IMMOBILIZATION OF RADIONUCLIDES IN THE HANFORD VADOSE ZONE BY INCORPORATION IN SOLID PHASES

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Background

- Complex waste fluids produced during the extraction of Pu, U and other strategic elements from irradiated uranium fuels, represent potential point sources of contamination at a number of DOE facilities.

- Many of these fluids are extremely alkaline and contain unusually high concentrations of dissolved Al, radioactive fission daughter products, alkaline earths, alkali metal cations, etc.

- A substantial quantity of fluids are thought to have leaked from the tanks at Hanford, potentially transporting high temperature, highly alkaline, contaminant containing fluids into the subsurface.

- The chemical composition of the fluids within the tanks raises the possibility of a number of unusual geochemical reactions with the underlying geomatrix. Many of these reactions should lead to the formation of Al-rich solids which have the potential to remove several radionuclides from solution (through adsorption and/or precipitation reactions).

For example, alkaline dissolution of SiO_2 can be described as:

$$SiO_2(s) + H_2O + OH^-(aq) = H_3SiO_4^{1-}(aq) \quad \{1\}$$

$$SiO_2(s) + OH^-(aq) = H_2SiO_4^{2-}(aq) \quad \{2\}$$

Decreases in pH can cause precipitation of Al by:

$$Al(OH)_4^-(aq) + H^+ = Al(OH)_3(s) + H_2O \quad \{3\}$$

and Al-silicates may also form:

$$Al(OH)_4^-(aq) + xH_4SiO_4^0(aq) = [Al(OH)_{3(1-3)}[SiO_2]_x(s) + OH^-(aq) + xH_20 \quad \{4\}$$

- Reactions 1-4 are suggestive of processes that may occur beneath the high level waste tanks. Newly formed Al- and Al-Si-surfaces may serve as sorption sites for radionuclides in the tank leachates. Coprecipitation reactions with radionuclides are likely.

- In this project, we are studying the incorporation of representative contaminant species(Cs, Co, Sr, Tc, and U) in carefully controlled model systems to gain fundamental understanding of sorption, neo-formation, precipitation, and exchange processes that might immobilize these contaminants in sediment matrices impacted by alkaline tank fluids.

Specific objectives

1. Examine the effect of aging on the stability of **Co, Cs, Sr, Tc and U** sorption complexes on Al-oxide and Al-oxyhydroxide surfaces formed during neutralization and precipitation of alkaline aluminate solutions.

2. Examine the sorption/coprecipitation of **Co, Cs, Sr, Tc and U** in solids formed from reaction of alkaline aluminate solutions with representative minerals and mineral coatings found in the soils and sediments at the Hanford Tank Farm (e.g., quartz, micas, feldspars, clay minerals, magnetite, hematite, Fe(III)-oxyhydroxides, and Mn(IV)-(hydr)oxides).

Specific objectives, continued…

3. Study the sorption/coprecipitation of **Co, Cs, Sr, Tc and U** in solids formed from reaction of alkaline aluminate solutions with uncontaminated soil and sediment samples obtained from the Hanford site.

4. Compare laboratory data to solid-phase speciation measurements for **Co, Cs, Sr, Tc and U**, to be made on selected sediment samples obtained from beneath the high level waste tanks.

Research is being performed within four tasks.

Task 1. Precipitation Studies in Tank Simulant Solutions – **OSU, Stanford**

- Examine the solid-phase speciation of Al, Co, Cs, Sr, Tc and U in aged tank simulant solutions (TSS). Solution composition will be measured with ICP-MS and solid phase speciation will be studied with X-ray absorption spectroscopy, XAS and NMR (for Al). Solids will also be examined with SEM/TEM and XRD.

Task 2. Sorption Studies with Model Minerals and Hanford Sediments – **Stanford, OSU**

- Examine the solid-phase speciation of Al, Co, Cs, Sr, Tc and U in TSS reacted with selected model minerals.

- Examine the solid-phase speciation of Al, Co, Cs, Sr, Tc and U in TSS reacted with uncontaminated sediment samples from Hanford. Samples will be examined as described in Task 1.

Task 3. Flow studies of Co, Cs and Tc in Hanford sediments reacted with TSS. – **PNNL, OSU, Stanford**

- Identify changes in porosity and major element chemistry in the leachates.
- Identify changes in bulk mineralogy with XRD and SEM.
- Identify spatial ("chromatographic") distribution of Co, Cs and Tc in the reacted sediment columns.
- Identify changes in Co, Cs and Tc speciation with XAS (macro and micro).

Task 4. Geochemical, mineralogical and spectroscopic characterization of contaminated sediments in areas impacted by high-level waste-tank plumes. – **PNNL, OSU, Stanford**

- Contaminated sediment samples from beneath SX-108 (and other high level waste tanks) will be examined for bulk mineral and geochemical properties at PNNL.
- Selected XAS studies will be conducted at SSRL and at APS to determine the solid phase speciation of target elements in the field samples. Samples for this activity will be provided by the River Protection Program.

Task 1: Precipitation studies:

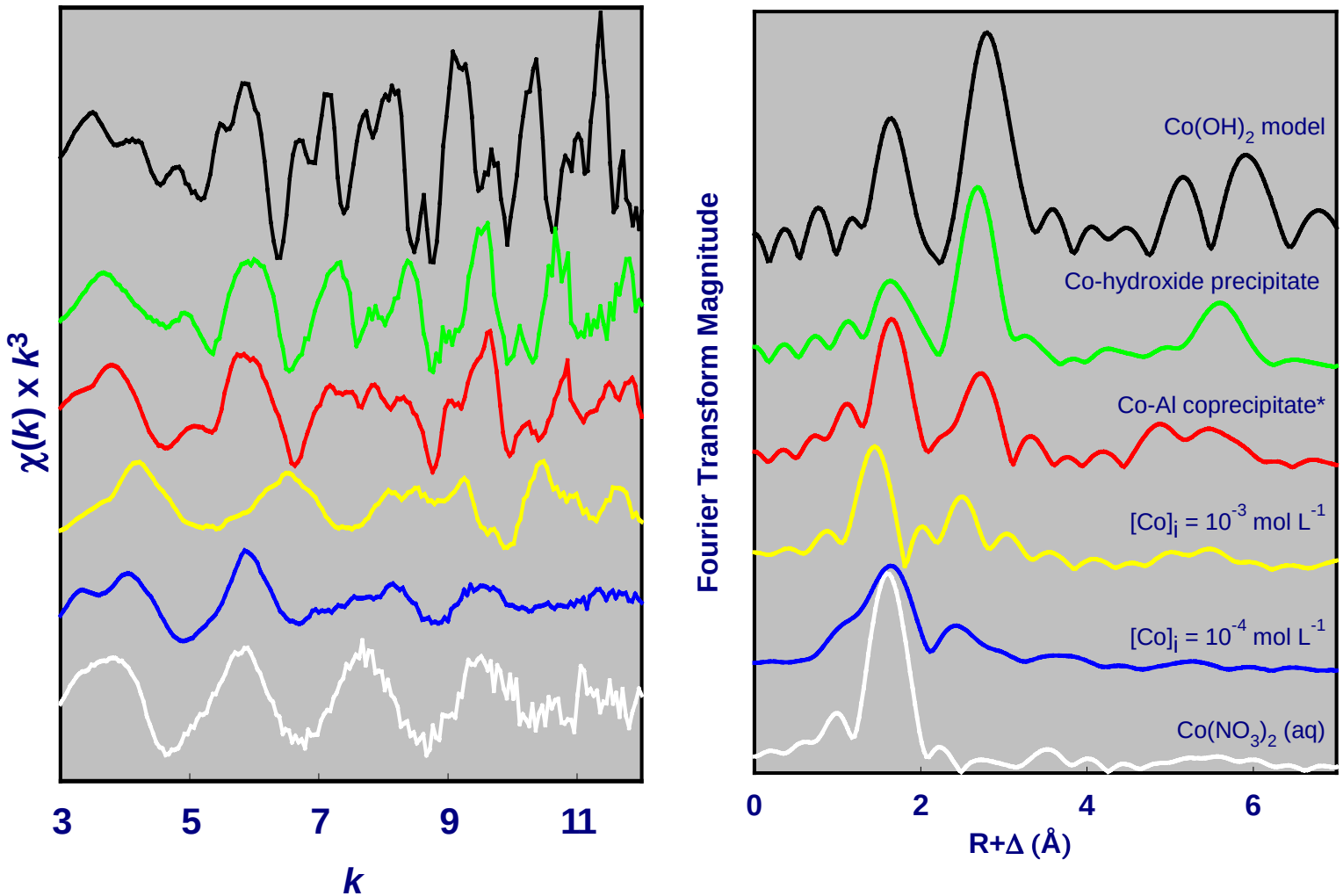
Objective of Task 1 is to ascertain the potential for incorporation of Co, Cs, Sr, Tc and U into Al-precipitates. The approach is to age homogeneous tank simulant solutions (TSS), with and without CO_2, at 50°C (indicative of near field subsurface temperatures) and examine speciation of Co, Cs, Sr, Tc and U in resulting precipitates.

Initial studies have been conducted on solutions with the following composition; $[Al]_i$ = 1 mol L^{-1}, $[Na]_i$ = 4 mol L^{-1}, $[NO_3]_i$ = 3 mol L-1, $pH_i \simeq 13$, $[Co]_i$, $[Cs]_i$, or $[Sr]_i$ = 0.01 to 1 mmol L^{-1}, T = 50°C.

Preliminary results

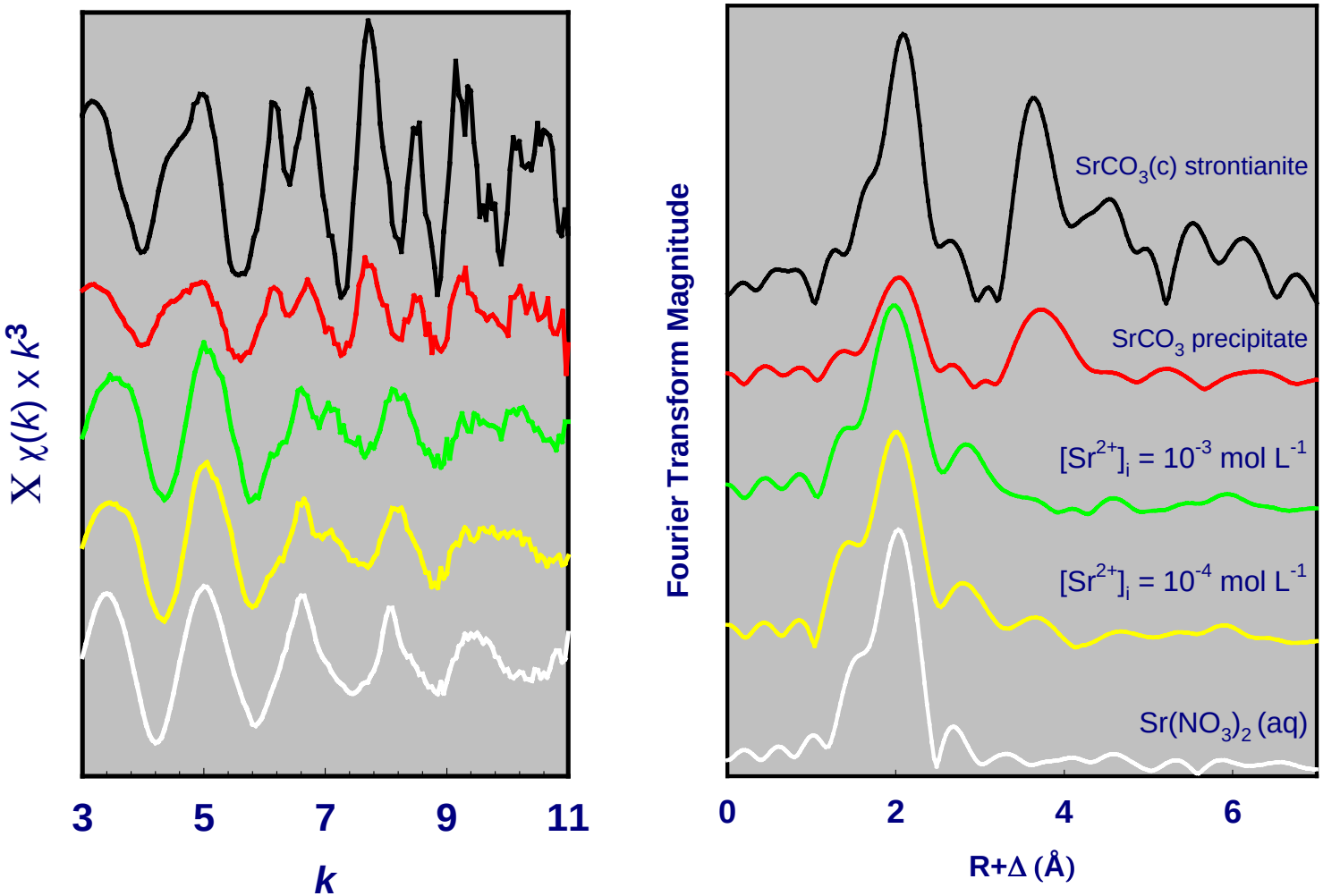
Visible precipitates formed after 3 days of reaction. After 2 months, XRD showed gibbsite and possibly corundum and/or bayerite present. EXAFS measurements on Co and Sr showed unique solid-phase speciation.

Co EXAFS in hyper-alkaline Al-precipitates and model compounds



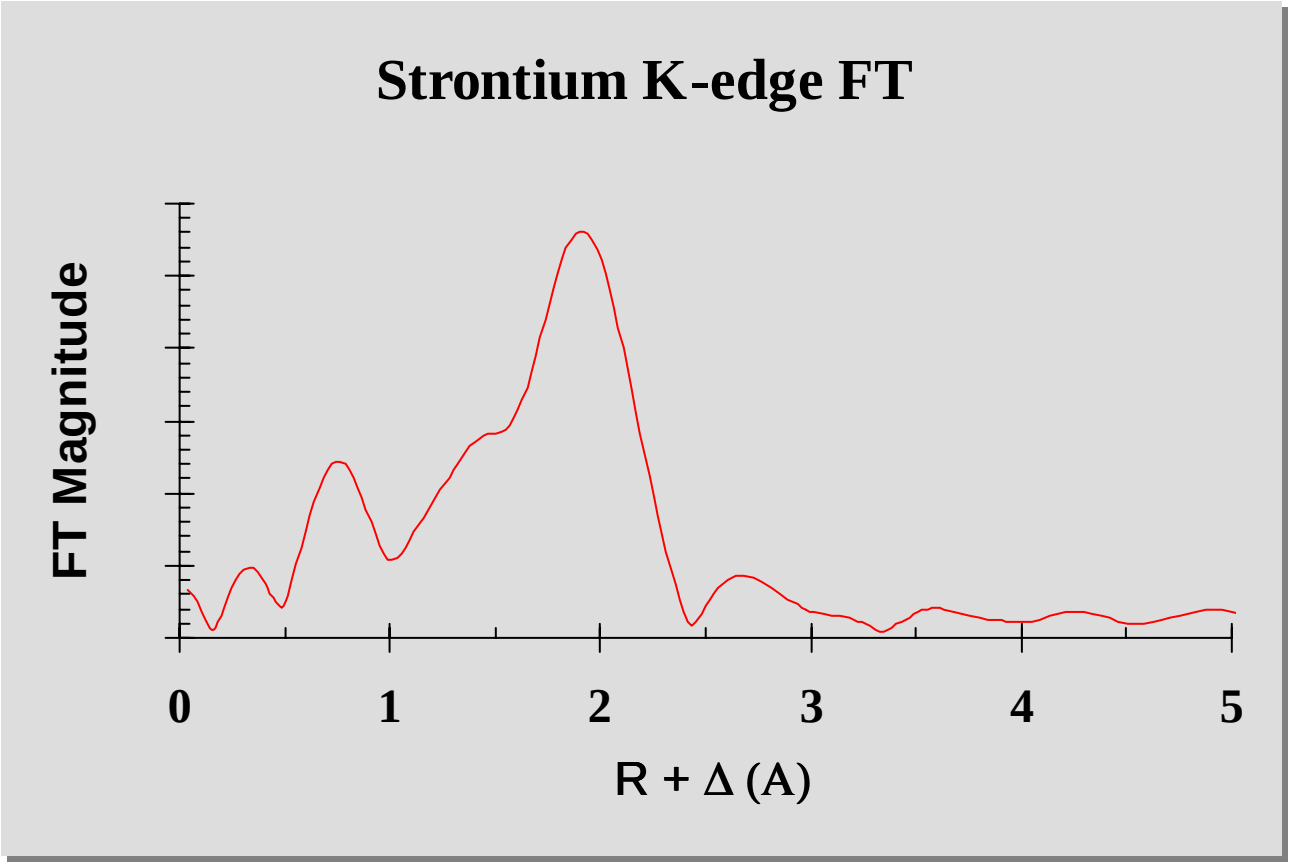
•Co EXAFS in the hyper-alkaline Al-precipitates ($[Co^{2+}]_i = 10^{-3}$ and 10^{-4} mol L^{-1}) are unique. *Co-Al coprecipitate prepared near pH 7.

Sr EXAFS in hyper-alkaline Al-precipitates and model compounds



- Sr EXAFS in the hyper-alkaline Al-precipitates ($[Sr^{2+}]_i = 10^{-3}$ and 10^{-4} mol L^{-1}) are unique.

Sr EXAFS in hyper-alkaline Al-precipitates



•Sr in hyper-alkaline Al precipitates has unique RDS. [Al]=0.4 M; [Sr] = 0.001 M, [OH]/([Al]+[Sr]) = 3; feature near R=2.75 occurs at many different [Al].

Future activities in Task 1

1. Expand initial solution composition to include Tc and U.
2. Expand the range of initial solution pH values.
3. Increase aging time.
4. Inclusion of CO_2 in selected reaction vessels.
5. Conduct NMR and XAS measurements on Al.
6. Expanded examinations of solid and solution-phase chemistry (i.e. XAS, NMR, electron microscopy, vibrational spectroscopy, etc.).

Task 2: Sorption on model minerals and Hanford sediments:

Objective of Task 2 is to ascertain the potential for sorption of Co, Cs, Sr, Tc and U by existing vadose-zone particle surfaces and by surfaces formed upon reaction with the tank leachates. The approach is to react TSS, with model solids and with target sorbents, with and without CO_2, at 50°C and examine uptake and solid phase speciation of Co, Cs, Sr, Tc and U. The coating of preexisting mineral surfaces by Al-precipitates is of particular concern.

Initial Sr sorption studies have been conducted on K-feldspar, a major component of the Hanford vadose-zone and δ-MnO_x, in the absence of dissolved Al.

Preliminary results

Outersphere uptake of Sr on K-feldspar. Precipitation of $SrCO_3$ When CO_2 is present. Innersphere sorption complexed formed on δ-MnO_x.

SURFACE PRECIPITATES OF STRONTIUM

HOMOGENEOUS PRECIPITATES

e.g. $SrCO_3$

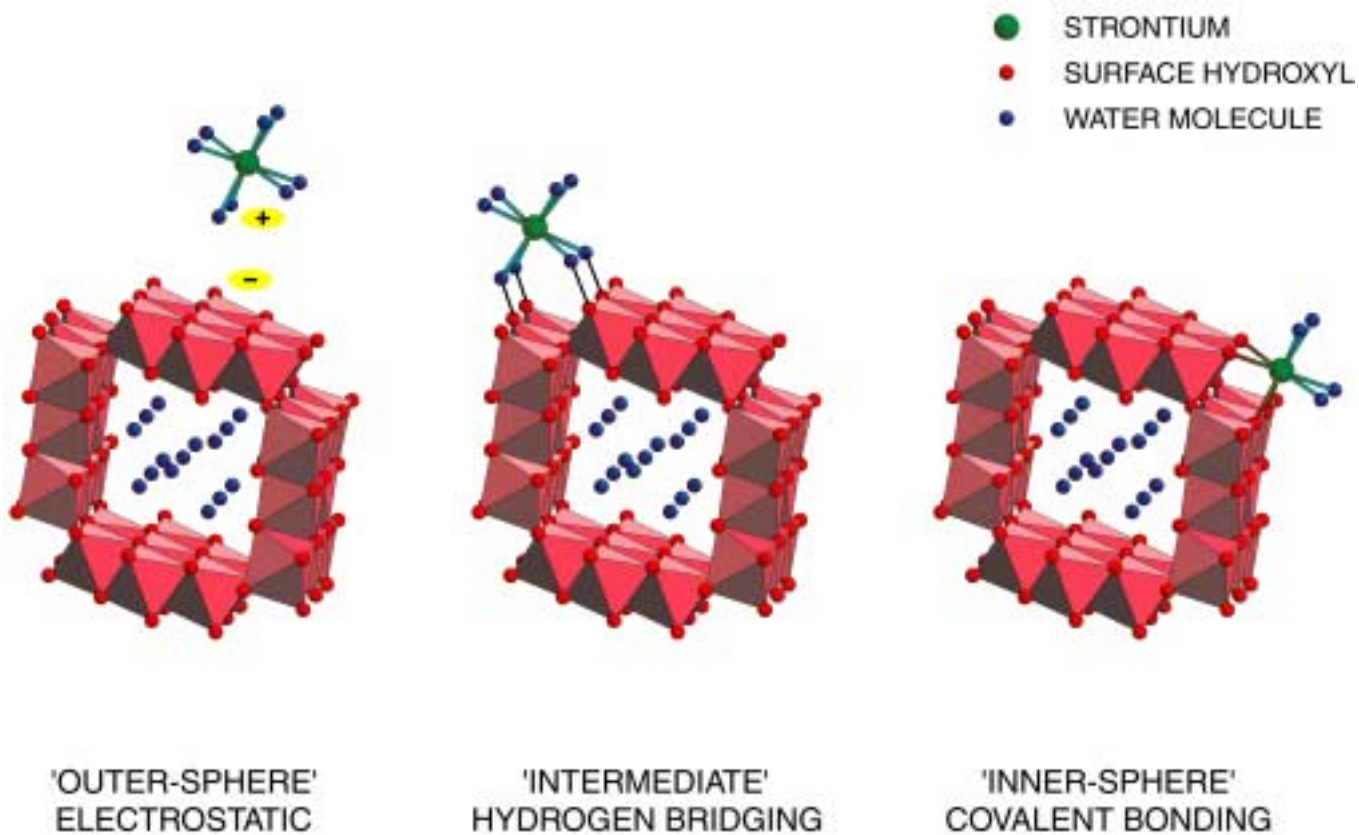
HETEROGENEOUS PRECIPITATES

e.g. $(Ca, Sr)CO_3$ SOLID-SOLUTIONS, MIXED PRECIPITATES

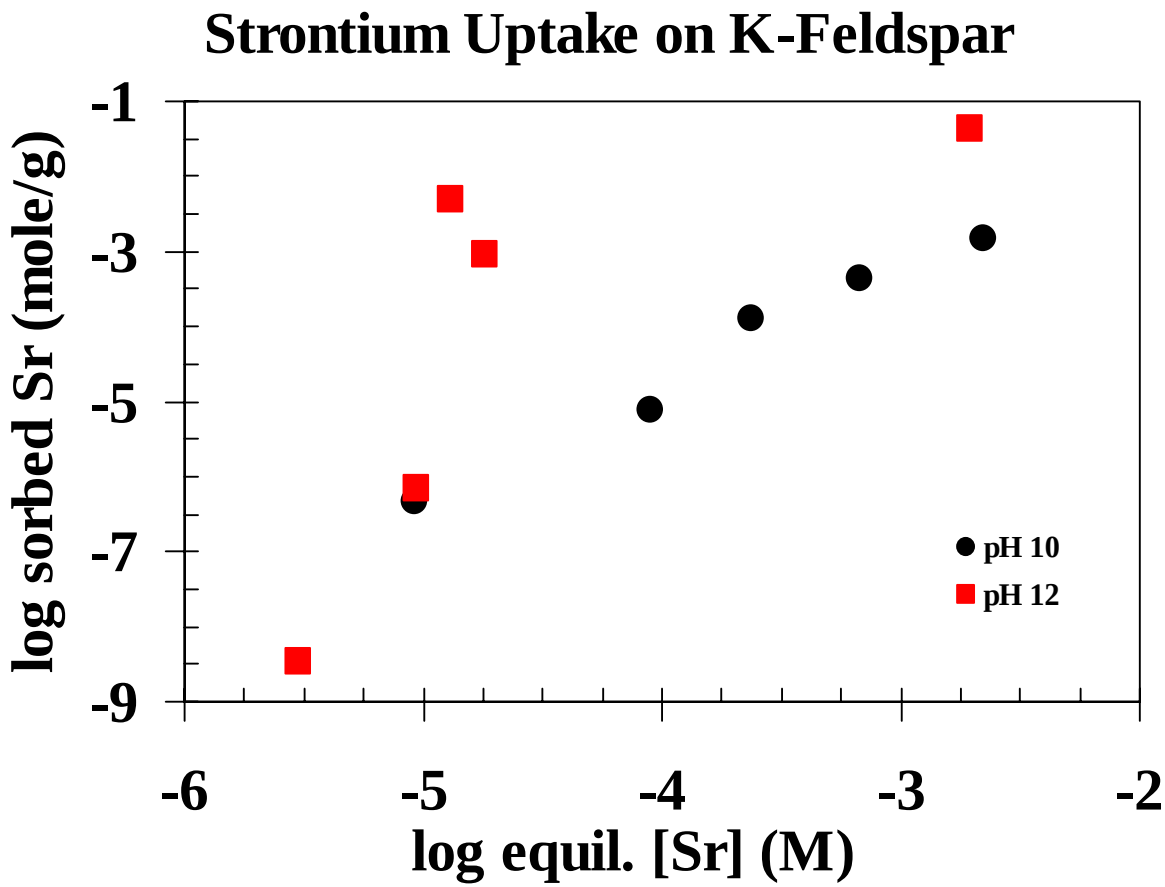
AGGREGATES | EPITAXIAL GROWTH | SURFACE COATINGS

•A metal ion can precipitate as a pure phase, a pure coating or as a coprecipitate.

MODES OF SORPTION OF Sr(II) ON δ-MnO_x

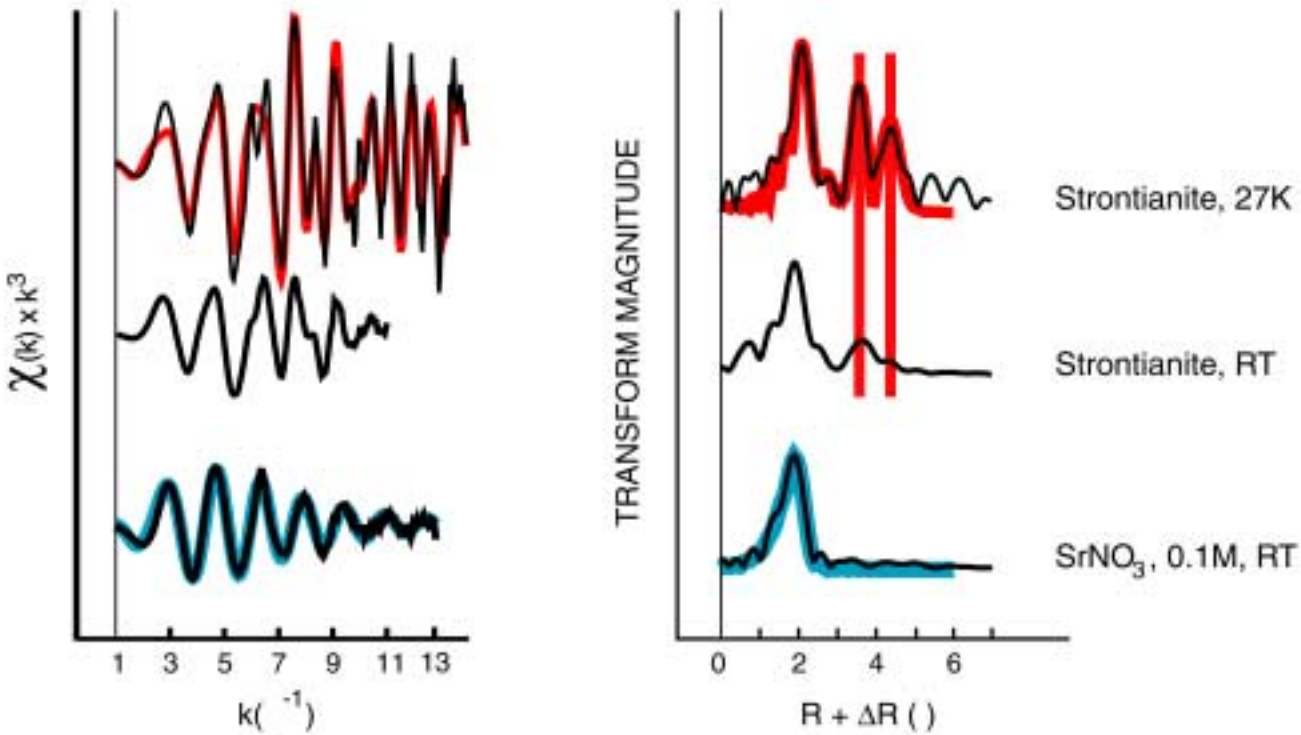


- Adsorption can result in different types of surface complexes

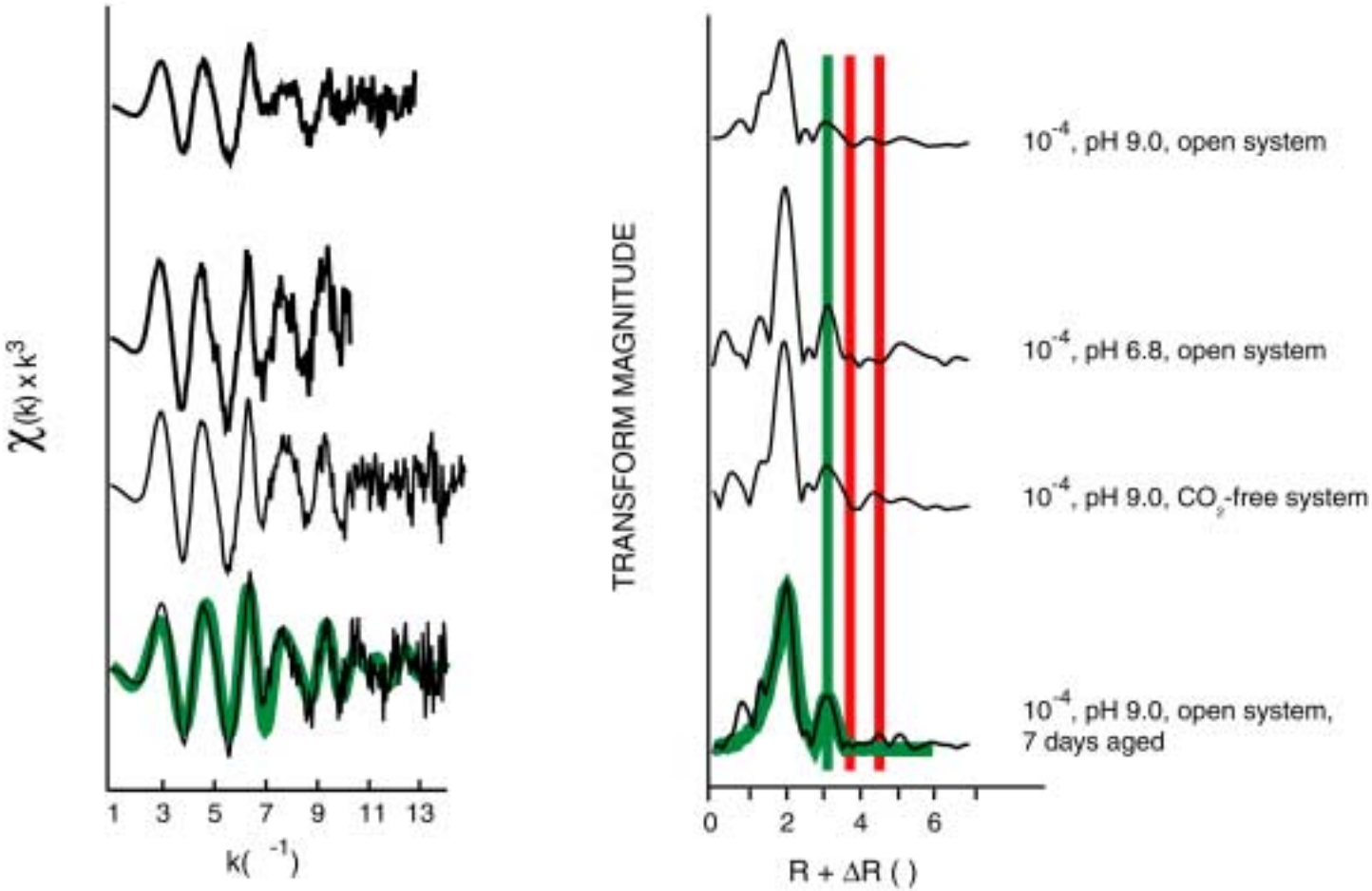


•Sr uptake on feldspar increases with pH

STRONTIUM - MODEL COMPOUNDS

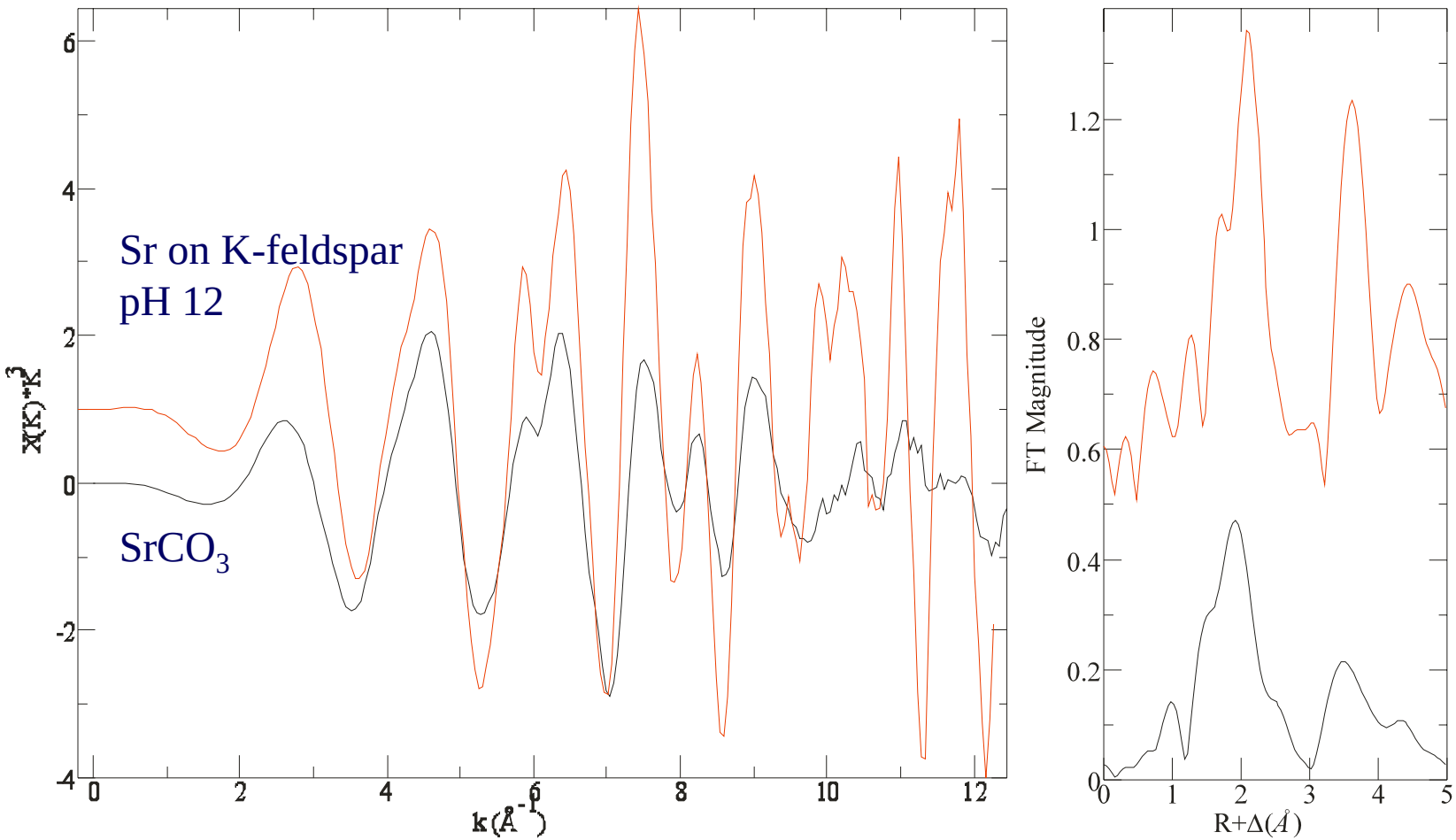


INTERFACIAL STRONTIUM ON δ-MnO_x



- Sr on δ–MnO_x is distinct from $SrCO_3$

Sr EXAFS on K-feldspar and in Strontianite ($SrCO_3$)



•Sr on feldspar similar to Sr in $SrCO_3$. [Feldspar] = 8.3 g L^{-1}, [Sr]=1mM in 50 mM $NaNO_3$. Data collected at 25 K

Task 3: Flow Studies

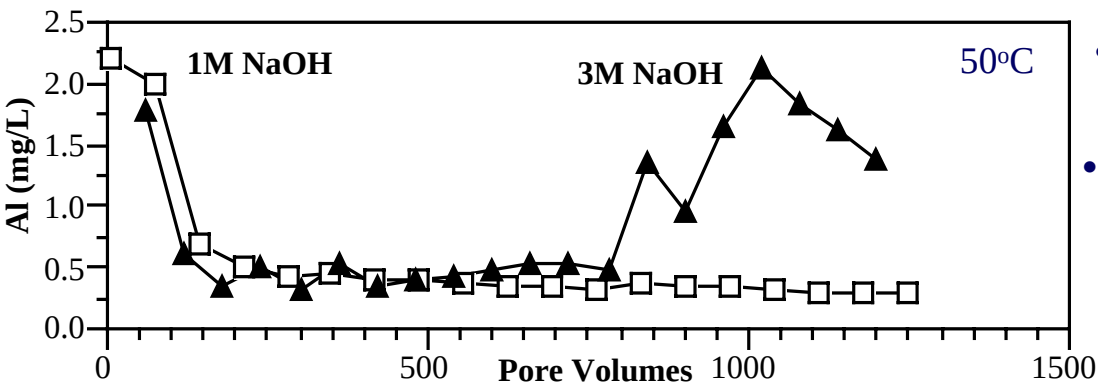
Initial objectives: Assess major mineralogical changes - Al, Si dissolution, physical changes (density, porosity), and effects on the sorption of radionuclides (^{99}Tc, ^{137}Cs, ^{60}Co).

Design of 1-D transport studies: a) 6 flow experiments varying NaOH, KNO_3, and $NaNO_3$, b) maximize leaching by fast flow over long time period through columns (1600 pore volumes), and 50°C. Measure: a) Si, Al in effluent, changes in bulk density and porosity, changes in sorption of ^{99}Tc, ^{137}Cs, ^{60}Co for untreated and 6 different treatments.

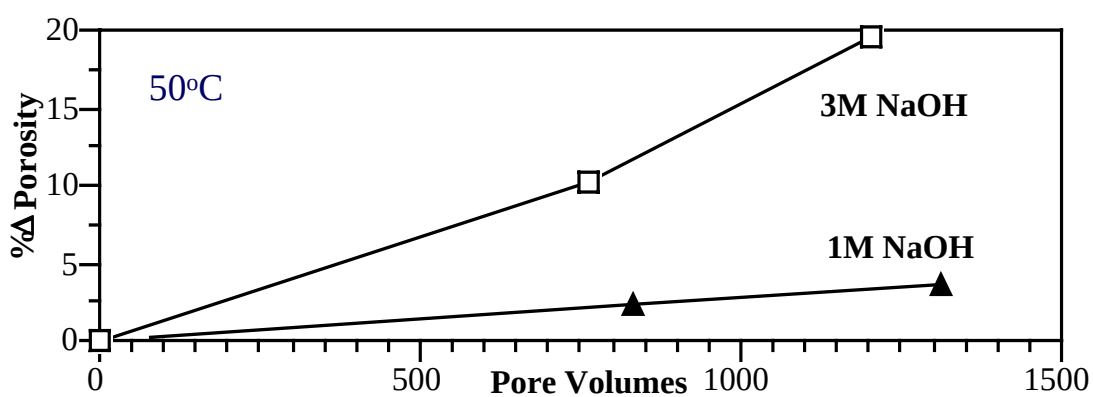
Preliminary results

Significant dissolution of sediment Al has occurred. Concomitant increases in porosity and decreases in bulk density were observed.

Effect of NaOH on dissolution/precipitation



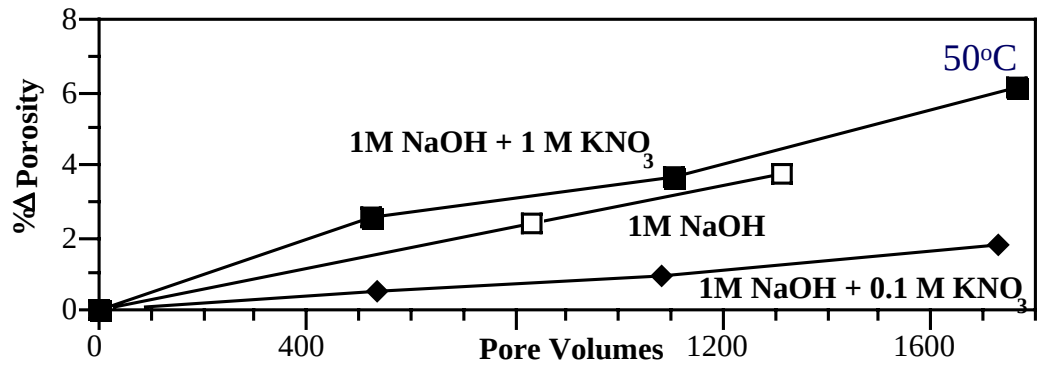
- initial Al dissolution (<50 pv) likely removes highly soluble Al phases
- 3M NaOH may be removing less soluble phases at later times (>800 pv) that were precipitating and redissolving



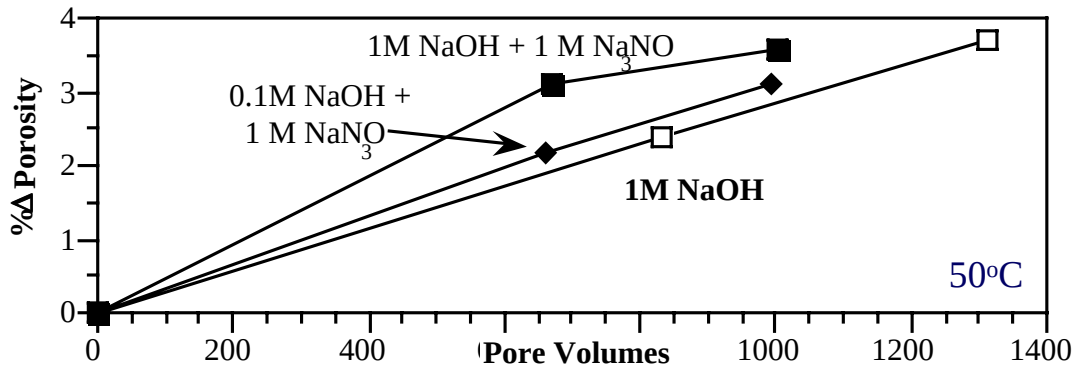
- a significant volume of sediment is being dissolved:
  porosity up 4% with 1M NaOH (bulk density down 6%)
  porosity up 20% with 3M NaOH (bulk density down 26%)

- preliminary results show considerable Al dissolution and possibly some Al precipitation

Effect of nitrate on sediment dissolution



- KNO_3 addition to NaOH appeared to decrease dissolution, based on change in porosity and bulk density



- $NaNO_3$ addition to NaOH increased dissolution, resulting in increased porosity and decreased bulk density

Future Flow Studies of TSS Leachate

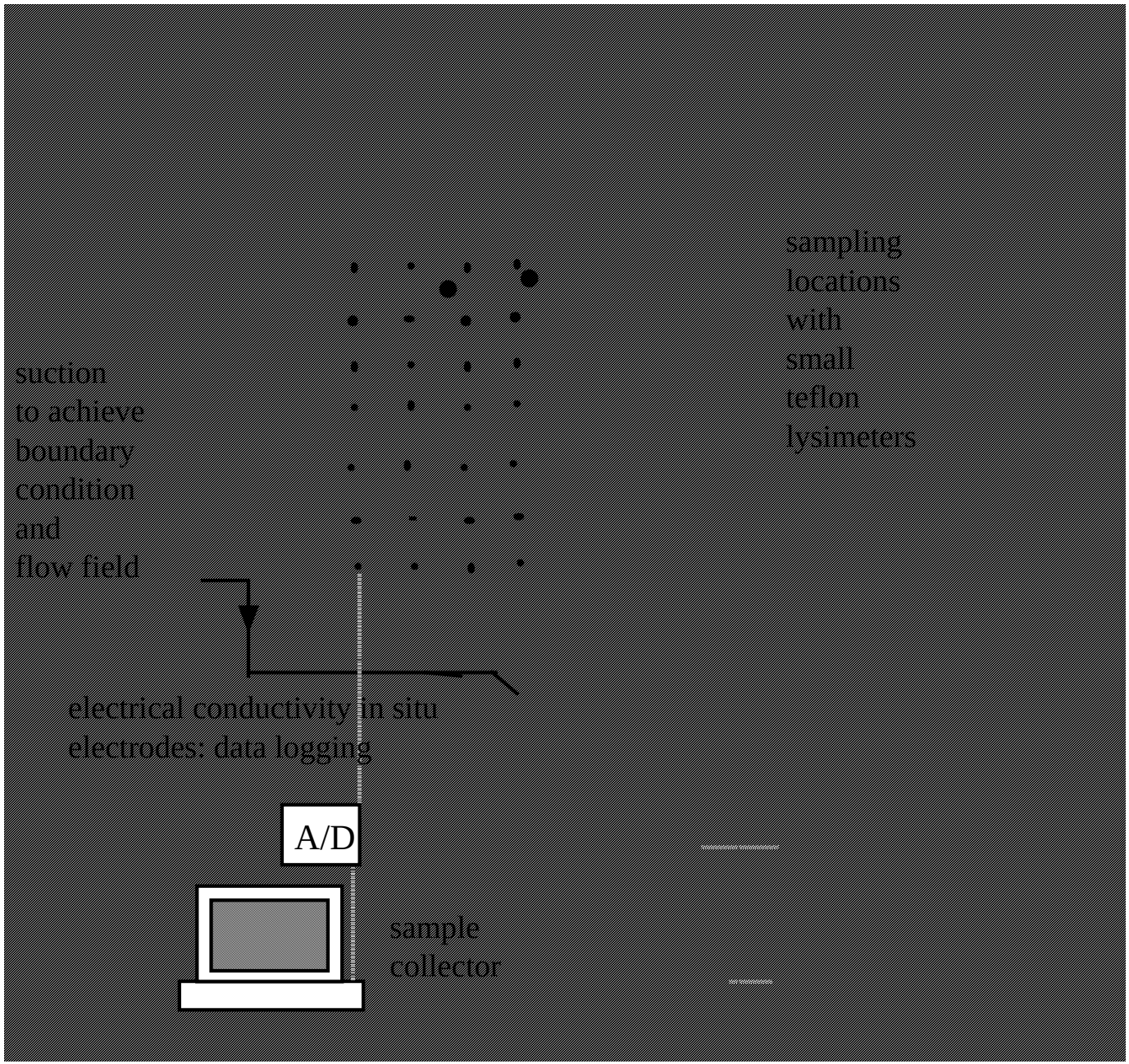
1-D flow experiments

- gamma attenuation for porosity change (dissolution in near field; precipitation in far field migration)
- mineral phase analysis along column length to evaluate sequences of reactions (destructive sampling)
- evaluation of dissolution/precipitation rates in flow systems by experiments with differing liquid/solid contact time
- radionuclide transport during dissolution and precipitation

2-D flow experiments

- gamma attenuation for 2-D porosity changes
- sequential precipitates may differ in 2-D/3-D systems as flow is diverted by precipitation

XAS analyses of Co, Cs and Tc will be conducted on selected samples from both1-D and 2-D flow experiments.


sampling
locations
with
small
teflon
lysimeters
suction
to achieve
boundary
condition
and
flow field
electrical conductivity in situ
electrodes: data logging
A/D
sample
collector

Task 4. Characterization of contaminated sediments in areas impacted by high-level waste-tank plumes.

Activities under this task will begin in late summer - early fall of 2000, when we expect to receive sediment samples from the drilling activities to be conducted in the vicinitiy of SX-108. Selected subsamples will be examined with SEM, bulk XAS and micro XAS.