Tc Removal using Goethite Precipitation

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Pacific Northwest National Laboratory

EM Waste Processing Technical Exchange

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Immobilization Methods of Hanford Nuclear Wastes

- Hanford wastes stored in 177 (149 single-shell and 28 double-shell) underground storage tanks will be treated by vitrification processes after separation into HLW and LLW fractions.
- Vitrification is a high-temperature immobilization method (Glass waste form for high and low level waste)-Waste Treatment Plant (WTP)
- Low-temperature immobilization technologies for mixed radioactive and hazardous waste
- Secondary waste forms to treat volatile radionuclides
- (Tc and I) using low-temperature (<150 °C) immobilization technologies for Hanford WTP off-gas caustic scrubber solution

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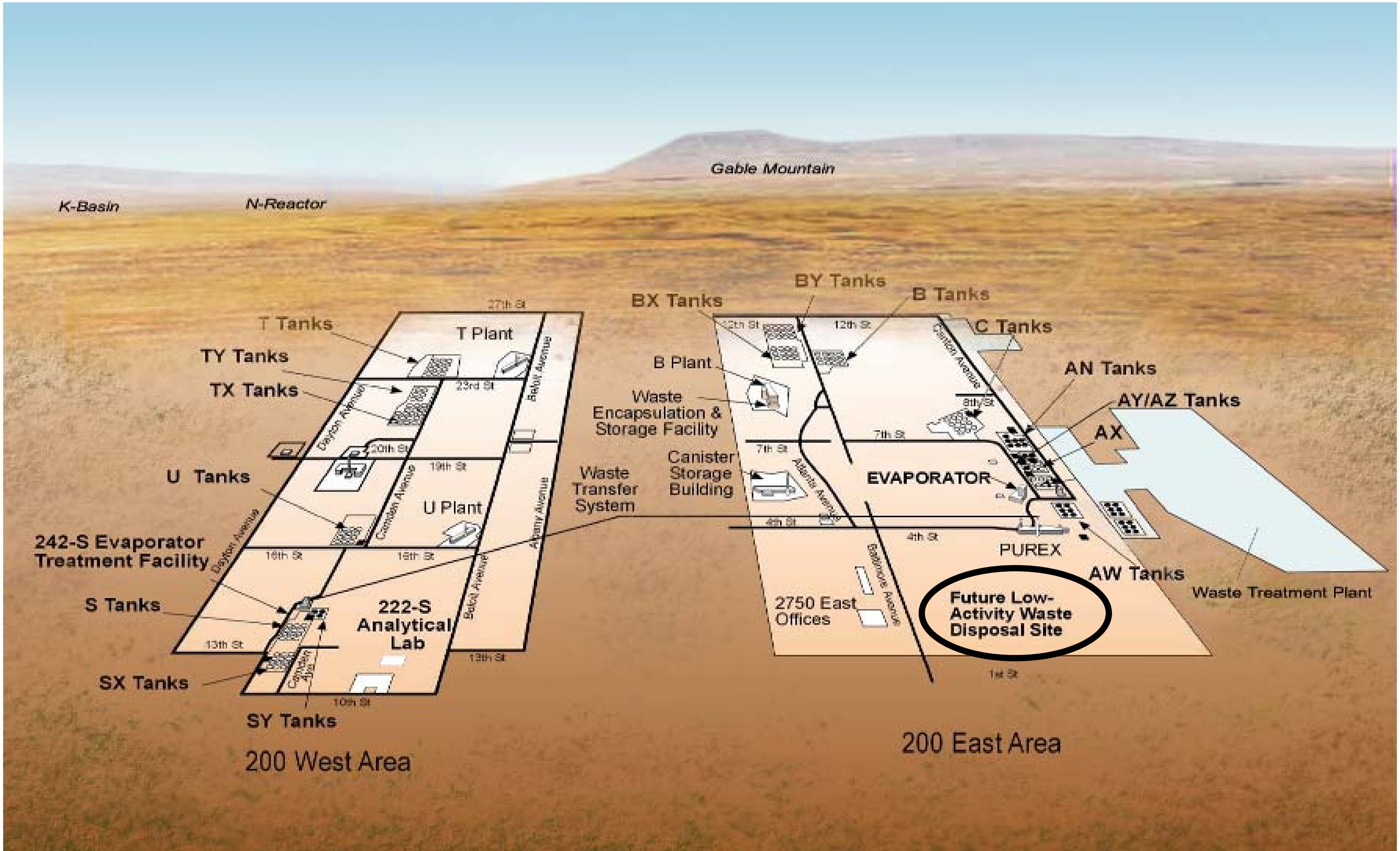
Hanford’s Central Plateau (200 Areas)



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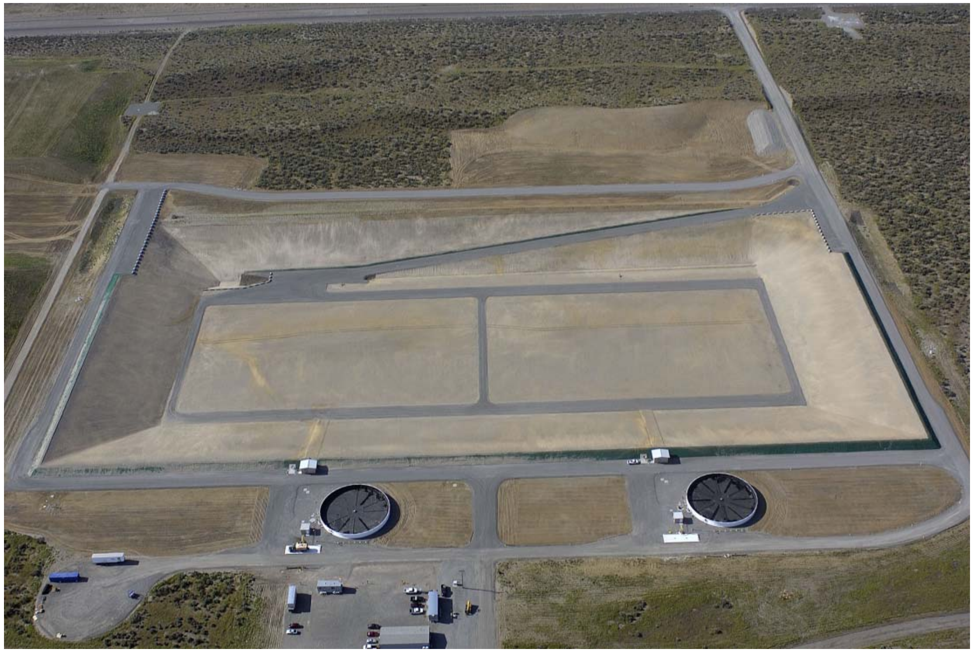
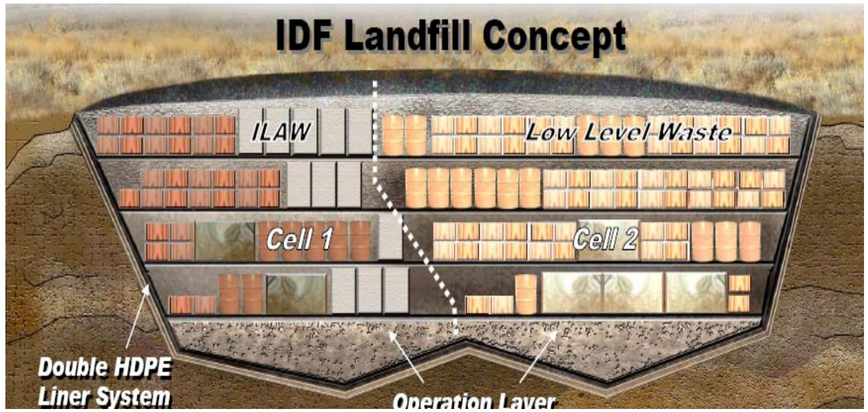
History of immobilized low activity waste (ILAW) disposal

- ILAW disposal has evolved from grout poured into concrete vaults to glass in steel containers disposed in engineered landfills.
- IDF started as disposal for WTP ILAW only, but was expanded to include other low-level and mixed waste.
- The IDF, an engineered shallow land lined- trench approximately 410 m wide by up to 13.2 m deep





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Why is Tc-99 a Concern?

- Long-lived radionuclide present in Hanford tank waste
  - Beta emitter (long half-life: 2.13×10^5 years)
  - A radioactive fission product of ^{235}U and ^{239}Pu fuel
  - Causes unfavorable health effects when ingested through food or water
    - Concentrates in thyroid and gastrointestinal tract
  - Dissolves in nitric acid and some other acids
- Tc may enter the environment if it leaches out of solid waste forms in the Integrated Disposal Facility (IDF)
  - Could travel through groundwater to Columbia River (K_d=0 mL/g)
  - Plants could uptake it from soil or water

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What is Goethite?

- Goethite [α-FeO(III)OH]
- Stable iron oxyhydroxide
- Similar bond length between Fe(III)—O and Tc(IV)—O (2.06 and 2.01 Å, respectively)
- Similar Eh values (ca. +20 mV at pH=7) for redox couple between Tc(VII)/Tc(IV) and Fe(III)/Fe(II)
- Possibility of direct substitution of Tc(IV) for Fe(III) in the goethite mineral lattice

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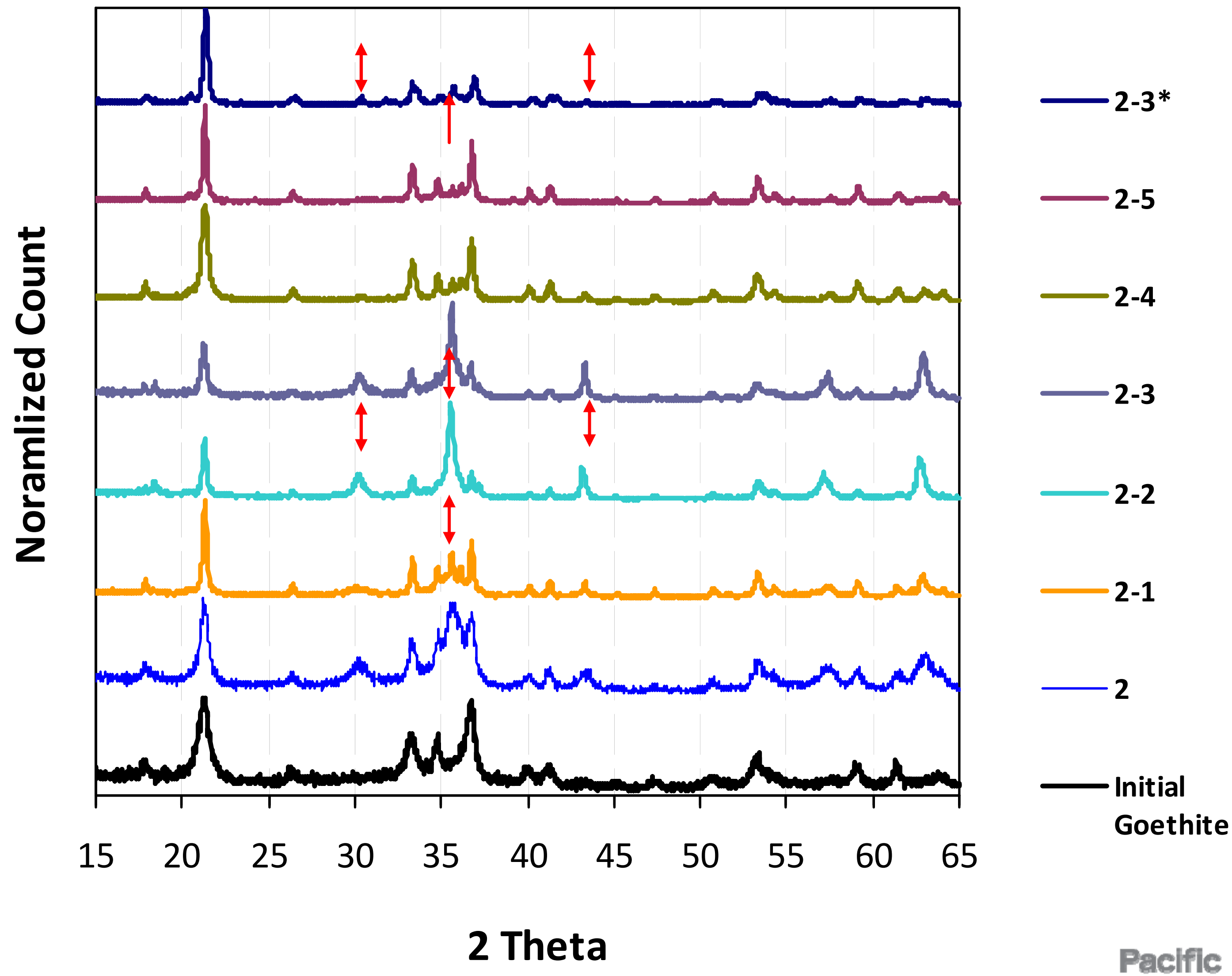
Synthesis and Characterization

- Use synthesized (Schwertmann and Cornell, 2000) or commercial goethite
- Acidify initial goethite slurry
- Add $FeCl_2 \cdot 4H_2O$ as reductant
- Mix with either Tc-99 spiked DI or off-gas scrubber simulant
- Additional Goethite armoring process as option
- Heating in a oven at 80 ^{o}C for 7 days
- Characterize mineral phases, total Tc content on solid, and binding mechanism of Tc on goethite using XRD, SEM, TEM, Mössbauer, and XAFS
- Batch Tc leaching at different solutions (pH buffer 4, 7, and 10 solutions, IDF pore water, and IDF glass leachate) using powder Tc-goethite sample
- Characterize the reacted Tc-goethite solid

Summary of Synthesis

Test description and Tc removal				Sample IDs			
	2	**2-1**	**2-2**	**2-3**	**2-3***	**2-4**	**2-5**
Additional Fe(III) armoring	**Yes**	**Yes**	**No**	**No**	**No**	**Yes**	**Yes**
Initial solution [1]	DI	DI	DI	SSS-1	SSS-2	SSS-1	DI
Initial pH	1.78	1.47	1.47	1.47	1.58	1.47	1.47
Initial spiked-Tc mass (μg)	**597**	**551**	**501**	**522**	5547	**546**	**615**
pH after mixing Fe(III) and NaOH	13.0	13.3	13.3	13.0	13.3	13.3	13.4
Final solid mass (g)	**6.53**	**6.05**	**3.24**	**3.51**	**5.10**	**6.43**	**6.41**
Final Tc removal on solid (µg/g) [3]	85.7	84.4	149.1	143.1	1020	78.9	96.0
Tc uptake in goethite (%)	**93.7**	**92.7**	**96.5**	**96.3**	**93.8**	**92.9**	**100.0**
XAFS sample collection	NSLS	n.a.	SSRL	SSRL	SSRL	n.a.	SSRL

XRD for initial goethite and final Tc-goethite



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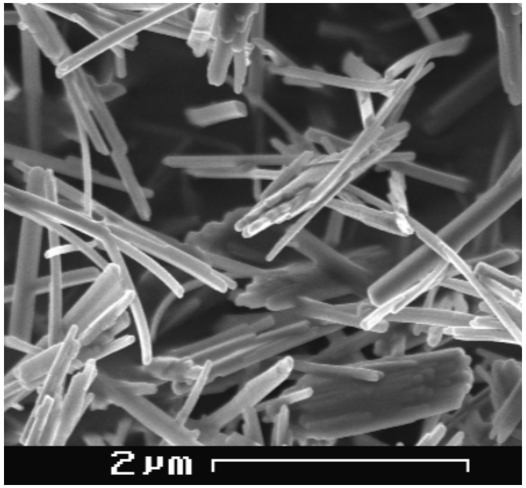
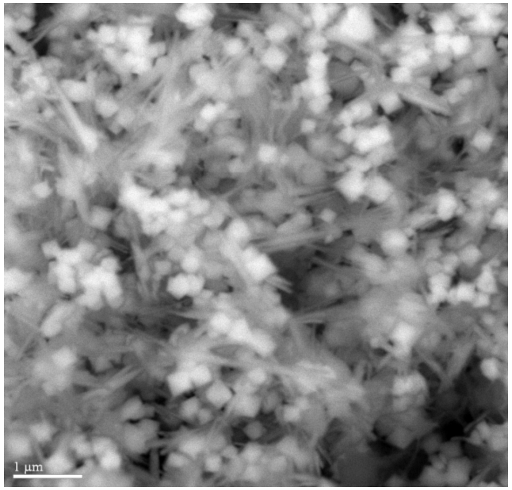
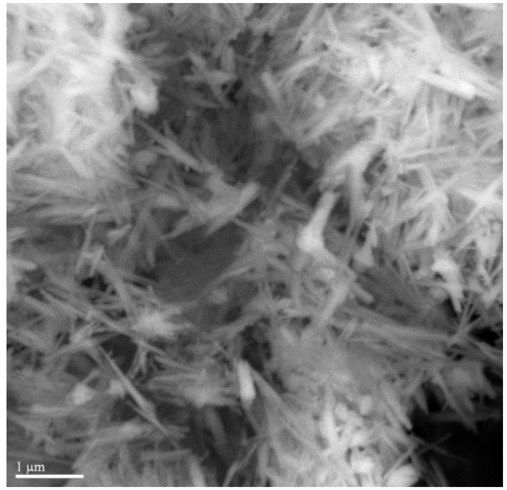
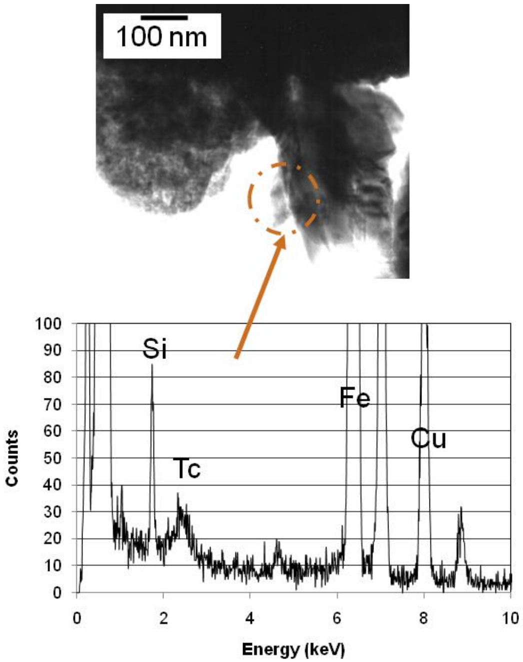
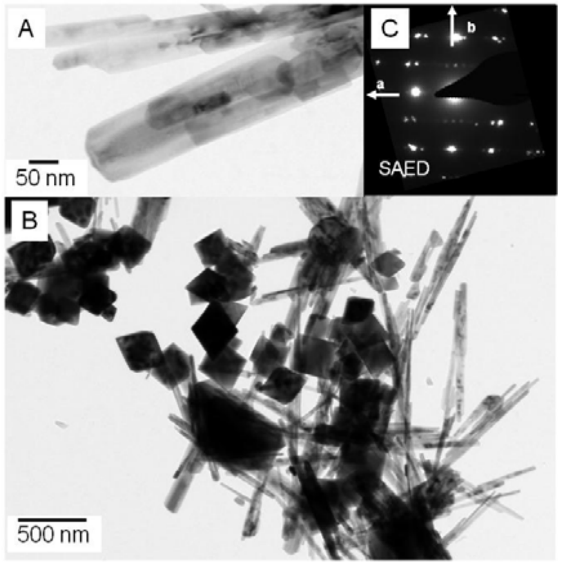
SEM and TEM Results

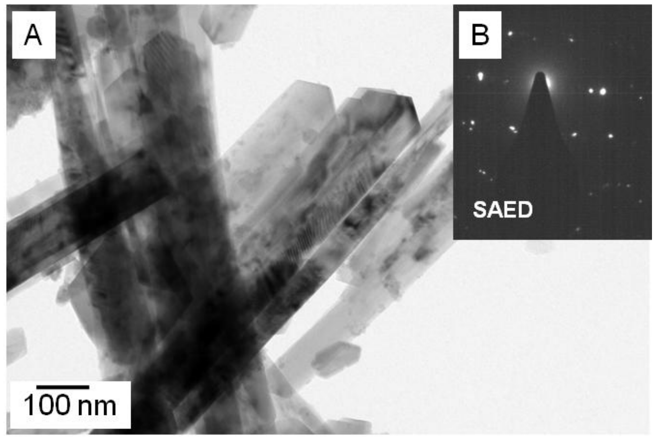












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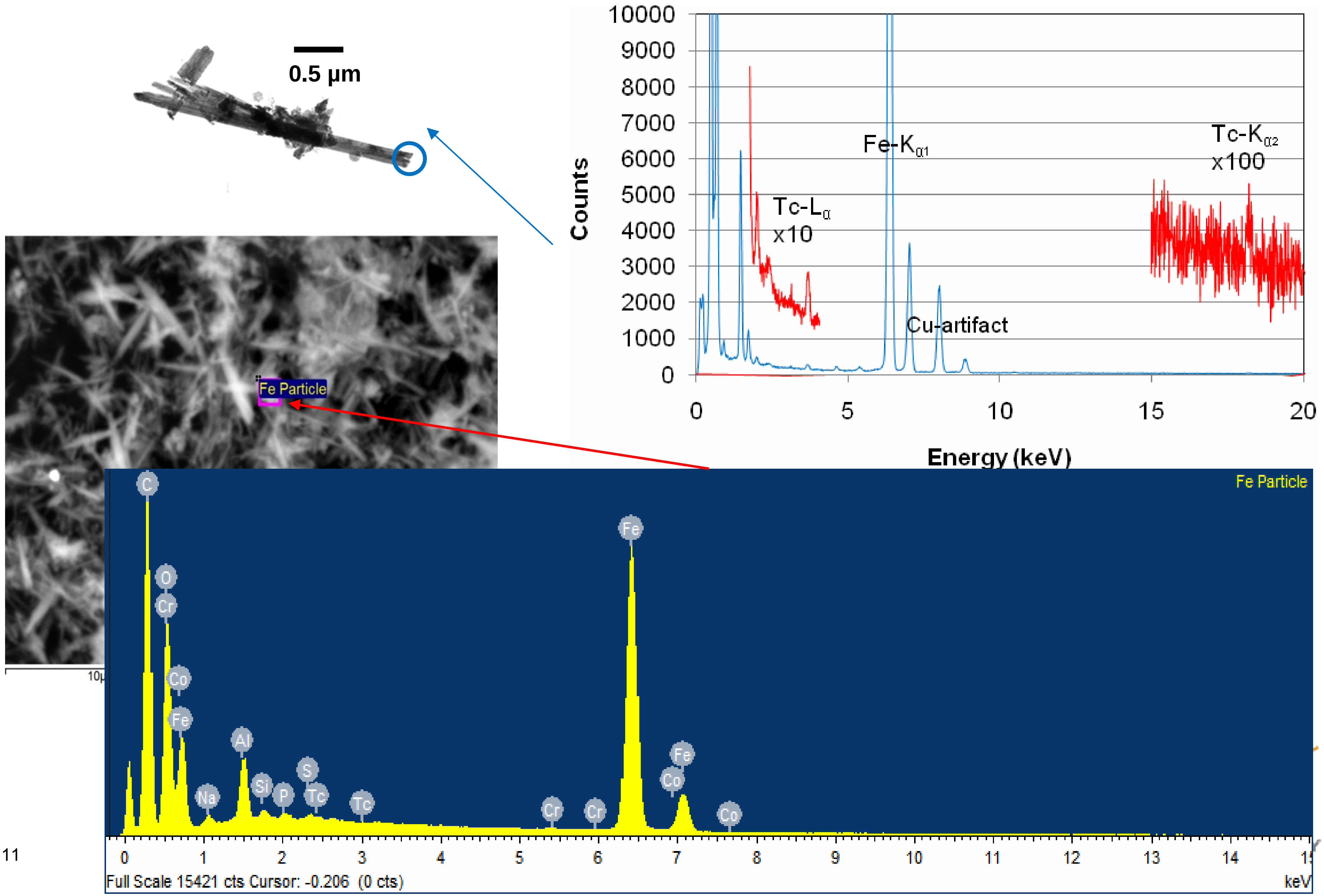
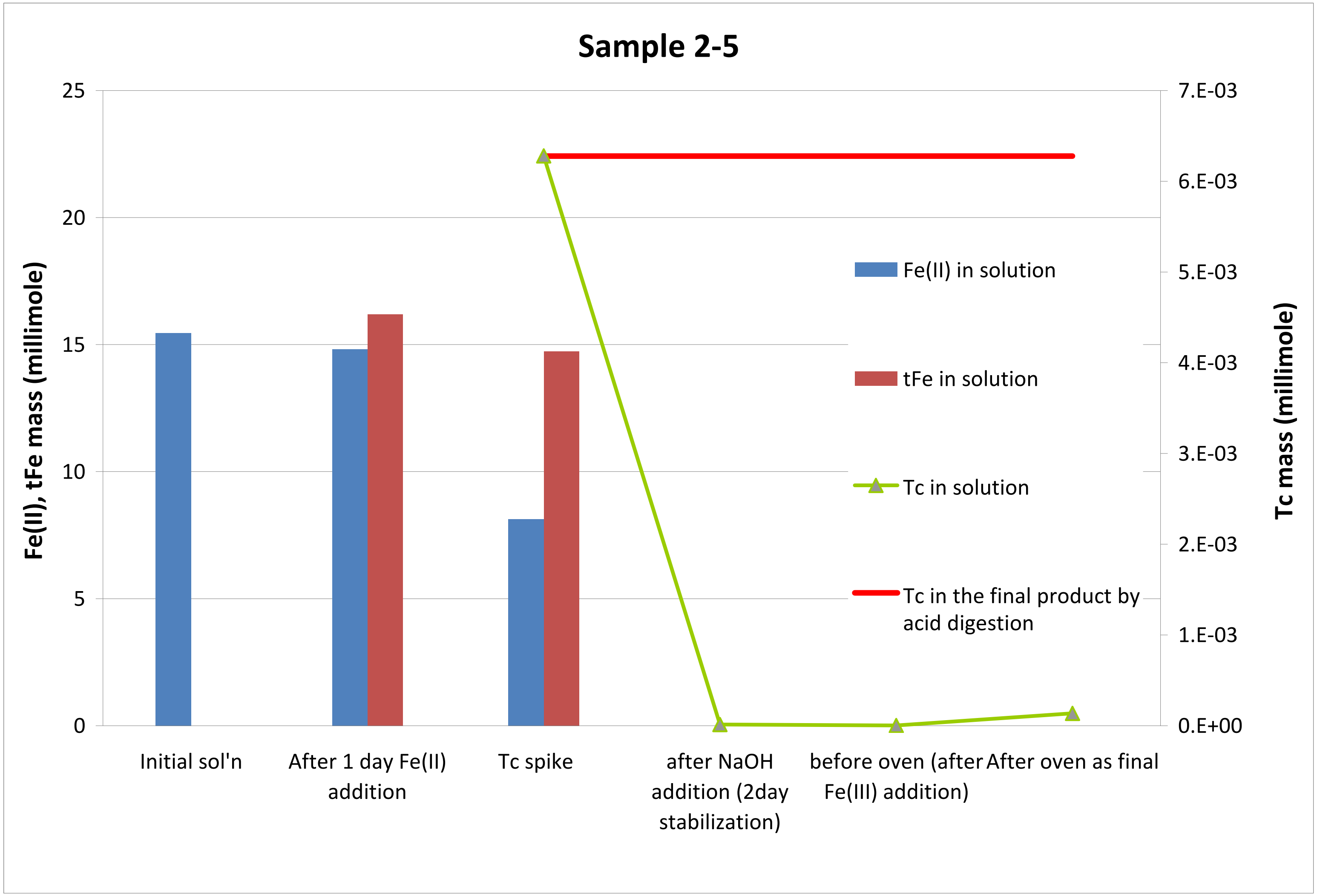
SEM and TEM Results (Sample 2-3*)



Concentrations of Fe and Tc



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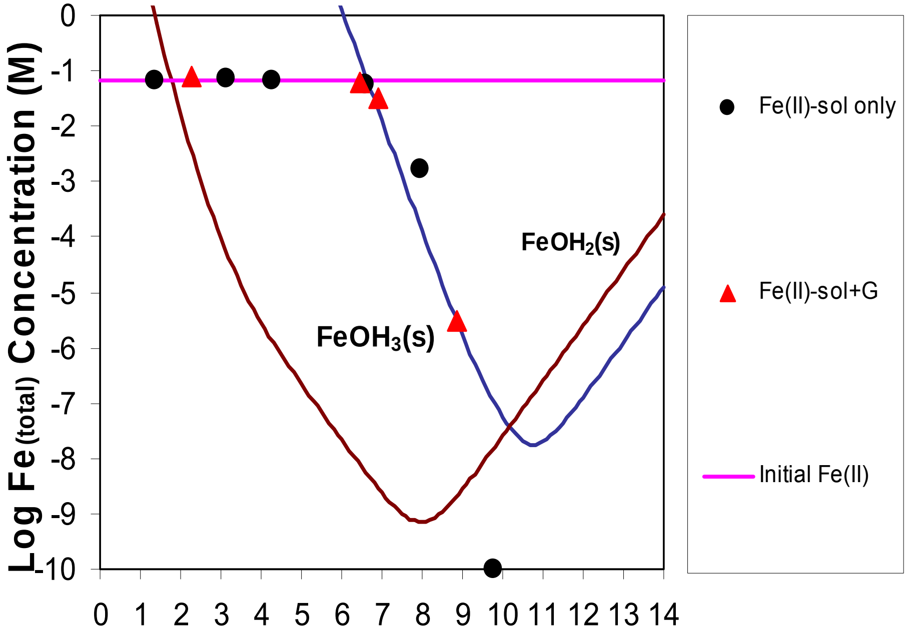
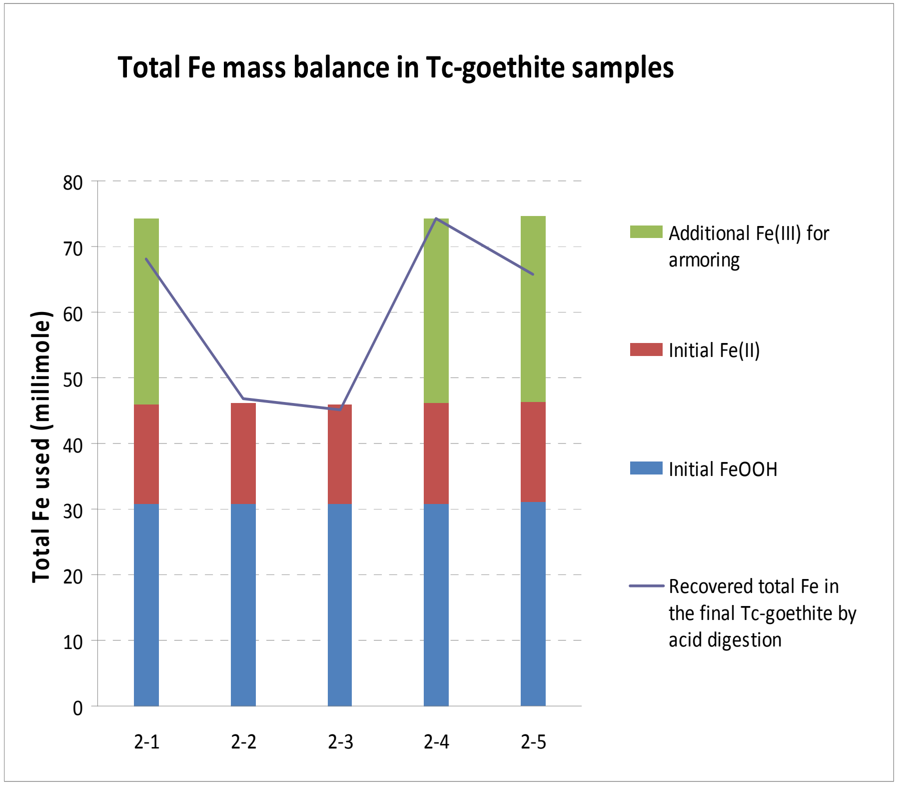
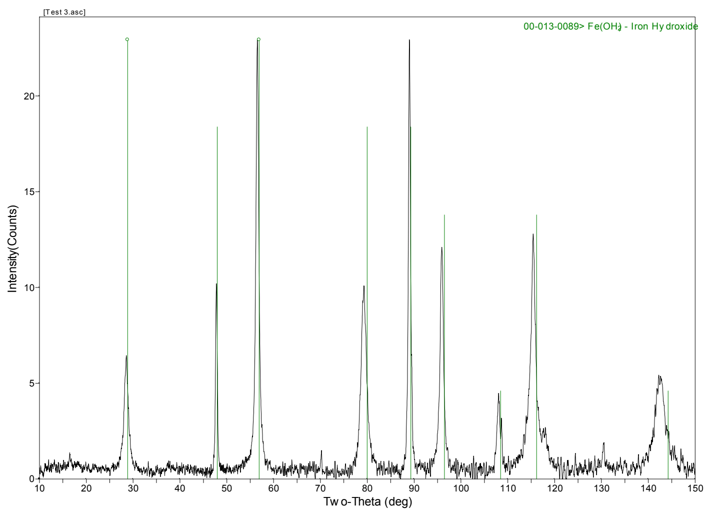
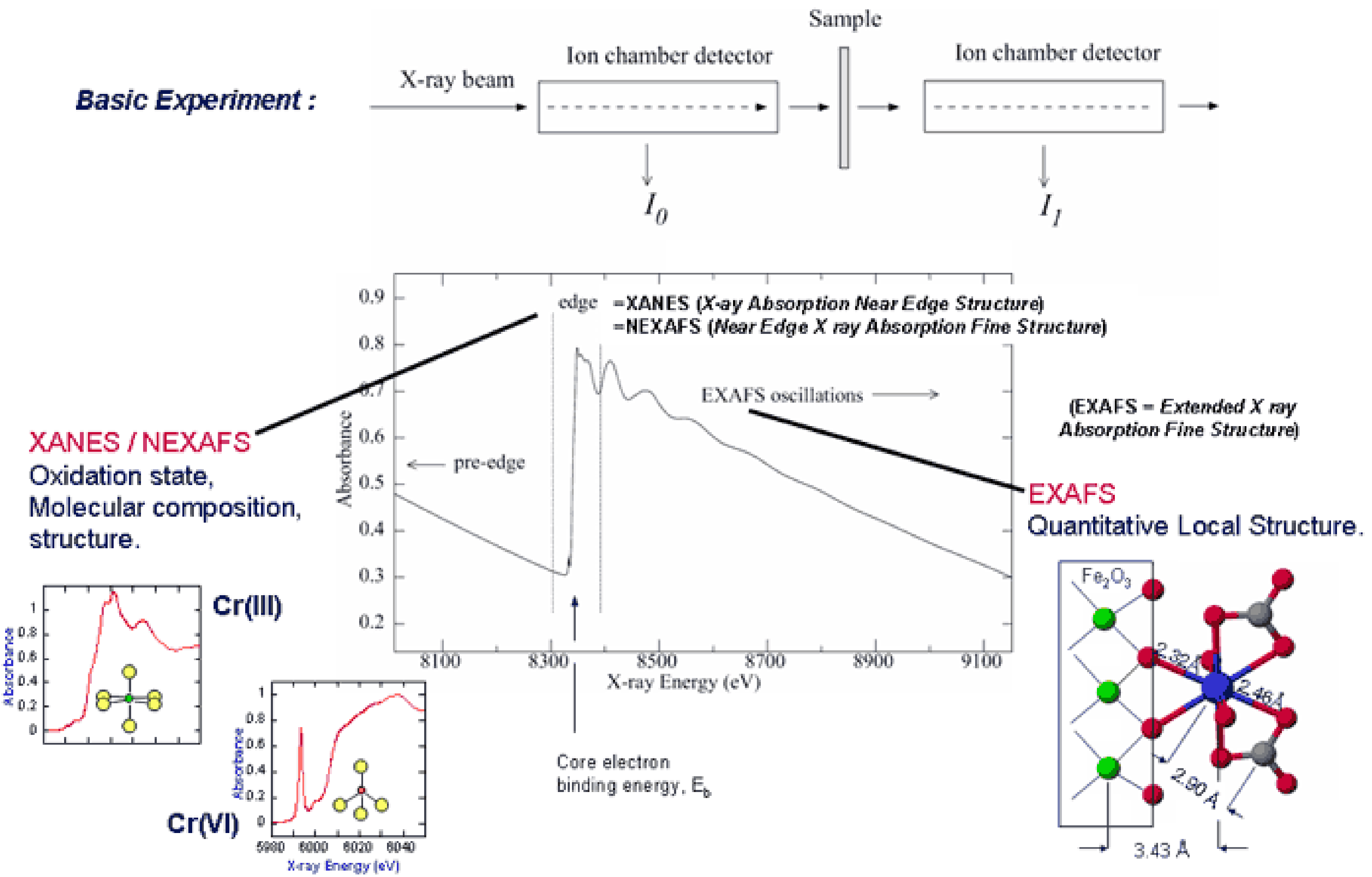
Solubility Diagram and Fe mass Balance







X-ray Adsorption Spectroscopy



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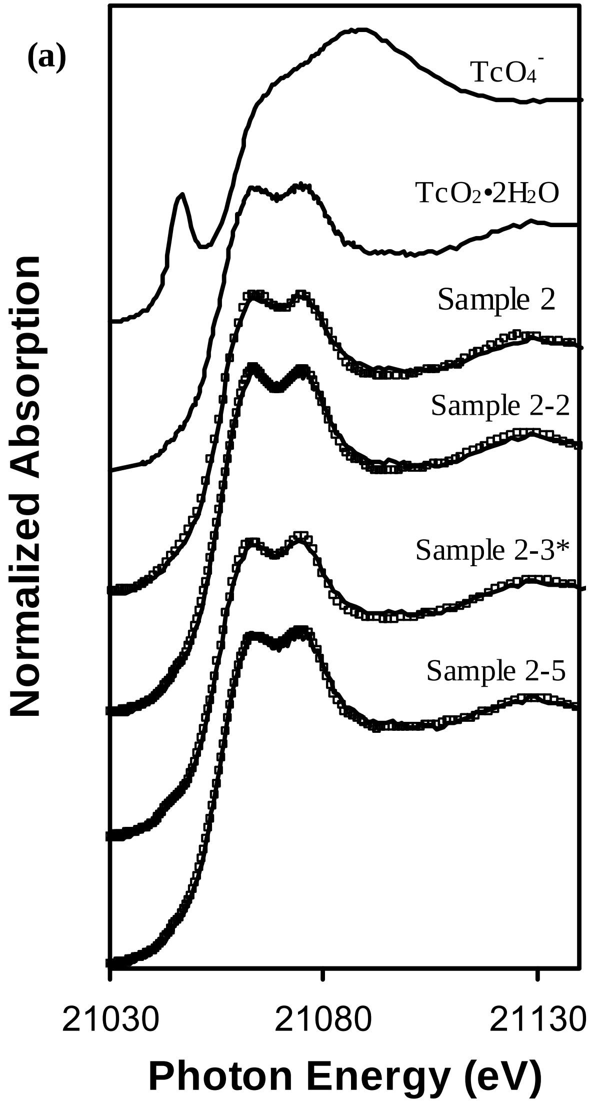
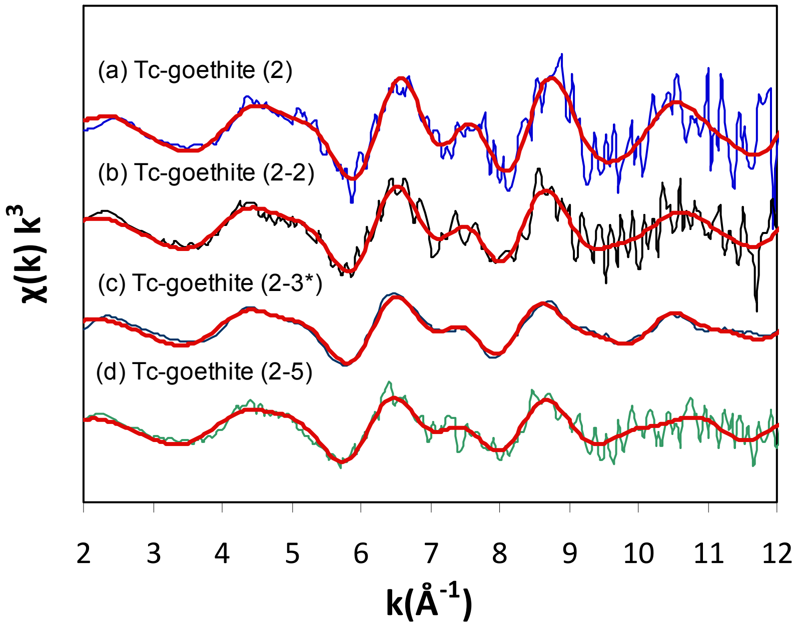
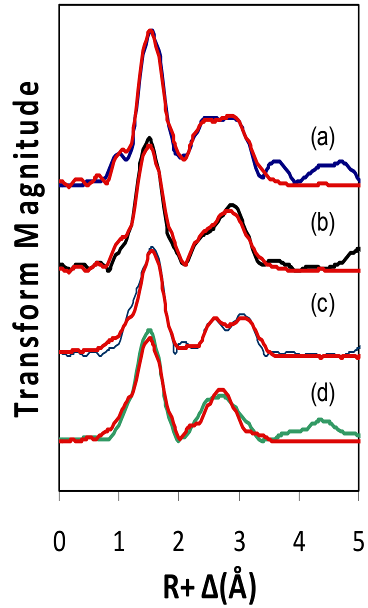
XAFS Results







EXAFS Fit Results

Samples	Neighbor atoms	CN	R(Å)	σ^2	ΔE_0	p(F)
Tc-goethite	O	6	2.017(5)	0.0023(3)	0(1)	<0.001
Sample 2	Fe	4	3.074(8)	0.0064(6)	0(1)	<0.001
(R-factor =	Fe	4	3.52(2)	0.0064(6)	0(1)	<0.001
0.006)	Tc	0.5(2)	2.51(2)	0.0064(6)	0(1)	0.046
Tc-goethite	O	6	2.020(6)	0.0040(4)	-2(1)	<0.001
Sample 2-2	Fe	4	3.09(1)	0.0084(7)	-2(1)	<0.001
(R-factor =	Fe	4	3.53(1)	0.0084(7)	-2(1)	<0.001
0.011)						
Tc-goethite	O	6	2.014(8)	0.0049(5)	-3(2)	<0.001
Sample 2-3	Fe	4	3.08(2)	0.013(2)	-3(2)	<0.001
(R-factor =	Fe	4	3.54(2)	0.008(1)	-3(2)	<0.001
0.033)						
Tc-goethite	O	6	2.02(1)	0.0060(6)	-2(1)	<0.001
Sample 2-5	Fe	4	3.10(2)	0.009(1)	-2(1)	<0.001
(R-factor =	Fe	4	3.53(5)	0.017(6)	-2(1)	0.25
0.037)						
Goethite‡	O	6	1.95-2.09			
	Fe	2	3.01			
	O	1	3.23			
	Fe	2	3.28			
	Fe	4	3.59			

- * S_o^2=1.0; coordination number (CN); interatomic distance (R); disorder parameter (σ2); energy shift (ΔE0); goodness of fit parameter (R-factor); F-test [p(F)].

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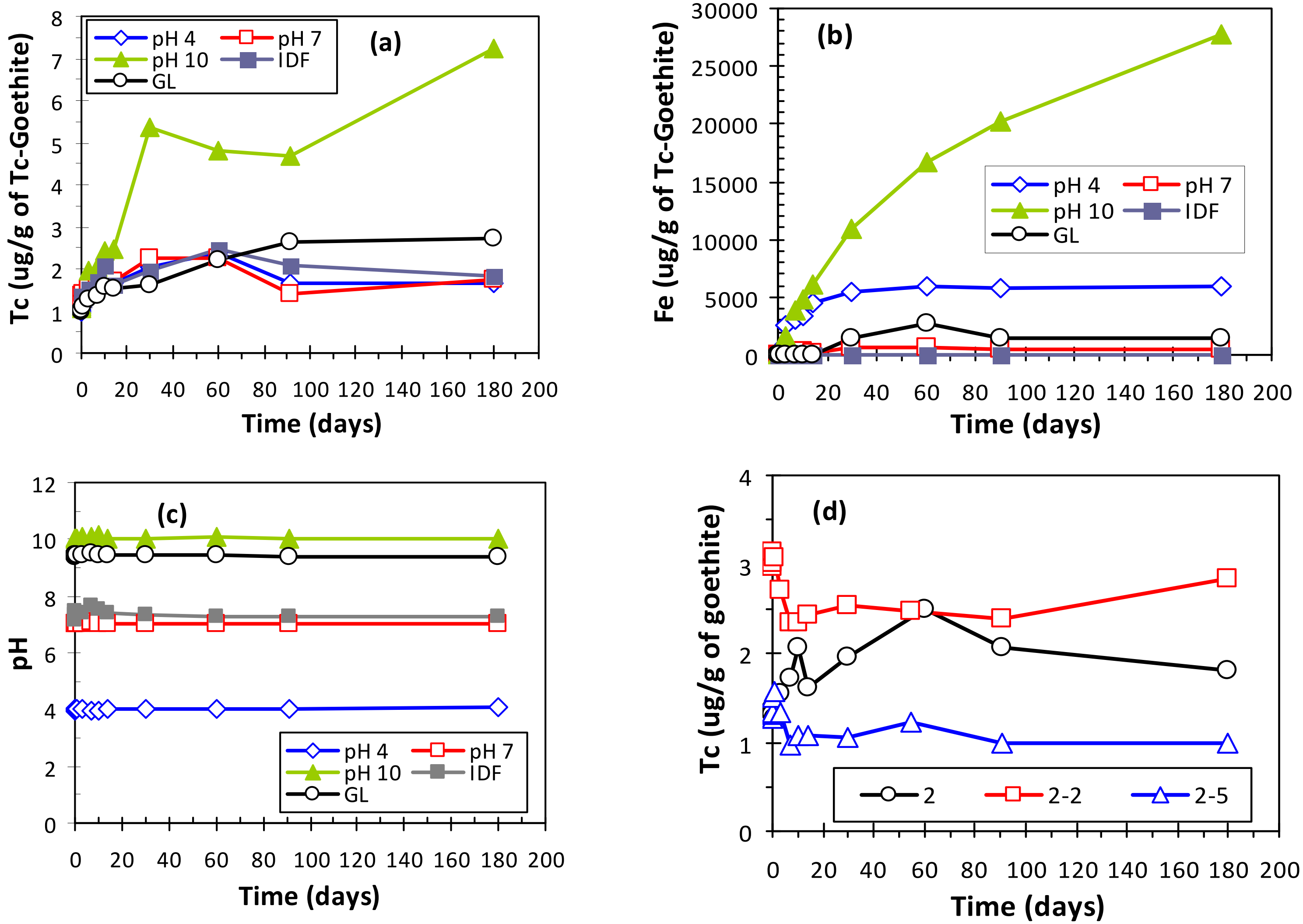
Batch Leaching Tc Results



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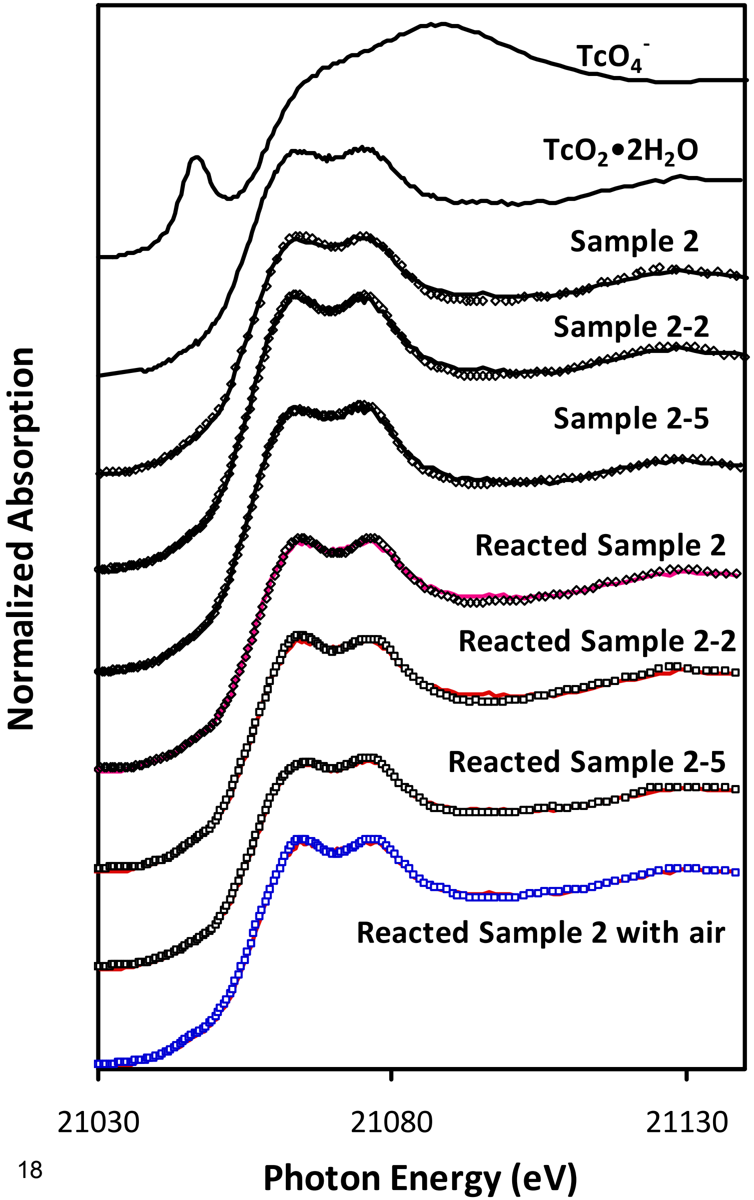
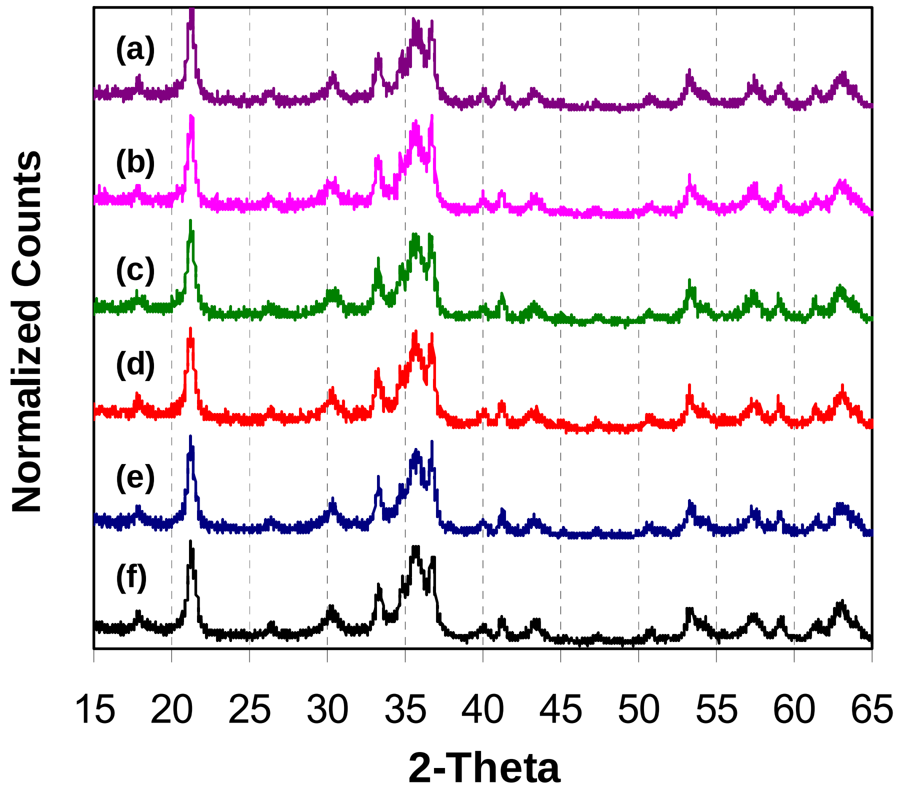
XANES and XRD Results for Reacted Samples





(a) reacted Tc-goethite sample 2 with pH=4 solution after 180 days; (b) reacted Tc-goethite Sample 2 with pH=7 solution after 180 days; (c) reacted Tc-goethite Sample 2 with pH=10 solution after 180 days; (d) reacted Tc-goethite Sample 2 with IDF pore water after 180 days; (e) reacted Tc-goethite Sample 2 with glass leachate after 180 days; (f) non-reacted initial Tc-goethite Sample 2 before leaching tests

Conclusions

- Removal of Tc(VII) from solution is most likely a result of heterogeneous surface-catalyzed reduction to Tc(IV) and subsequent co-precipitation onto the goethite

- The final Tc-bearing solid was identified as goethite-dominated Fe(III)-(oxy)hydroxide based on XRD analysis, confirming the widespread observation of its characteristic acicular habit by TEM/SEM images.

- Analysis of the solid precipitate by XAFS showed that the dominant oxidation state of Tc was Tc(IV) and was in octahedral coordination with O and Fe-O. The Tc-Fe bond distances are consistent with direct substitution of Tc for Fe in the goethite structure.

Conclusions (Cont.)

- Although Tc-sequestered goethite samples were exposed to various fluids and different leaching conditions (air and water), the reduced Tc(IV) was not re-oxidized to Tc(VII) even after 180 days of reaction in both solution and air.

- The more stabilized and strongly coordinated Tc(IV) within the goethite lattice in the Tc-sequestered goethite, especially after precipitating additional goethite as an armoring layer, provides significant advantages for slowing the release of Tc disposed in the nuclear waste repositories.

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Acknowledgement

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- Thank You for your attention !

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