^{233}U (Eckert & Ziegler) - 100 Bq/sample
- Analysis by Liquid Scintillation Counting
- Batch Experiments – Common Parameters
  - 10 mL:1g solution to graphite ratio
  - 10 samples per data point (7 samples, 3 blanks)
  - I = 0.01M NaCl
  - pH controlled by addition of 0.01 M HCl or NaOH
    - Borax buffer used for pH 7 to 10 region
  - FEP Tubes used from pH 6 to 8 to minimize sorption
  - Mixed on Hematology Mixer for 5 days, Centrifuge to Separate

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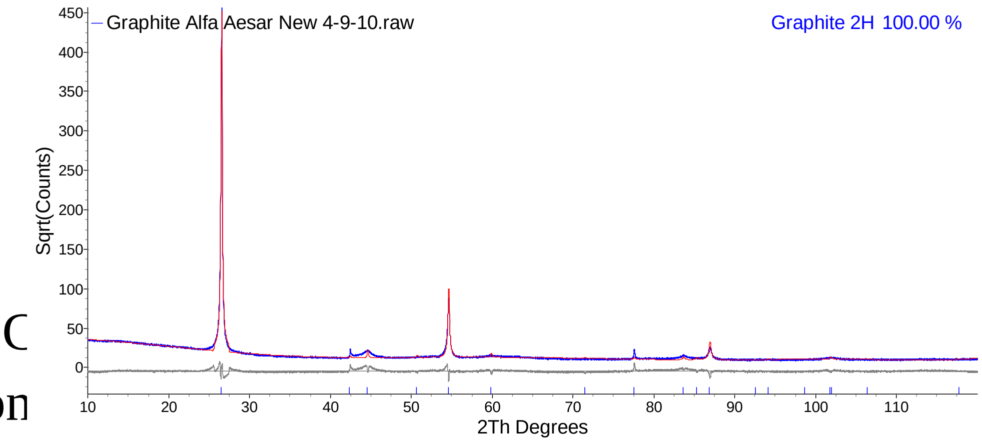
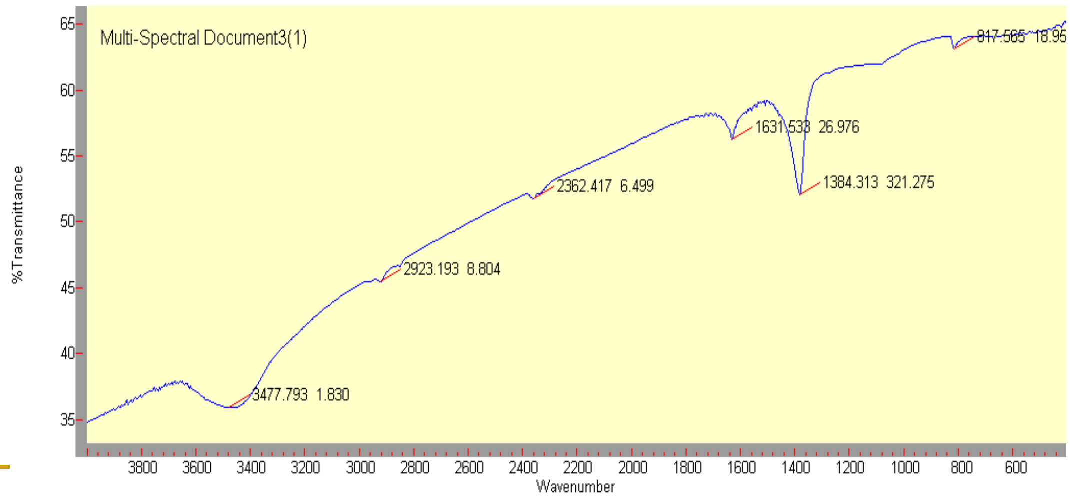
Graphite Characterization

- Alpha Aesar (-20/+100)
- X-Ray Diffraction
  - No minor phases observed
- FTIR Spectroscopy
  - 1631 suggests sp^2-hybridized C
  - 1384 suggests C-OH formation
  - 3477 suggests surface water or hydrogen-bonded OH groups
- BET Surface Area
  - $0.554 \pm 0.027\ m^2/g$
- Proton Exchange Capacity
  - 0.25 ± 0.15 cmol/kg
- Point of Zero Charge
  - pH = 9.3





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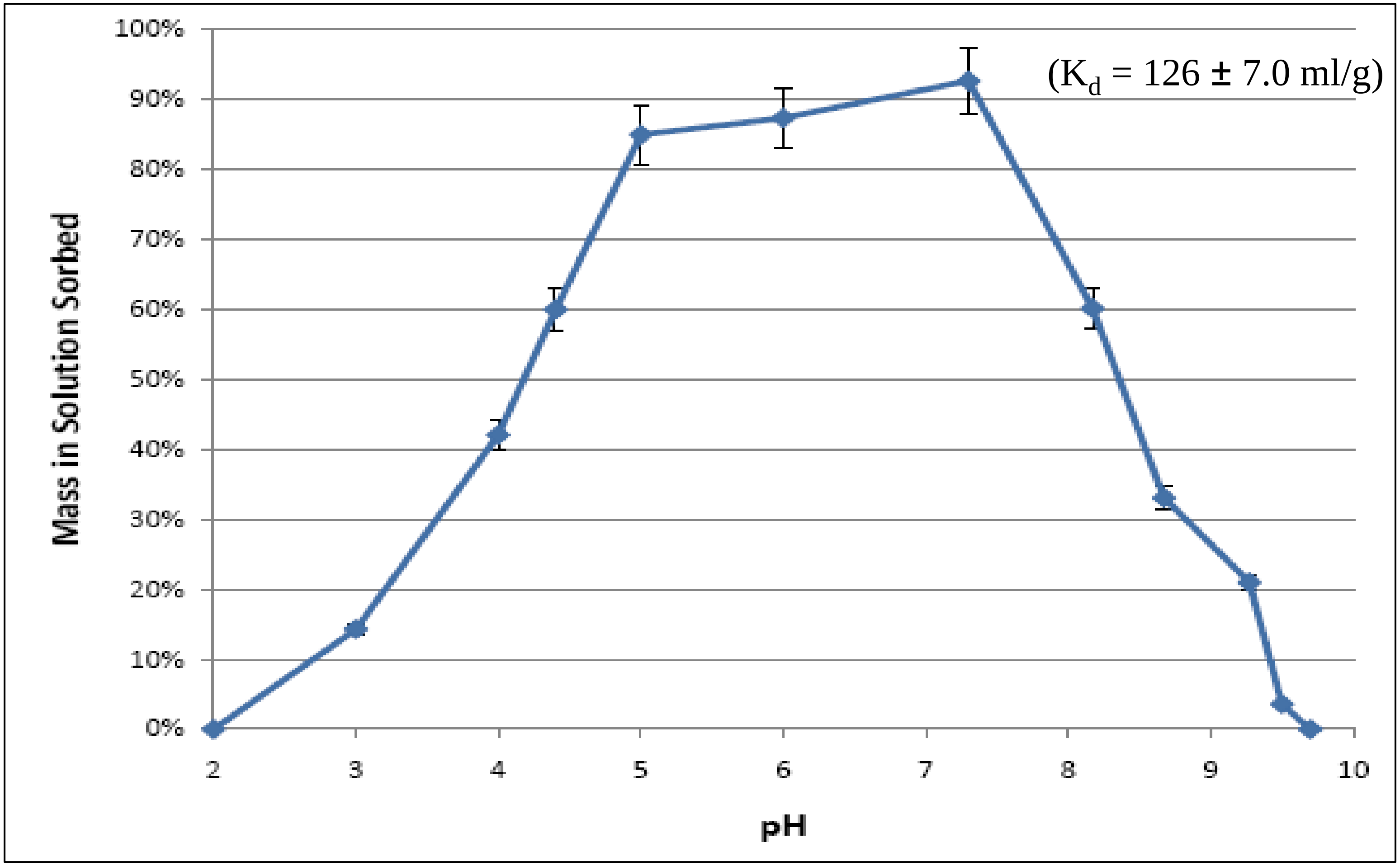
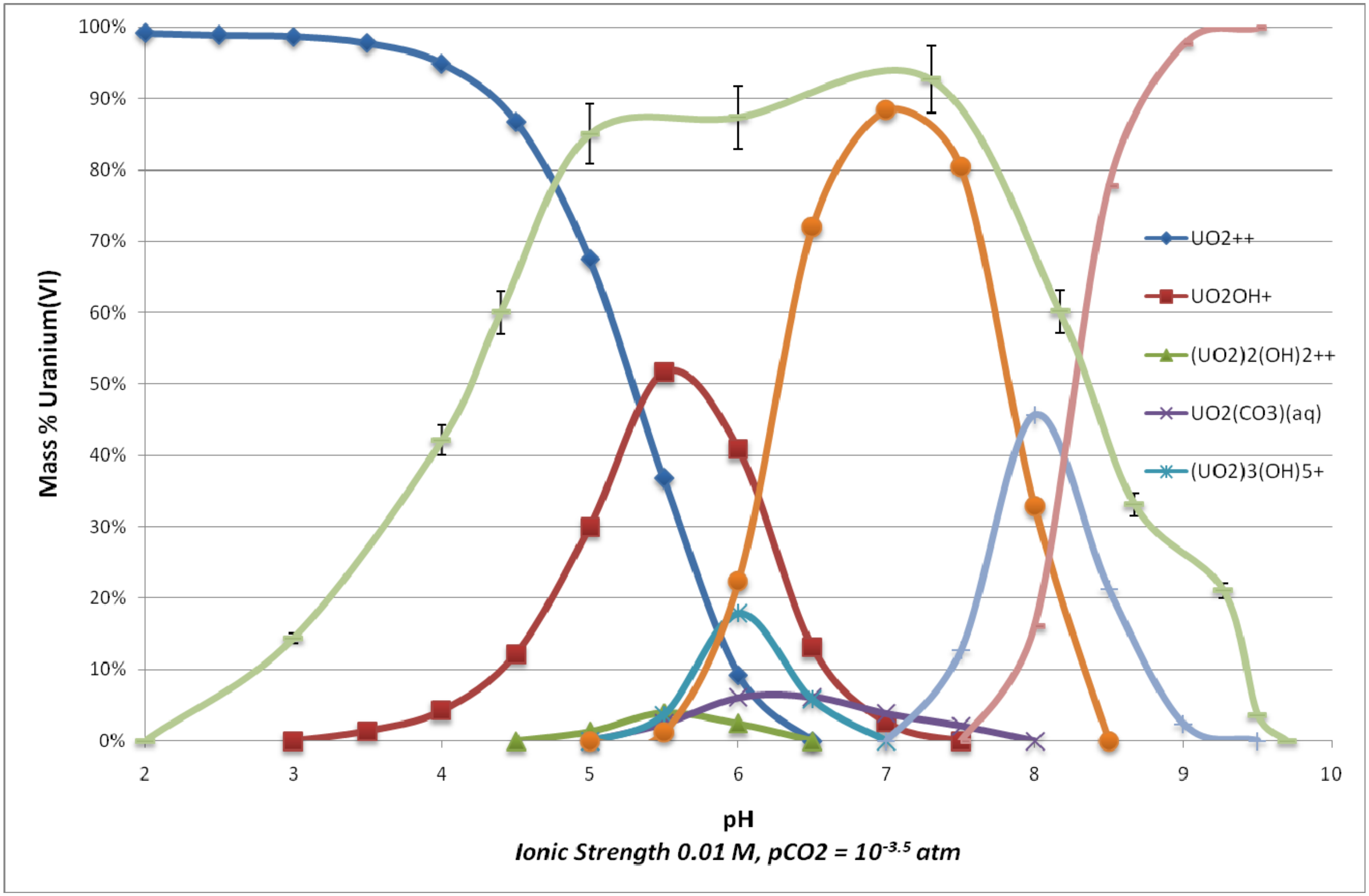
Equilibrium Sorption – pH Effects



Equilibrium Sorption vs. Speciation



Speciation Curve Generated using EQ3/6 with the YM Database

Effect of Ionic Strength

pH	[NaCl] (molal)	K_d (ml/g)
4.03	0.01	8.23 ± 0.08
4.06	0.05	8.58 ± 0.04
4.07	0.1	7.73 ± 0.05
5.07	0.01	51.43 ± 6.84
5.14	1	58.74 ± 15.5
5.16	4	59.84 ± 19.5

Effect of CO_2 on Sorption

$[CO_2]$, ppm	pH	Mass % Sorbed	K_d (ml/g)
Atmospheric	9.27	21.0% ± 2.27%	2.48 ± 0.25
< 1	9.30	36.7% ± 2.11%	5.48 ± 0.28
~1,000,000	9.28	~0%	N/A
Atmospheric	7.30	92.6% ± 0.97%	126.4 ± 0.28
~1,000,000	7.50	~0%	N/A
Atmospheric	4.85	75.3% ± 3.03%	39.3 ± 4.9
~1,000,000	4.75	28.78% ± 6.59%	4.43 ± 1.6

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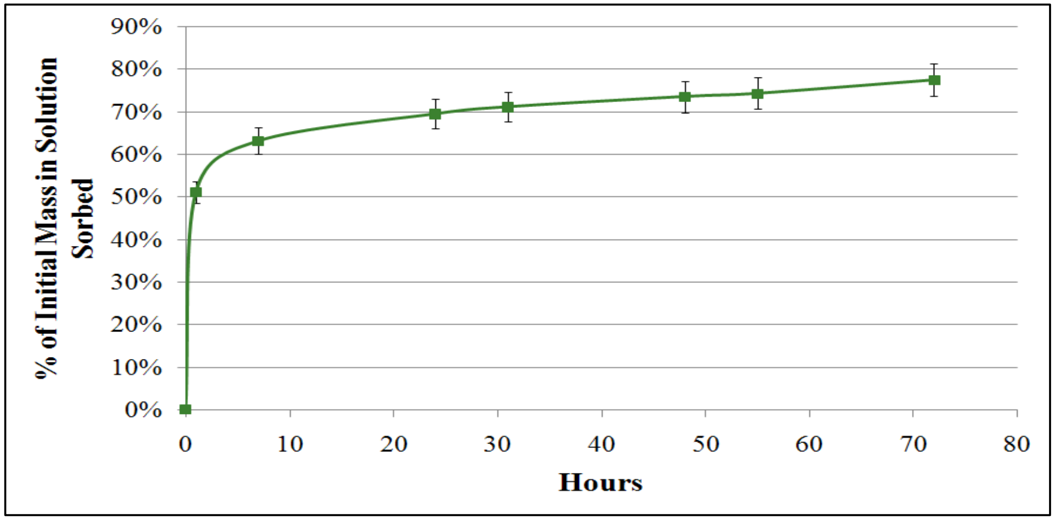
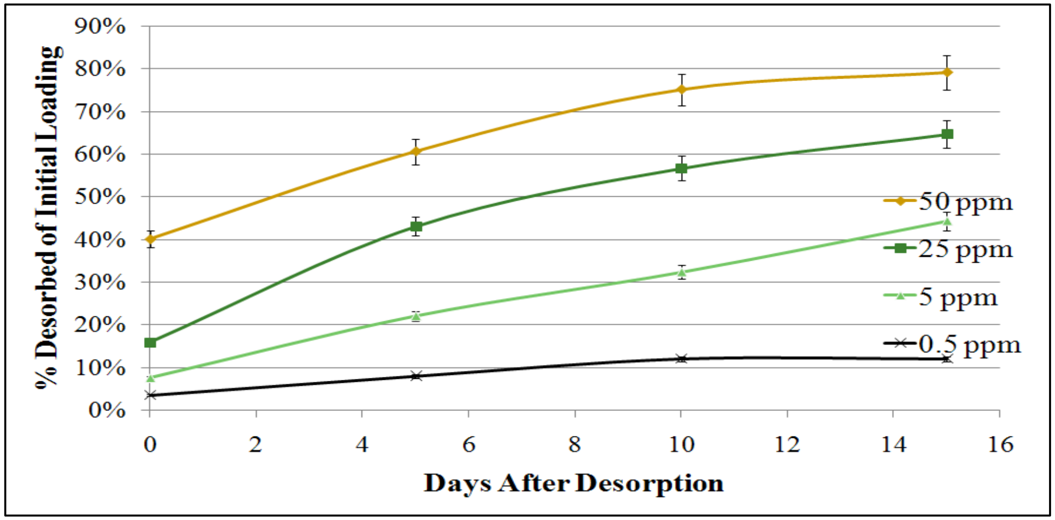
Kinetic Studies





- Two apparent partitioning phases
  - Rapid Initial Sorption
  - Slower “kinetic” phase
- Incomplete recovery during desorption
  - Approx. 10 µg U / g graphite remained sorbed

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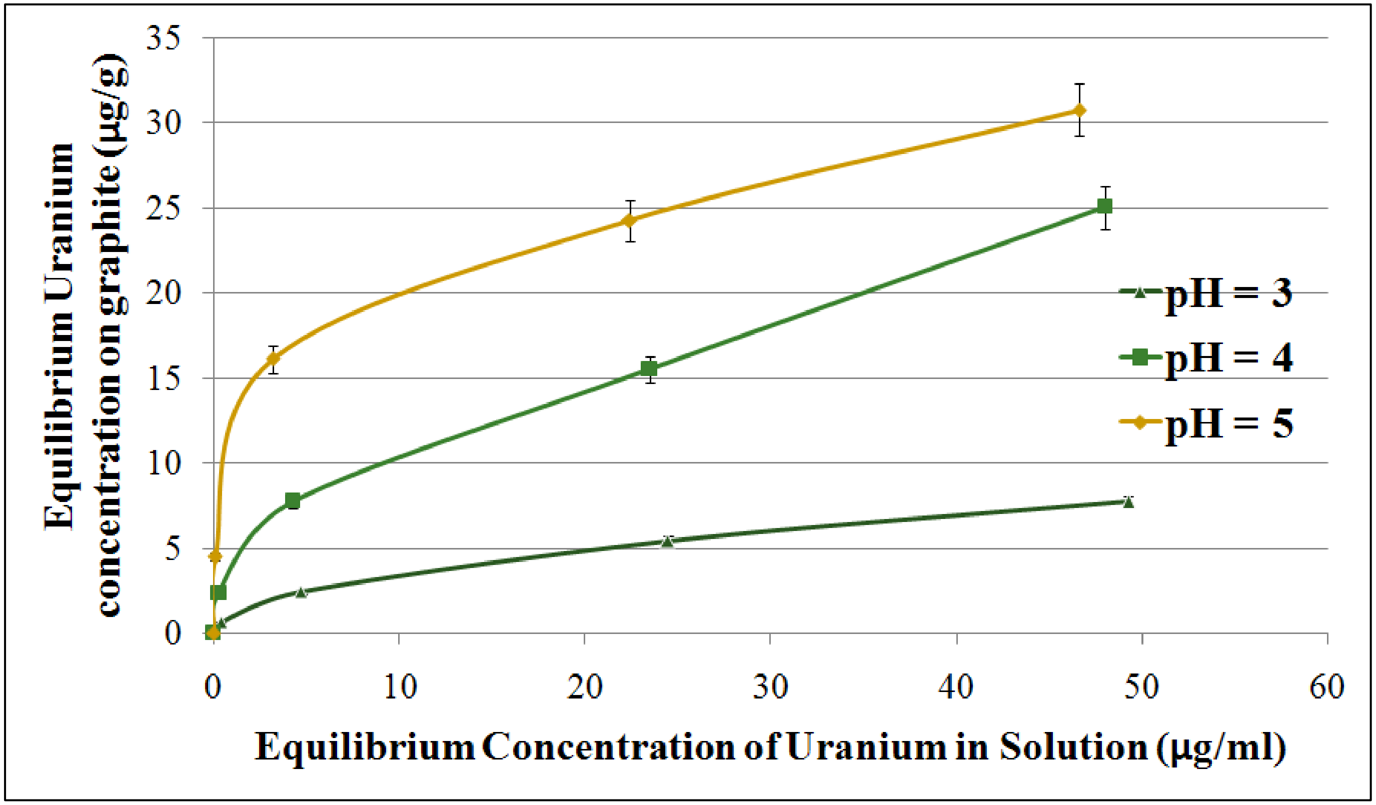
Sorption Isotherms



- Kinetic sorption and desorption data suggest at least 2 sites
- Fit w/ Freundlich Isotherm, $q = (0.930)c_{eq}^{0.37}$ (pH 5)

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Kinetic Sorption Model

- **Two apparent partitioning phases**
  - Incomplete recovery during desorption
  - Approx. 10 µg U / g graphite remained sorbed
- **Kinetic Sorption Model Features:**
  - Sorption behavior has an equilibrium and kinetic fraction
  - Eq. fraction has higher K_d than kinetic fraction
    - Can be sub-divided into a low/high solution mass region
  - Eq. fraction fills before kinetic fraction in partitioning
  - Kinetic fraction has first order rate constant of $\alpha = 0.01925\ hr^{-1}$
  - Equilibrium fraction maximum loading is 1.7 µg U / g graphite

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Slow Flow Column Experiment

Dispersion Coefficient	0.903 cm^2/hr
Column Area	0.3845 cm^2
Elution Rate	0.25 cm^3 / min
Column Length	9 cm
Graphite Mass	2.27 g
Graphite Bulk Density	1.794 g/cm^3
Porosity	0.365

- 45-60 minute flow times used at constant concentration
- Tritium used as conservative tracer

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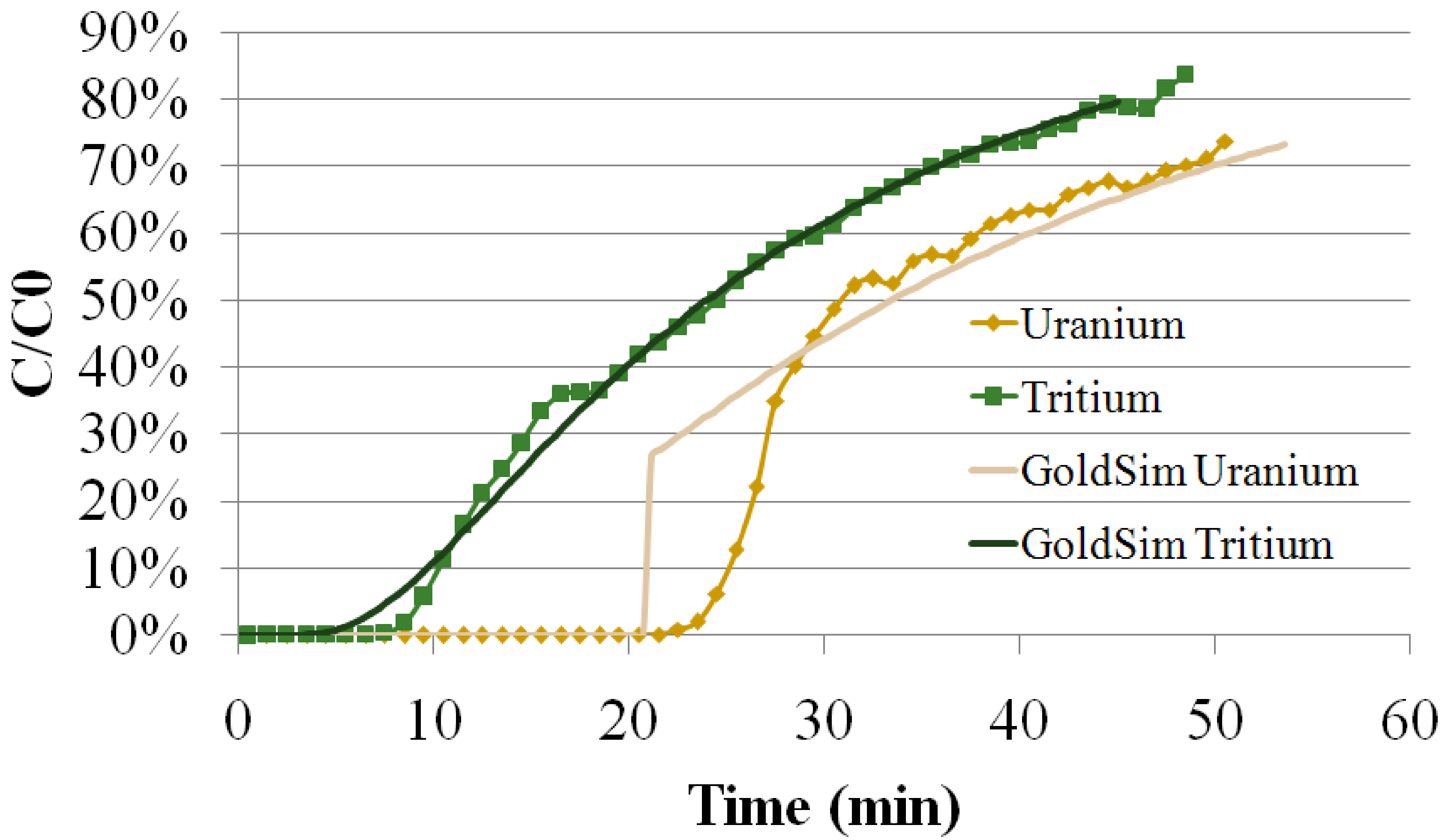
Model Prediction vs. Experimental Results



Conclusions and Future Work

- Sorption to graphite is not insignificant
  - Particularly at near neutral pH
  - "Irreversibility" of sorption can provide additional barrier to release
- Carbonate complexation appears to suppress sorption
- **Future Work**
  - Sorption mechanism is still unknown
  - Effects of graphite surface preparation needs to be examined
    - particularly surface oxidation
  - Need longer term desorption data to bound desorption kinetics
  - Data needed at elevated temperatures
  - Isotherms need to be extended to lower concentrations
  - Need to extend to other elements (Np, Pu, I, Tc)

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Questions?

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