Geochemical Evolution of Highly Saline and Alkaline Tank Waste Plumes in the Hanford Vadose Zone

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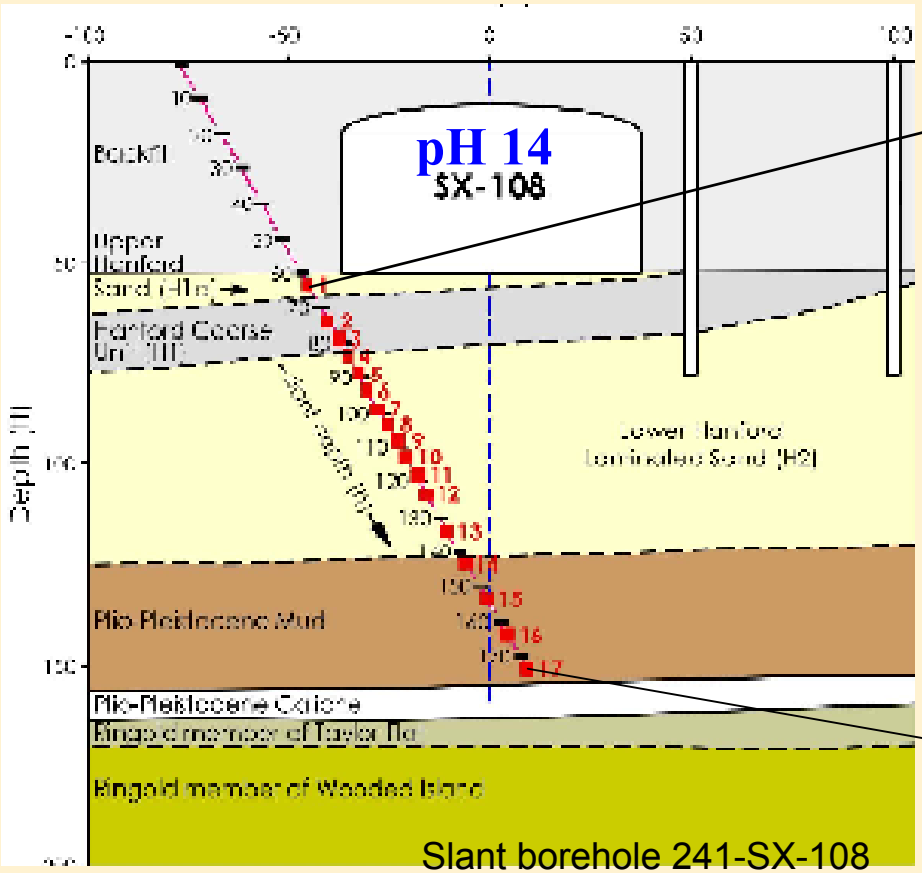
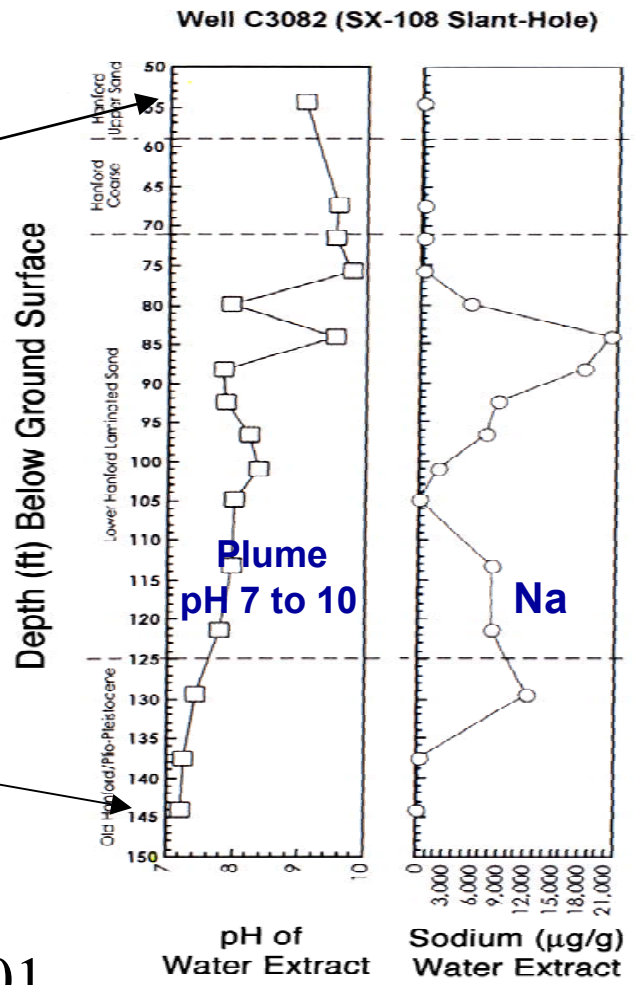
Motivation

"Where is all the caustic that was initially contained in the tank fluids?" -- Question raised by the Hanford Groundwater and Vadose Zone Integration Team.





After Serne et al., 2001

Objective

To understand how the tank waste plumes evolved geochemically as results of their reactions with the underlying sediments

- **Directly measure pH profiles of lab. simulated waste plumes**
- **Directly measure changes in chemical compositions of pore liquids and the sediments**
- **Identify the major secondary phases**
- **Is colloid formation/transport significant?**
- **A geochemical model for plume evolution**

General Approach

- We simulated the tank waste leakage event by infiltrating synthetic tank waste solution into Hanford sediment columns at elevated temperature (70°C, temperature was elevated because of radioactive decay). By doing so, the geochemical reactions and transport processes were studied simultaneously.
- We chose experimental conditions as close to the field conditions as possible, however the experimental systems were designed simple enough so that causes and effects could be identified.
- This led to a new column method to study waste plume evolution.

Methods and Material

Hanford Sediment

"coarse sand" Hanford formation 200 Area	Sand %	Silt %	Clay %	CaCO3 %	Moisture mass %	pH mass% (1:1 water extract)
	92.5	5.9	1.7	1	7	8.4

Other sediments used

Altamont soil: 40% clay and 5% calcium carbonate

Quartz sand: 99% quartz

Synthetic tank waste solution:

- **REDOX Waste Solution:** SX-111 supernatant (the historical measurements). Major ions include: 0.8 M Al^{3+}, 8 M Na^{+}, 5 M NO_3^-, I = 8 M, pH = 14.

Results

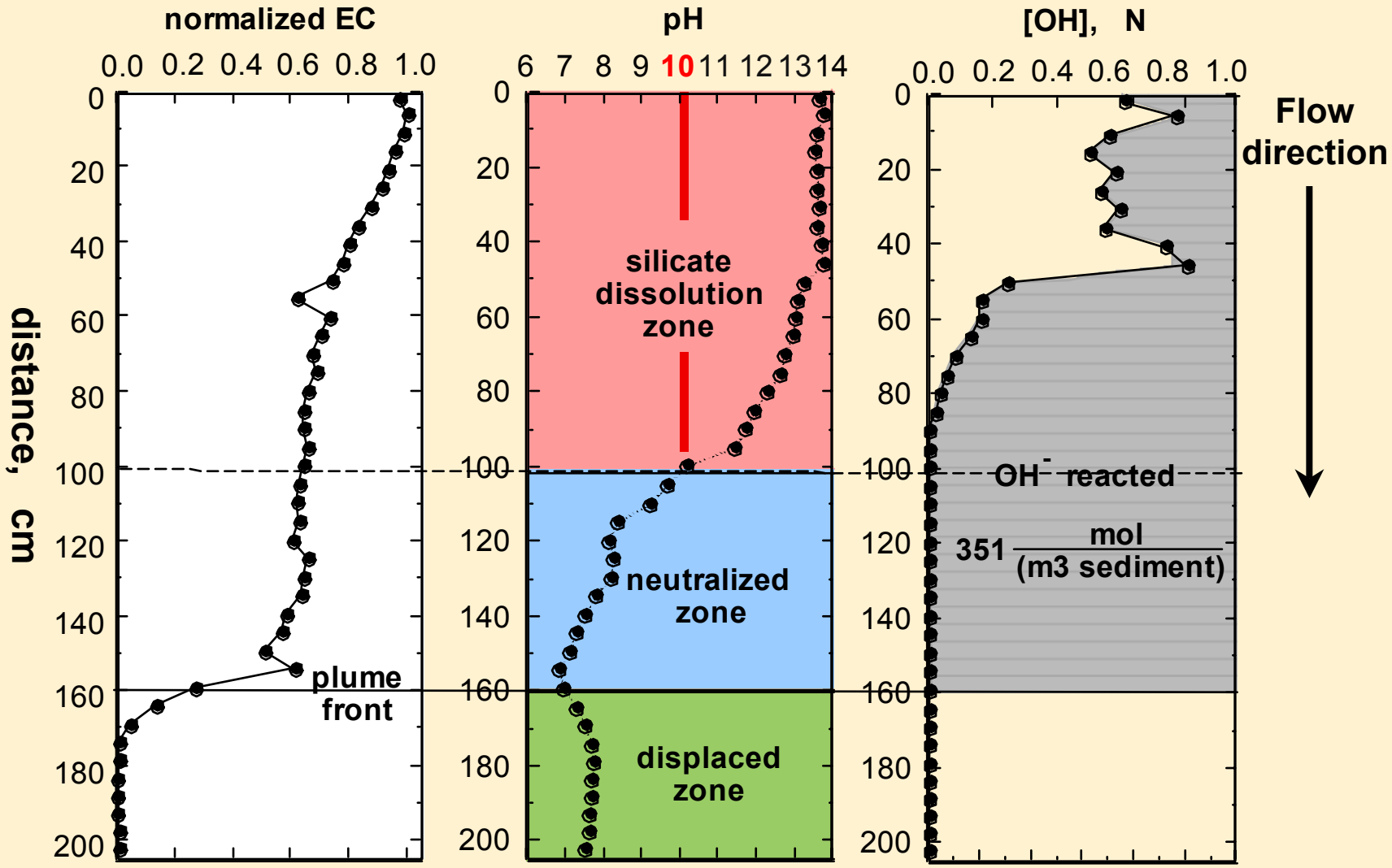
1. pH profiles of waste plumes
2. pH neutralization and zonation mechanisms
3. Evolution of major cation composition

   Plume liquid

   Sediments
4. Major secondary phases
5. Colloid formation and transport
6. Geochemical model of waste plume evolution

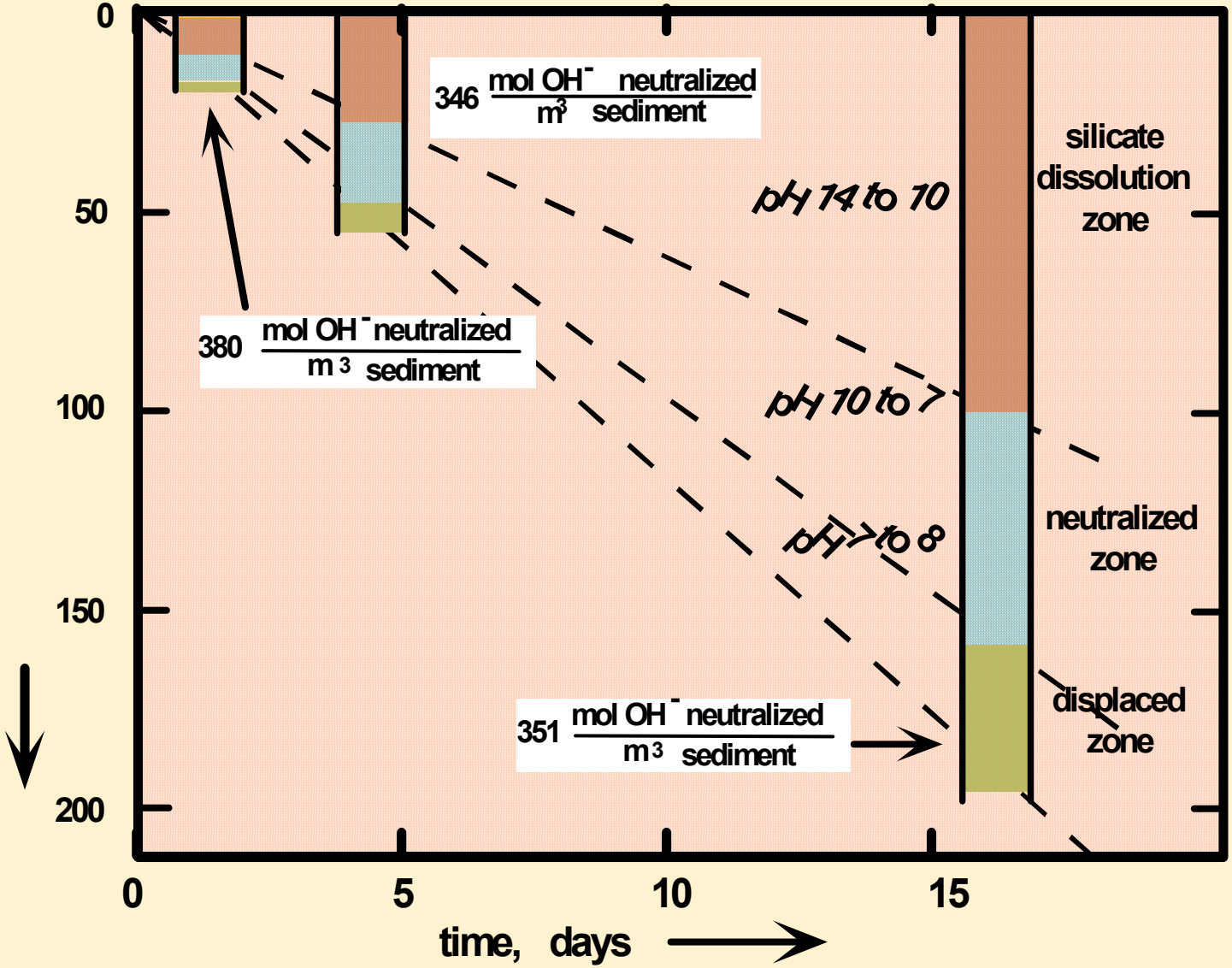
Results 1: pH profiles of waste plumes

EC, pH, [OH] profiles from 2 m column

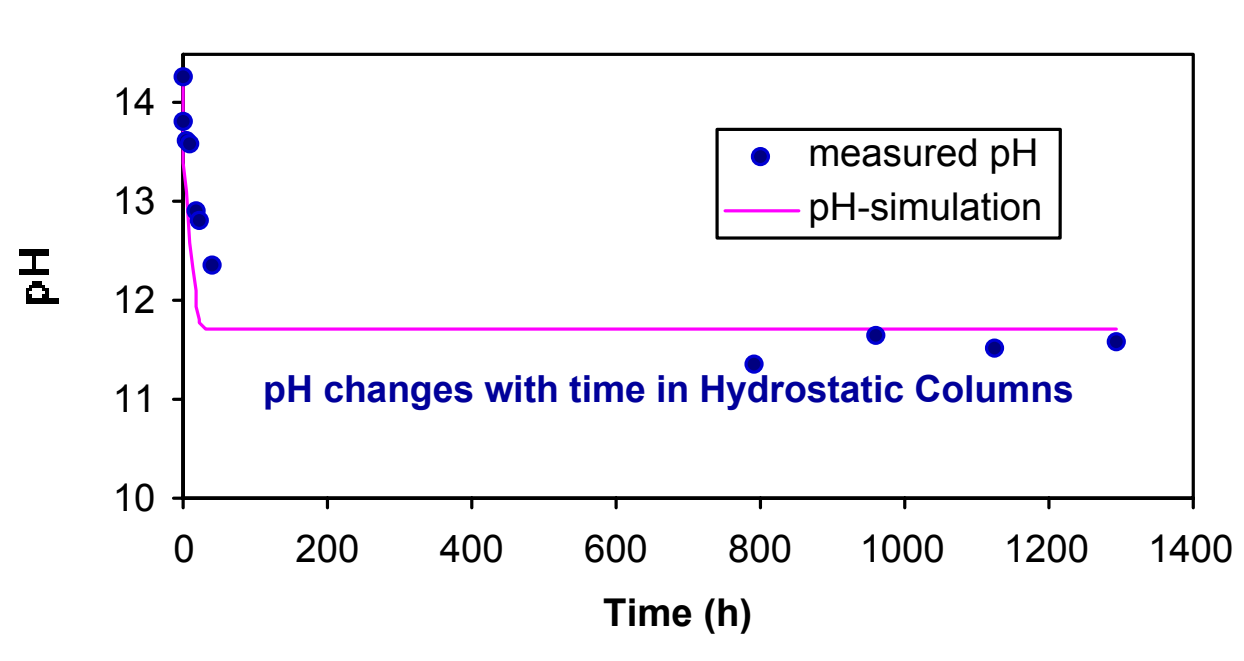


Results 1: pH profiles of waste plumes

Measured One-Dimensional Plume pH Profile



Can pH neutralization be understood through batch equilibrium studies?



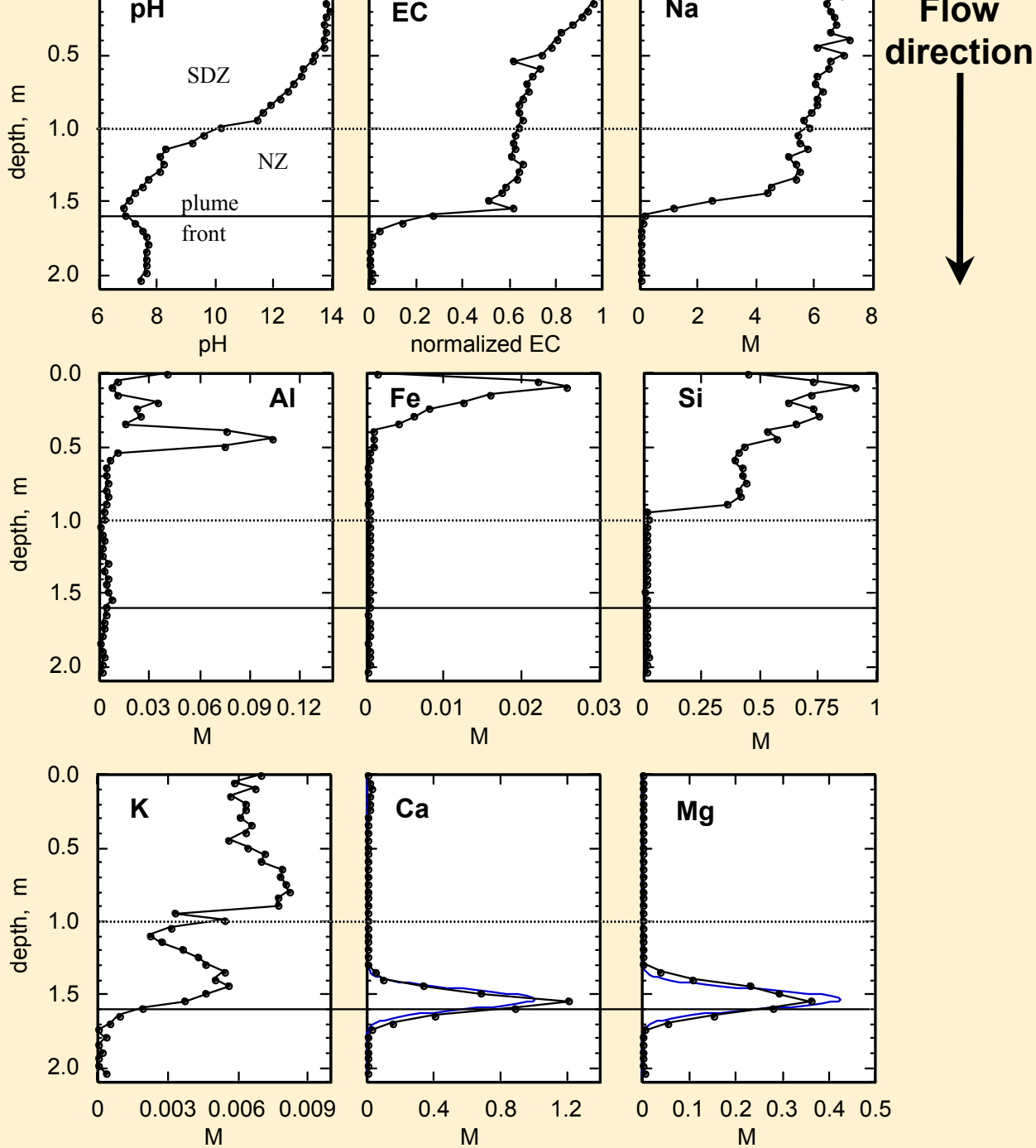
Hanford sediment; REDOX TWS; same packing density; same liquid:sediment ratio; 70˚C; no flow.

- **Equilibrium pH=11.5, from silicate dissolution and Na-metasilicate precipitation.**
- **The spectrum of geochemical conditions existing in dynamic plumes can not be captured in batch studies.**

Results 3

Evolution of major chemical composition of plume liquid phase

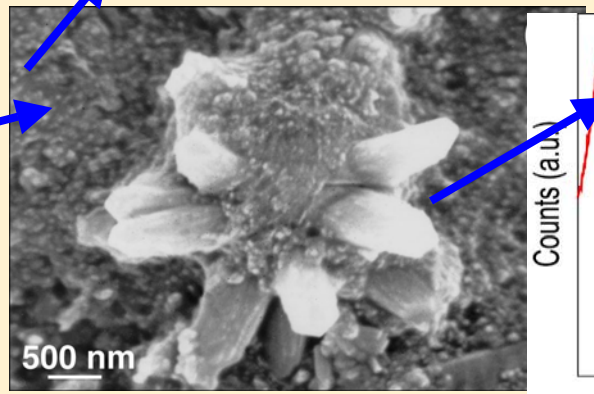
(2 m column)

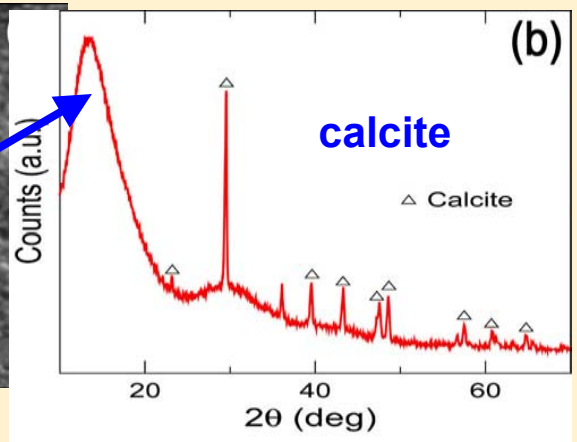


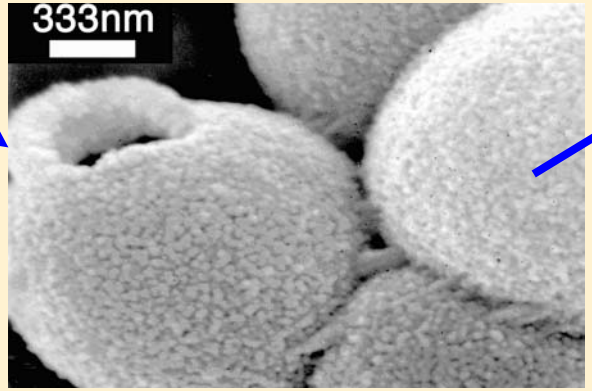
Results 4: Major Secondary Phases

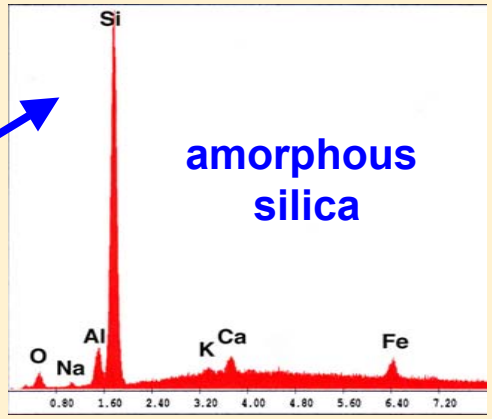
At the Plume Front

Amorphous Al-Si-Ca-O-OH



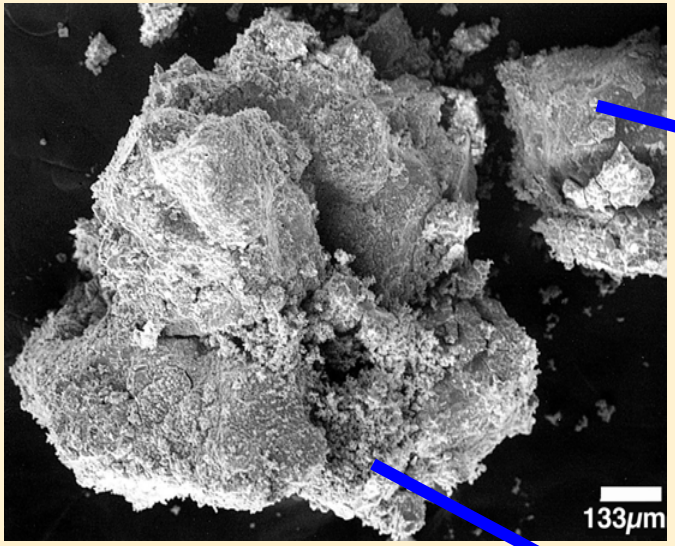




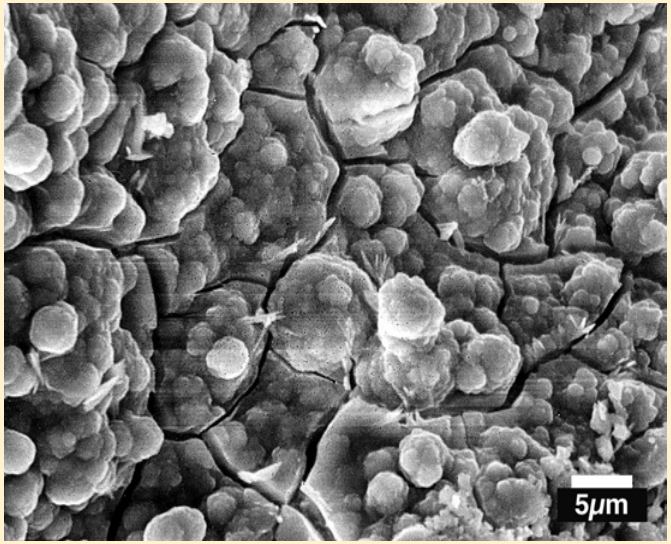


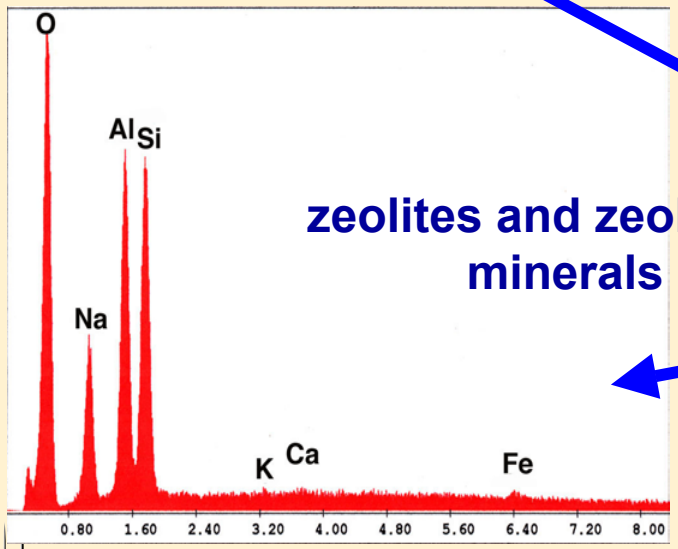
Results 4: Major Secondary Phases

At the Silicate Dissolution Zone

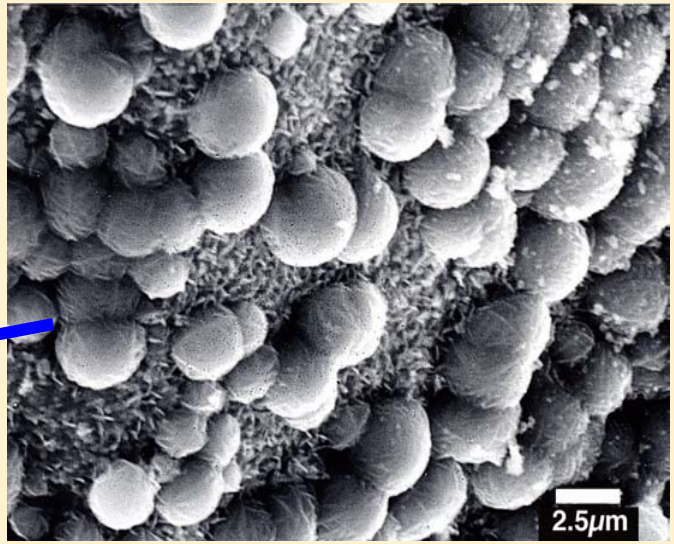


Amorphous Na-aluminosilicates

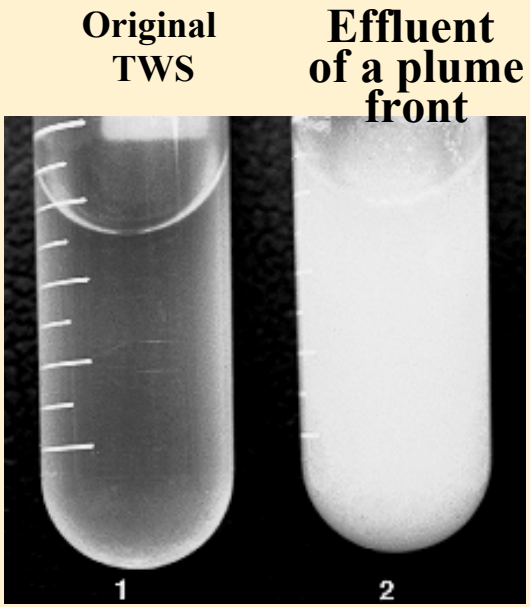


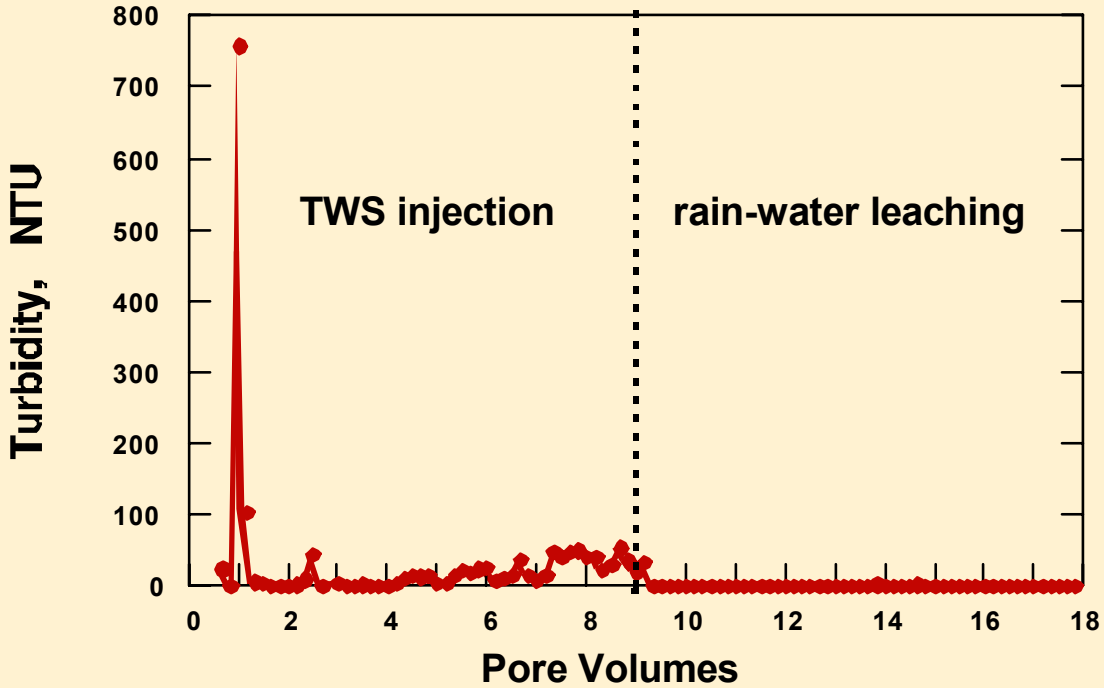


zeolites and zeolite-like minerals



Results 5: Colloid Formation and Transport





Conclusions

- pH neutralization and zonation of tank waste plumes were revealed, and mechanisms were identified. As the master geochemical variable, pH needs to be understood in order to understand and predict contaminant fate and transport.

- Extending the approach developed in this study to other types of tank waste plume problems will be beneficial.