Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions

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Problem – Hypothesis – Approach

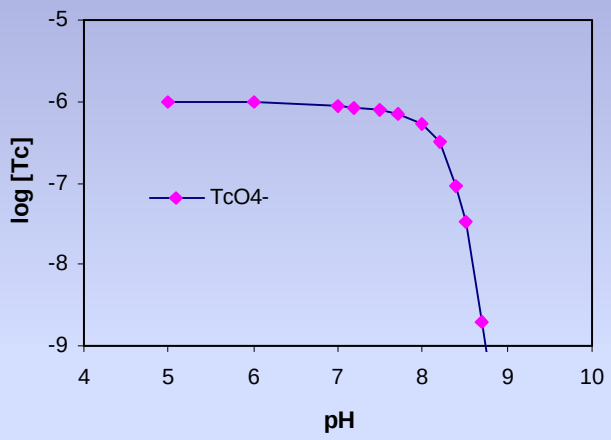
- Tc in the vadose zone is likely to be present as the soluble and mobile pertechnetate species. Are there mechanisms to retain Tc in the vadose zone?
- If Tc is retained, then Fe^{2+} in minerals are responsible for the reduction of Tc and precipitation as TcO_2(am).
- (1) Use existing thermodynamic data to predict Tc redox behavior in presence of Fe^{2+}/Fe^{3+} couple.

  (2) Evaluate TcO_2(am) solubility as function of pH.

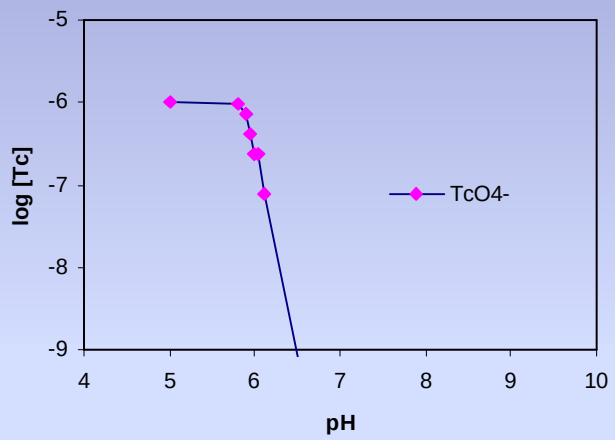
  (3) Test Hanford sediments capacity to reduce TcO_4^-.

Homogeneous Reduction of TcO_4^- by $FeCl_2$

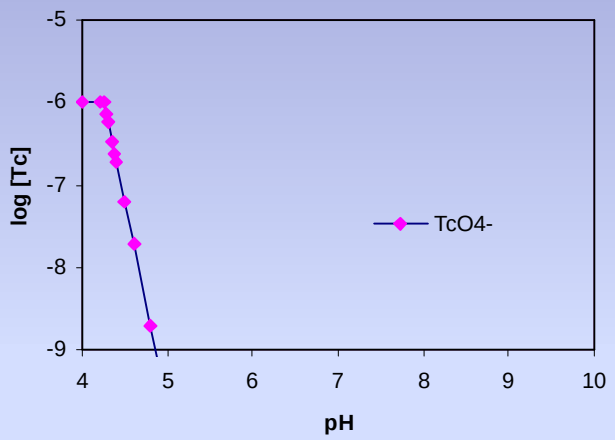
$$Tc^{7+} + 3Fe^{2+} = Tc^{4+} + 3Fe^{3+}$$



Suppress all Fe ppt.



Allow $Fe(OH)_3$ ppt.

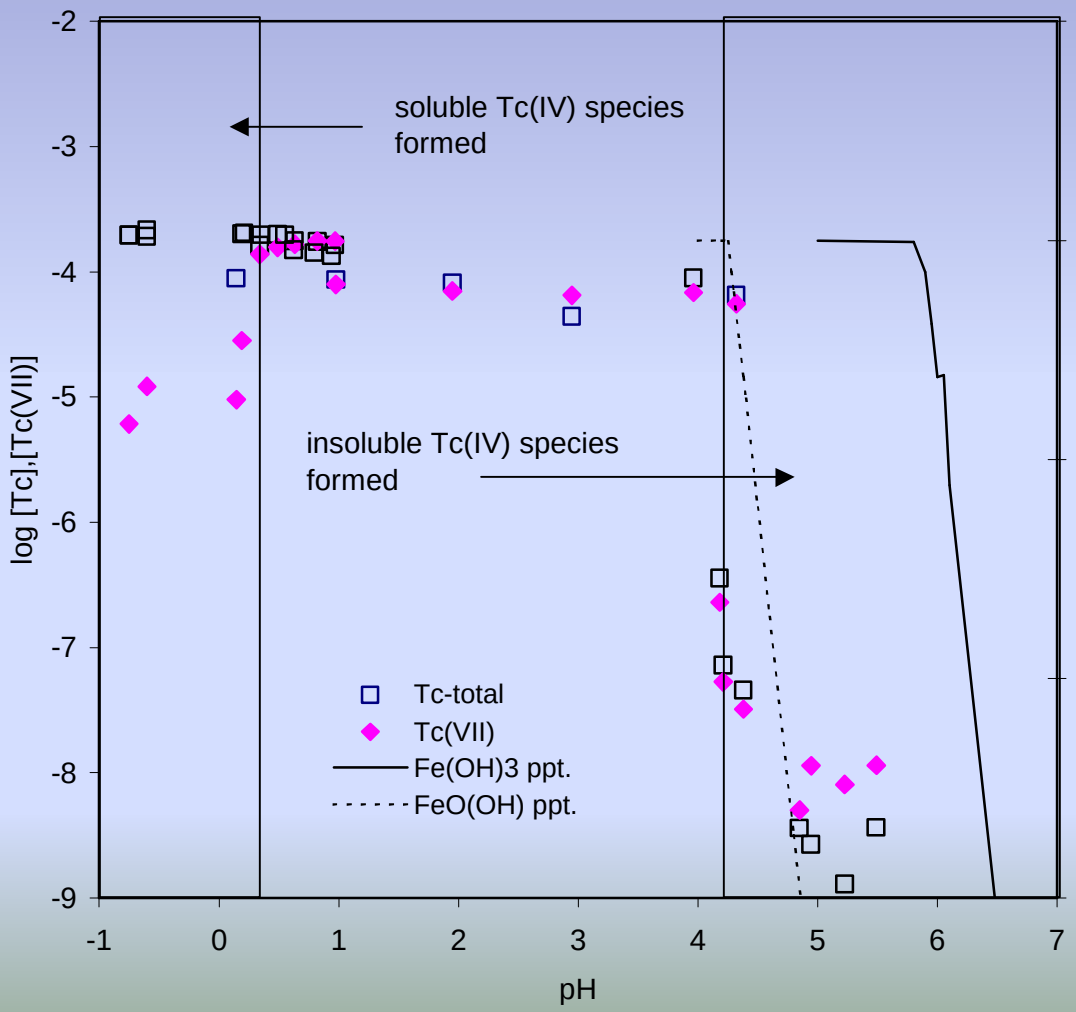


Allow FeO(OH) ppt.

- pH at which TcO_4^- reduction and TcO_2(am) ppt occurs depends on the free energy of the Fe solid phase that precipitates.

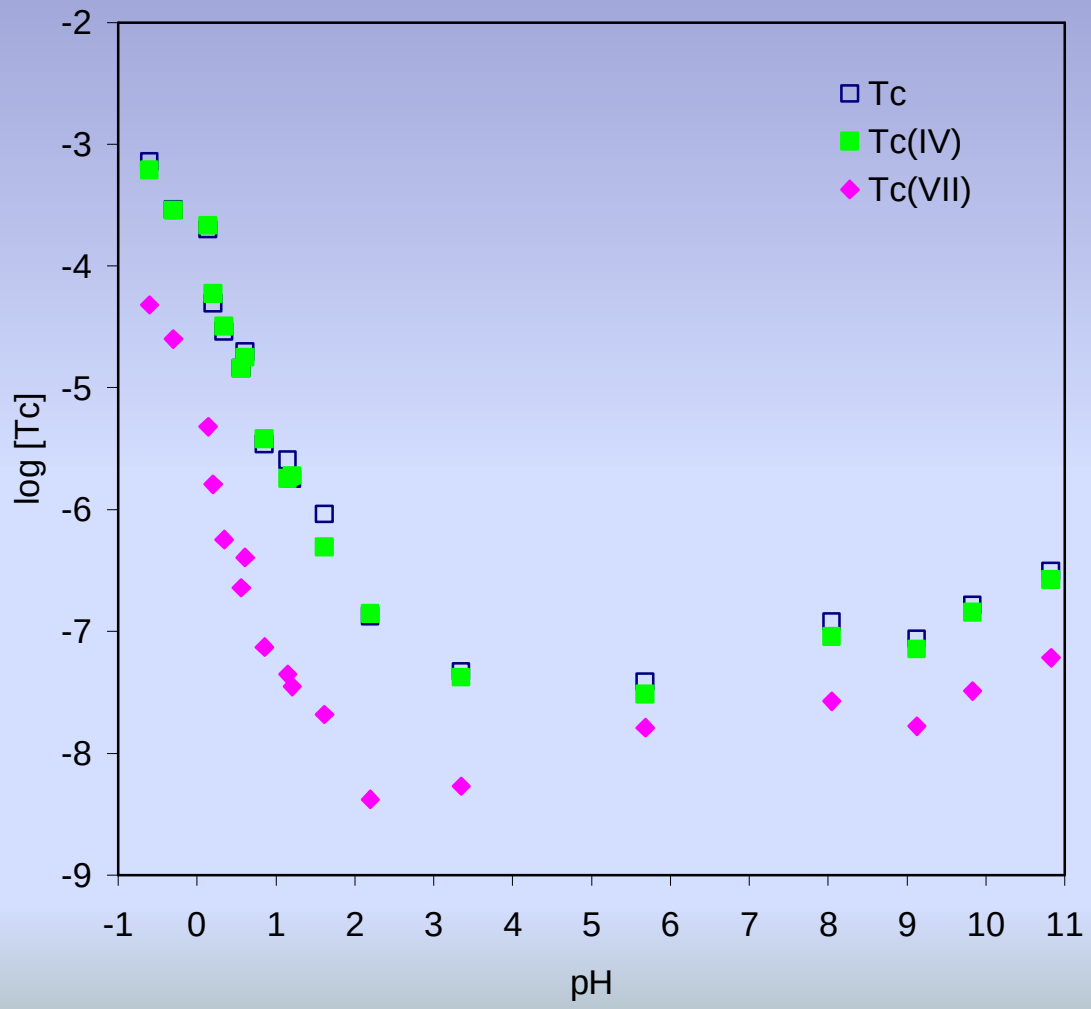
Experimental Result

TcO_4^- reduction by $FeCl_2$



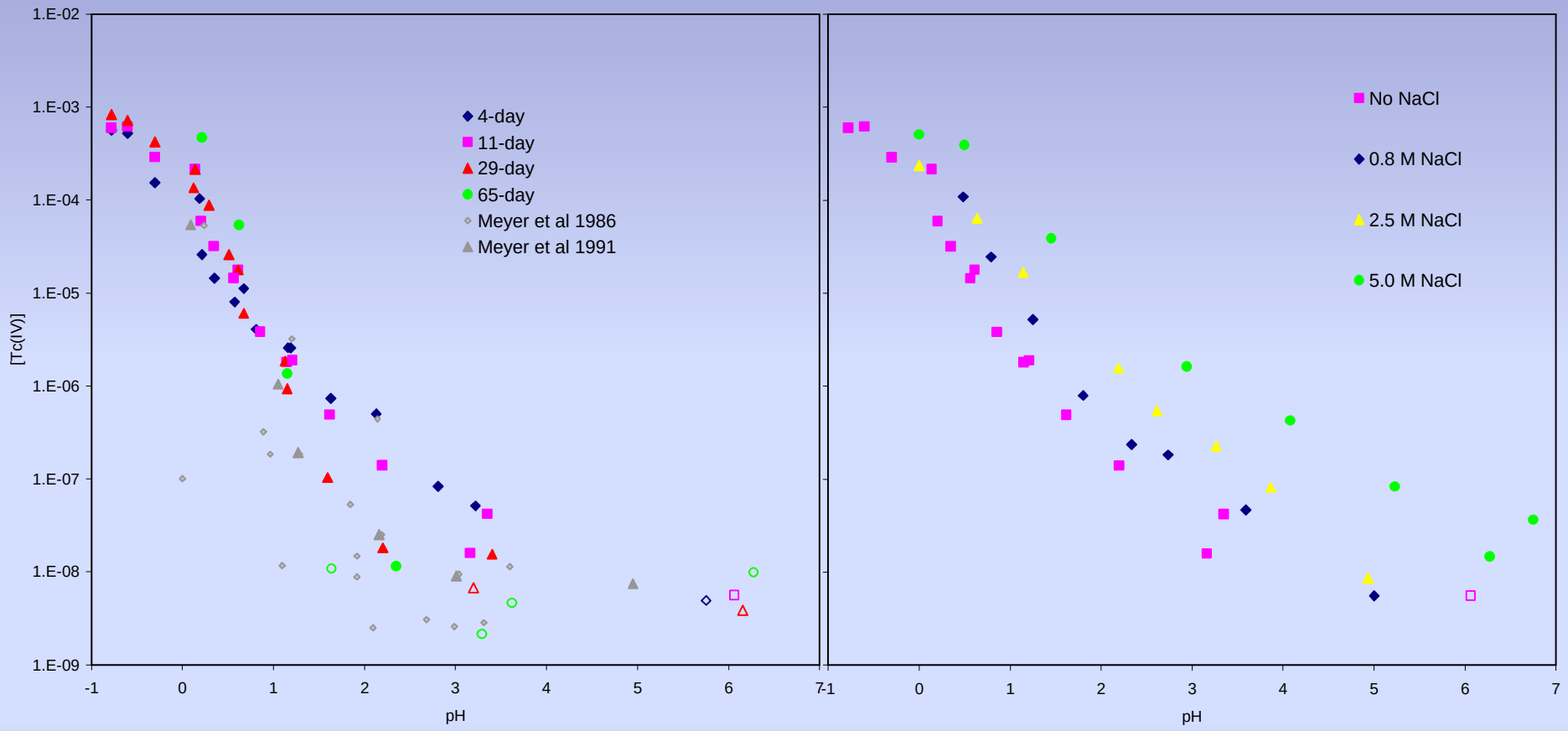
- Observe TcO_4^- reduction by $FeCl_2$ under very acidic conditions and above pH 4.
- Under very acidic conditions Tc(IV) exists as a solution species.
- Above pH 4 Tc(IV) precipitates as TcO_2(am).
- Modeling suggests that Fe(III) solid phase is FeO(OH).
- Suggests thermodynamic data for TcO_2(am) needs to be investigated.

Solubility of TcO_2(am) function of pH under reducing conditions

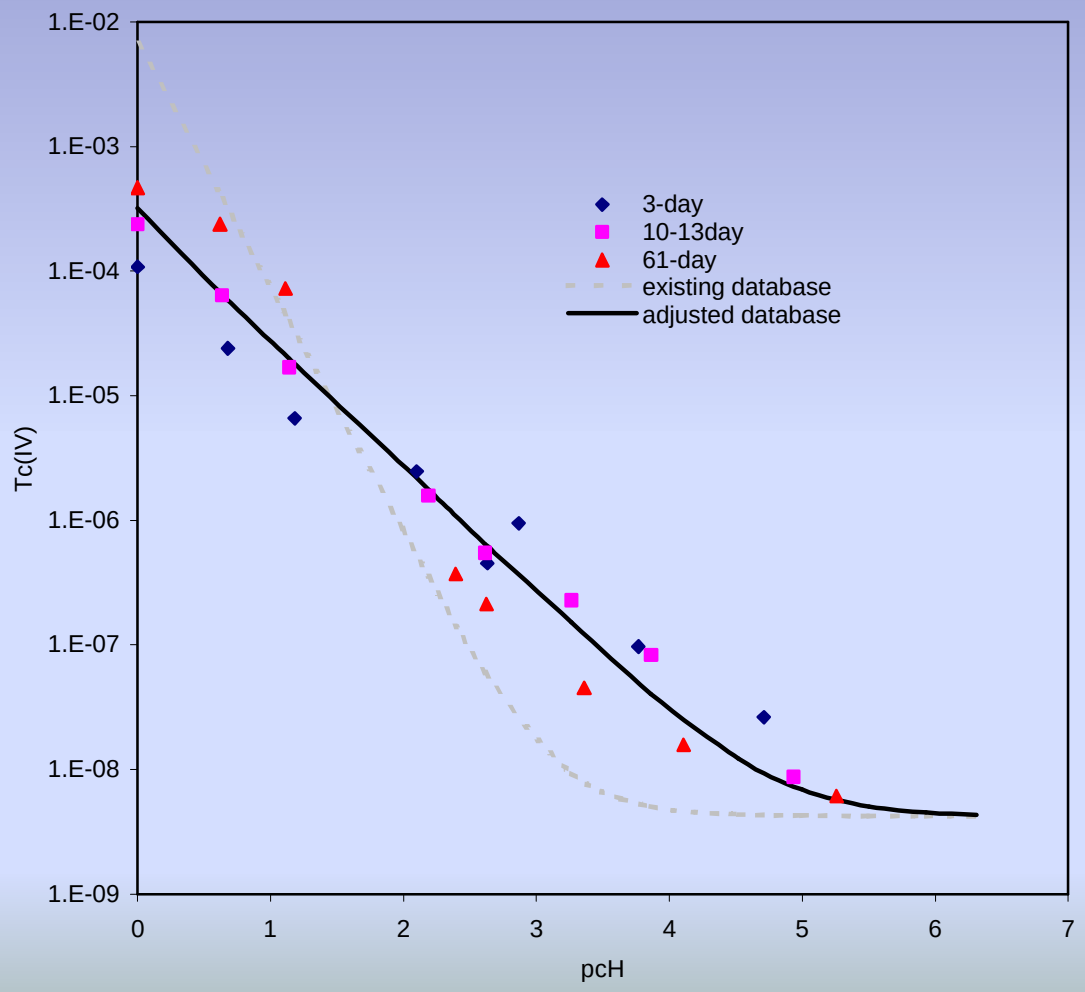


- TcO_2(am) displays weak amphoteric behavior.
- TcO_2(am) solubility in near neutral region is near or at the detection limit.
- Need to conduct solubility experiments under acidic conditions.

TcO_2(am) solubility under acidic conditions and as a function of chloride concentration



Solubility of TcO_2(am) in 2.5 M NaCl



Experimental data in good agreement with geochemical model based on existing thermodynamic data at low chloride concentrations.

At higher chloride concentrations need to make adjustments to thermodynamic values for some Tc(IV) species:

- Adjusted free energy for $TcO(OH)^+$ species
- Added Pitzer parameters for chloride ion interactions for TcO^{2+} and $TcO(OH)^+$ species

Continuing and Planned Work

- Verify solution speciation of Tc(IV) complexes where possible using X-ray absorption spectroscopy.
- Interpret results of homogeneous reduction experiments.
- Conduct studies of TcO_2(am) under highly basic conditions and in the presence of inorganic complexants.
  - Bicarbonate/carbonate
  - Nitrate

Pertechnetate Reduction during Transport at High pH in Natural Sediments

background:

- pertechnetate can be reduced by ferrous iron, typically near mineral surfaces

- NaOH dissolution of sediment minerals can generate sufficient ferrous iron to reduce chromate

purpose:

- is pertechnetate reduced by Fe^{2+} produced by NaOH dissolution of sediment minerals?

Hypothesis

- **pertechnetate reduction at high pH is controlled by dissolution / precipitation reactions limiting the ferrous iron production rate and not the pertechnetate reduction rate**

$$TcO_4^- + 3Fe^{2+} \Leftrightarrow TcO(OH)_2 + 3Fe^{3+}$$

$$\frac{\check{Z}Tc^{VII}}{\check{Z}t} = k_f [Tc^{VII}][Fe^{II}]^3$$

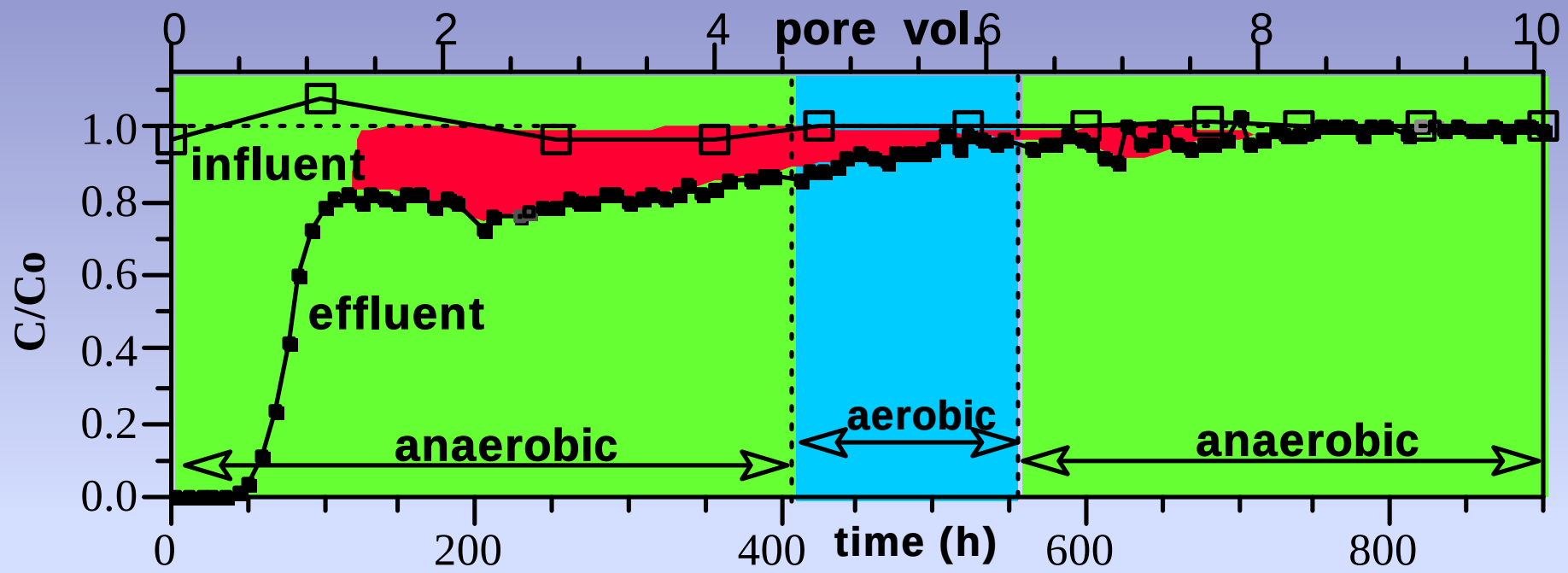
sediment components + xNaOH + y(K,Na)NO_3 <=> [Si] + [Al] + [Fe] ...

quartz, K-feldspar, biotite, magnetite

$$Al^{3+} + 3OH^- \Leftrightarrow AlOOH + H_2O \quad + \text{coprecipitation}$$

$$\frac{\partial Fe^{2+}}{\partial t} = k_{observed} [NaOH]^n [NaNO_3]^m - k_1 [O_2][Fe]^4 - k_2 [Tc^{VII}][Fe]^3$$

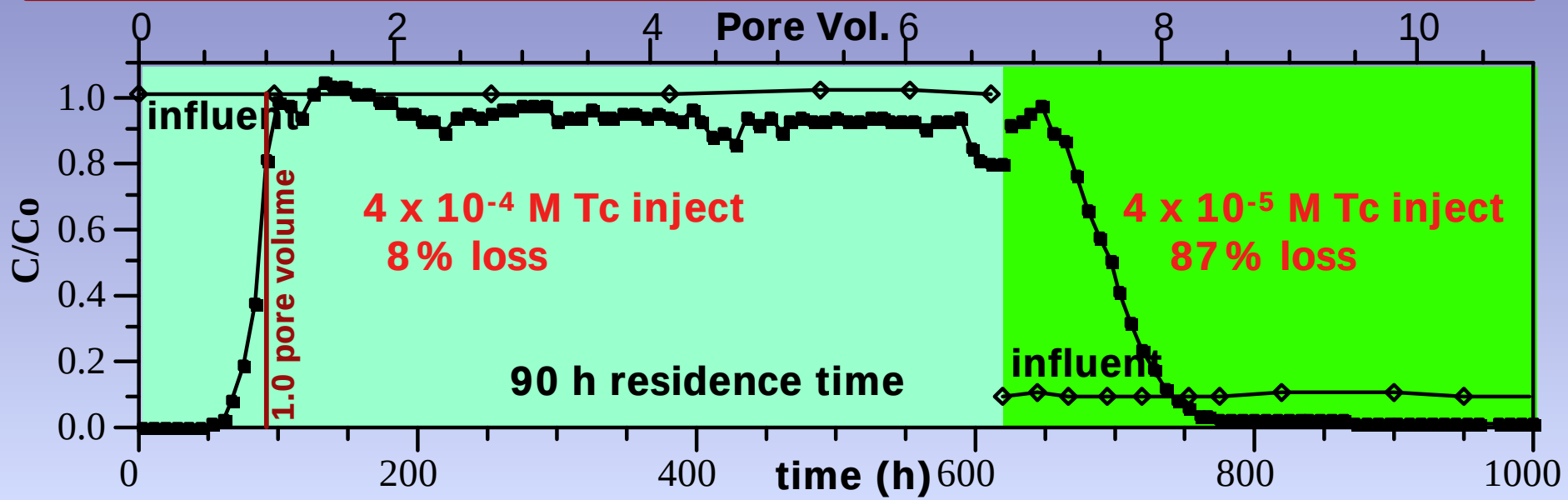
Pertechnetate Reduction at pH 8



influent: 4.4 x 10^{-6} mol/L pertechnetate, O_2 free (no base)
column exp.: Hanford sediment, O_2-free water, 90 h residence time

- slow and limited pertechnetate loss 9% or 3.32 x 10^{-10} moles Tc/h
- mass loss immediate (no lag, available ferrous iron)
- mass loss decreased > 300 h, suggesting limited ferrous iron was exhausted

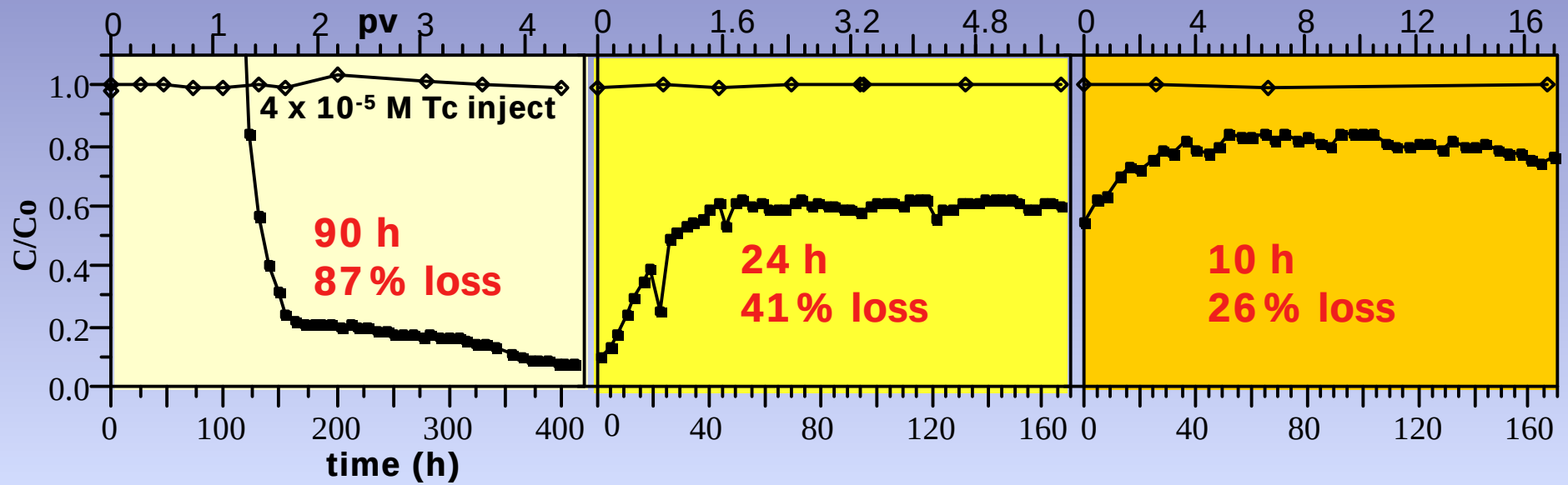
TcO_4^- Reduction with 4M NaOH



Tc inject	Tc removed	Tc loss rate (mol/h)
4×10^{-4} M	3.0×10^{-5} M	1.5×10^{-8}
4×10^{-5} M	3.3×10^{-5} M	1.7×10^{-8}

- pertechnetate removal (reduction/ppt?) lags after initial breakthrough (ferrous iron production)
- removal rate first order in Tc concentration

TcO_4^- Reduction and Reaction Time (4M NaOH)



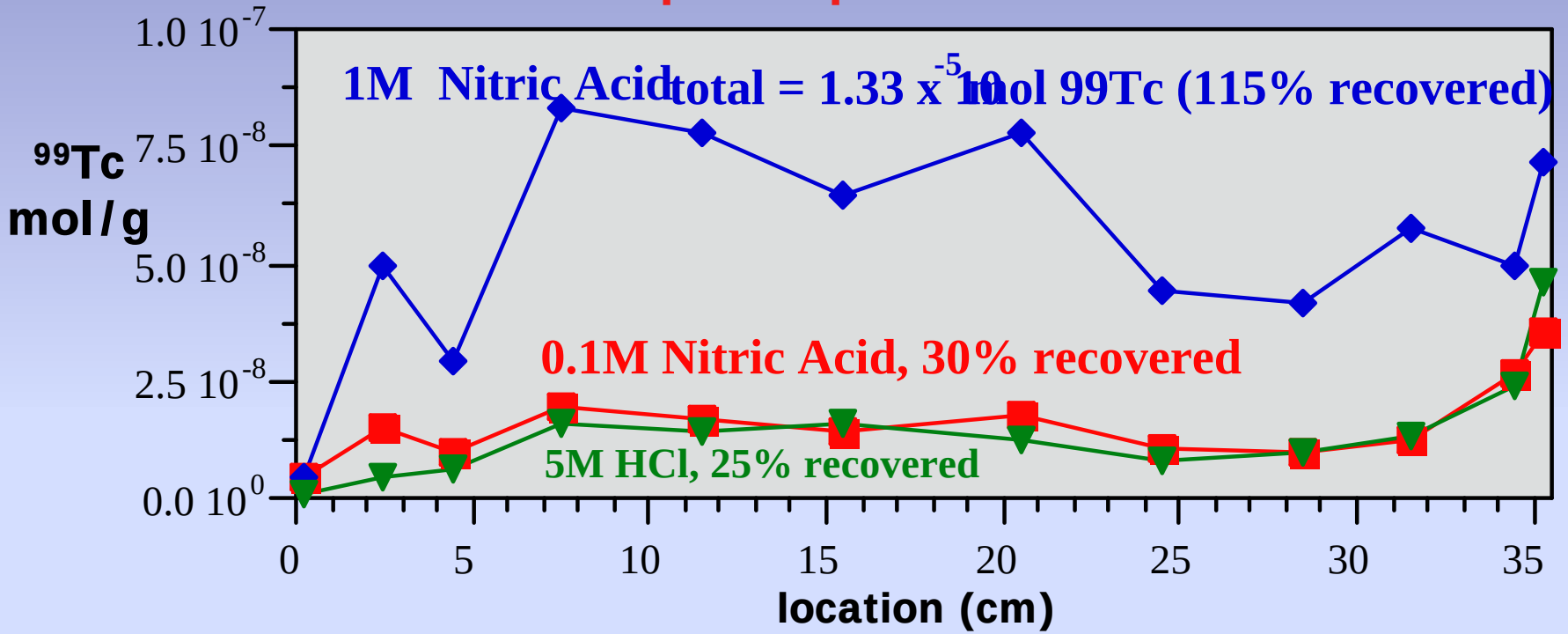
res. time	Tc loss rate (mol/h)
90	1.7×10^{-8}
24	2.9×10^{-8}
9.9	4.1×10^{-8}

- pertechnetate removal rate is greater at shorter contact times; ferrous iron availability partially controlled by Al hydroxide precipitation (less at faster velocity)

- Tc removal increases over time (not steady state)

Tc(IV) on Sediments

- 5 pv of oxygen-free water flushed through column to remove NaOH and aqueous pertechnetate before extraction



- Tc was likely reduced and precipitated on the surface, as oxidation was needed to solubilize the Tc precipitate

- little spatial variability of the Tc precipitate

Summary

- pertechnetate is removed in high base (4M NaOH) solutions in contact with sediments, likely reduction by ferrous iron produced by mineral phase dissolution

- pertechnetate removal rate appears to be controlled by the ferrous iron production rate (dissolution/precipitation rxns) and not limited by the pertechnetate reduction rate

Future Studies

- surface analysis: Tc(IV) identification and mineral associations
- measurement of ferrous iron produced by NaOH dissolution
- comparison of batch, column Tc reduction rates to ferrous iron production rates

Implications to Tank Releases

- a bimodal Tc distribution is likely to develop with:
  - initial conservative Tc transport followed by
  - a later pulse as precipitated Tc is reoxidized

- competition for ferrous iron by other redox reactive species will affect Tc movement:
  - chromate is likely reduced first (lag relative to Tc), then pertechnetate will be reduced
  - nitrate may also slow pertechnetate reduction

- Tc immobilization may be enhanced at shallow depths