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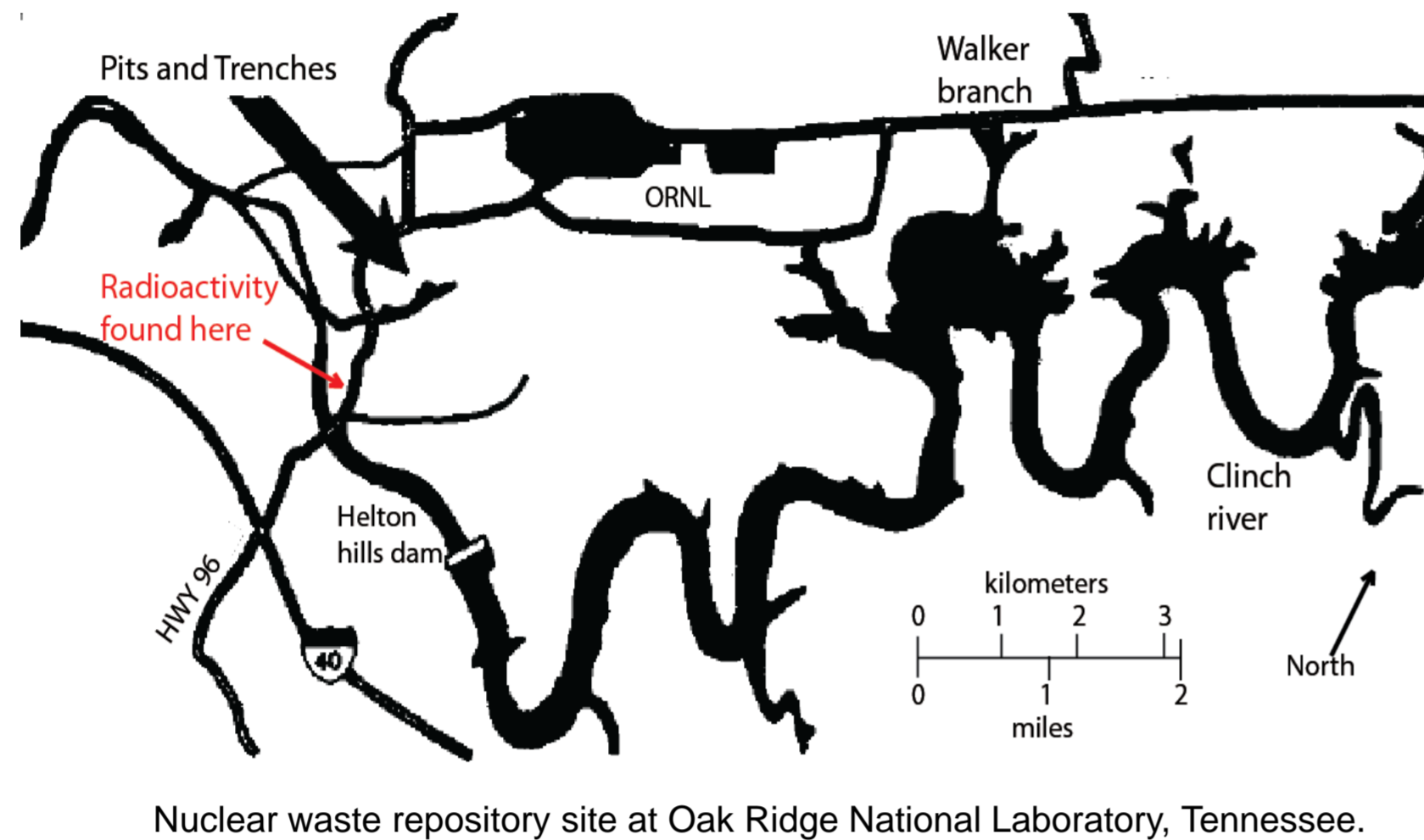
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## 1. Introduction

**Emergent phenomena** are of great concern in the risk analysis of nuclear waste storage sites. The unpredicted and **the fast transport of radionuclides** in the subsurface has been observed nearby some of the nuclear waste repositories in the United States. The phenomenon has been attributed to **physical factors** (e.g., precipitation and fracture flow) and to **geochemical reactions** (e.g., adsorption onto organic ligands, complexing agents in solution, acidic conditions, and colloid formation).

The **combination of flow transport and geochemical models** of the subsurface has been used in this contest and has highlighted the role of

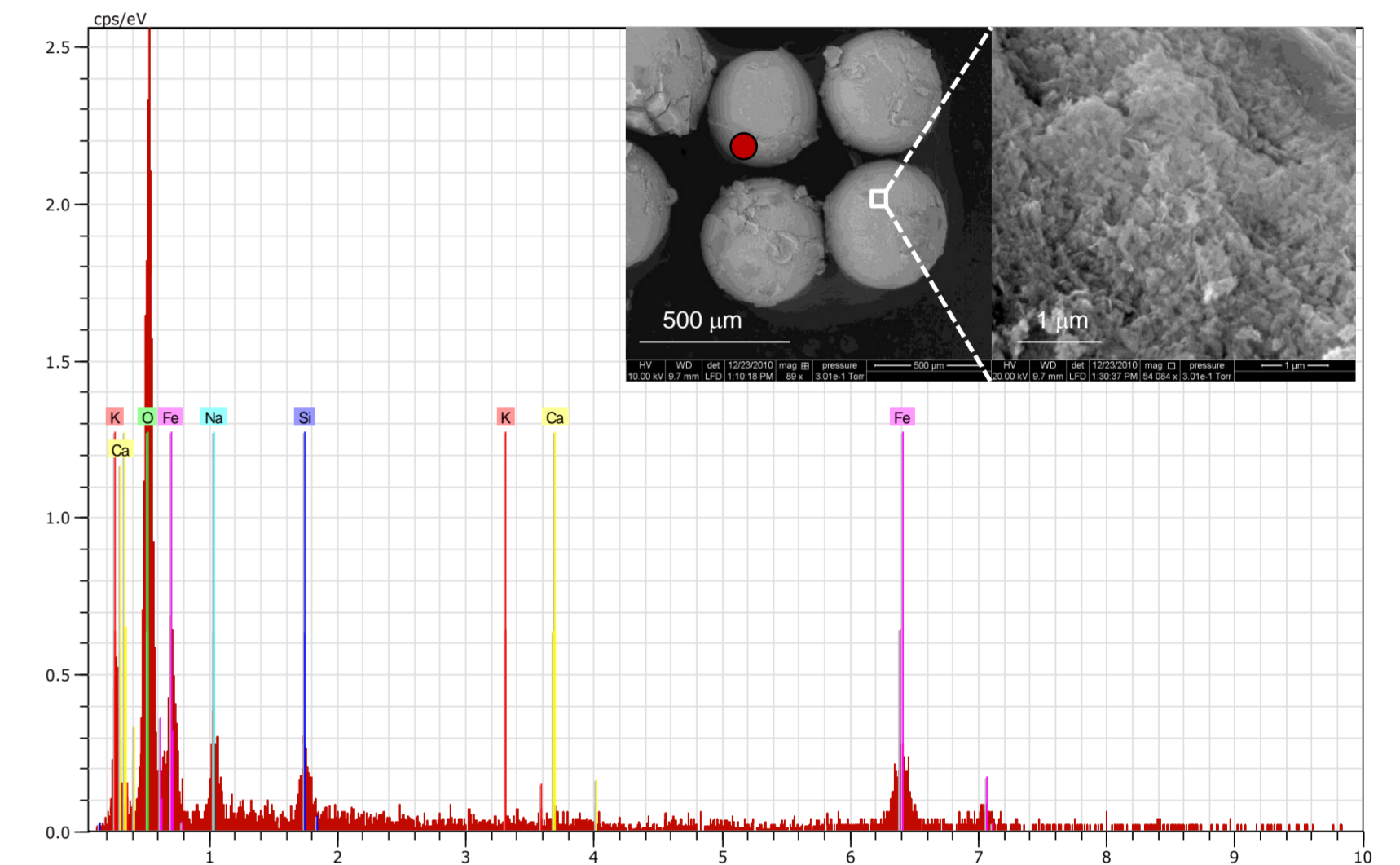
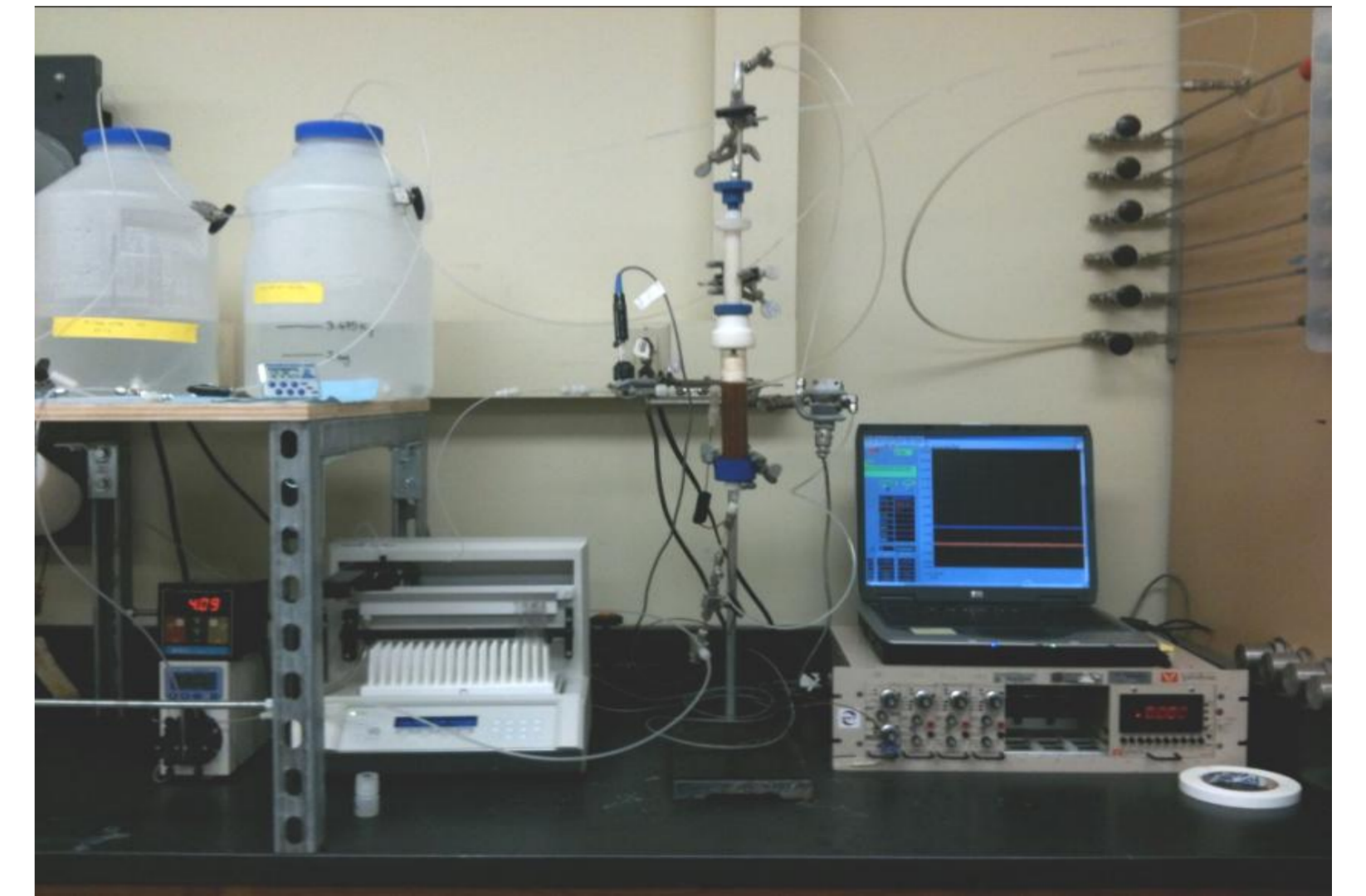
both the dispersion and the reactions at the liquid-solid interface on the affect of radionuclide mobility [1].



Nuclear waste repository site at Oak Ridge National Laboratory, Tennessee.

## 2. Experimental

**Transport experiments** were performed to investigate the transport of  $\text{Sr}^{2+}$  and  $\text{H}^+$  throughout a column packed with silica beads coated with **amorphous ferric oxide (HFO)**. The system is monitored with online pH, temperature, and pressure probes and samples are collected to determine the ion concentration with an ion chromatograph. HFO is synthesized in the lab, characterized with XRD, and used to coat 500  $\mu\text{m}$ -diameter silica beads. SEM-EDS analyses were performed to verify the distribution and the composition of the coating.



## 3. Modeling

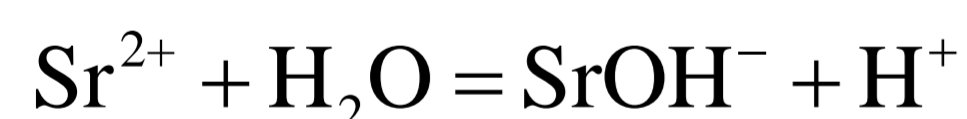
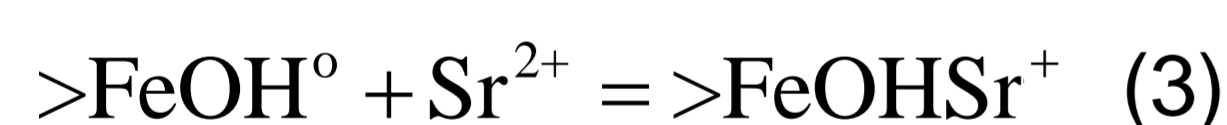
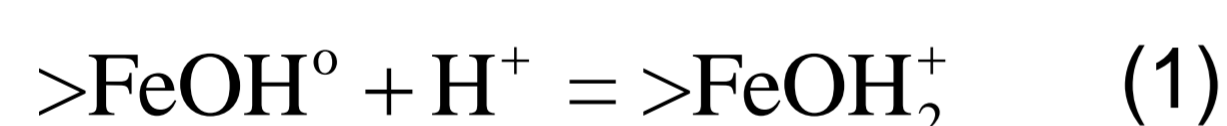
**Reactive transport equations, strontium ( $\text{Sr}^{2+}$ ) and acidity:**

$$\phi \frac{\partial (C_{\text{Sr}} + Z_{\text{Sr}})}{\partial t} + u \frac{\partial C_{\text{Sr}}}{\partial x} - D \frac{\partial^2 C_{\text{Sr}}}{\partial x^2} = 0$$

$$\phi \frac{\partial (C_{\text{H}} - C_{\text{OH}} + Z_{\text{H}})}{\partial t} + u \frac{\partial (C_{\text{H}} - C_{\text{OH}})}{\partial x} - D \frac{\partial^2 (C_{\text{H}} - C_{\text{OH}})}{\partial x^2} = 0$$

where  $C_i$  and  $Z_i$  are the concentrations of the aqueous and adsorbed specified species;  $u$  is the Darcy velocity;  $D$  is the dispersion coefficient;  $\phi$  is the media porosity.

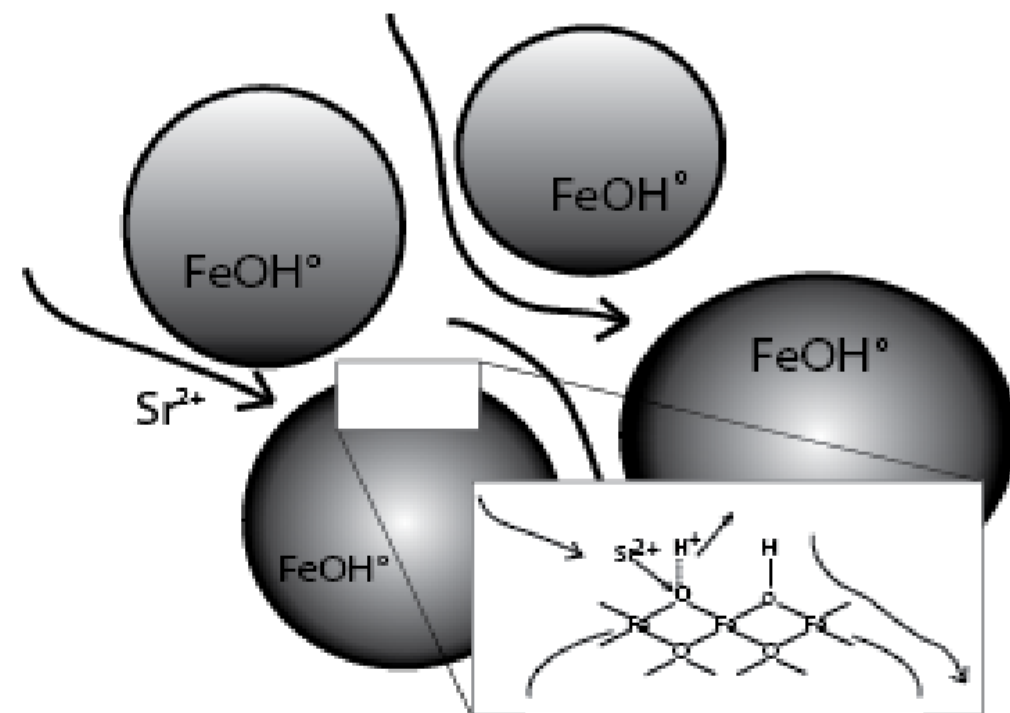
**Geochemical model:**



At 25°C:  $K_1=10^{7.29}$ ,  $K_2=10^{-8.82}$ ,  $K_3=10^{5.1}$ .

**Adsorption isotherms are:**

$$Z_{\text{Sr}} = \frac{a_{\text{Sr}} K_3 Z_{\text{tot}}}{1 + a_{\text{H}} K_1 + a_{\text{Sr}} K_3}, \quad Z_{\text{H}} = \frac{a_{\text{H}} K_1 Z_{\text{tot}}}{1 + a_{\text{H}} K_1 + a_{\text{Sr}} K_3}$$

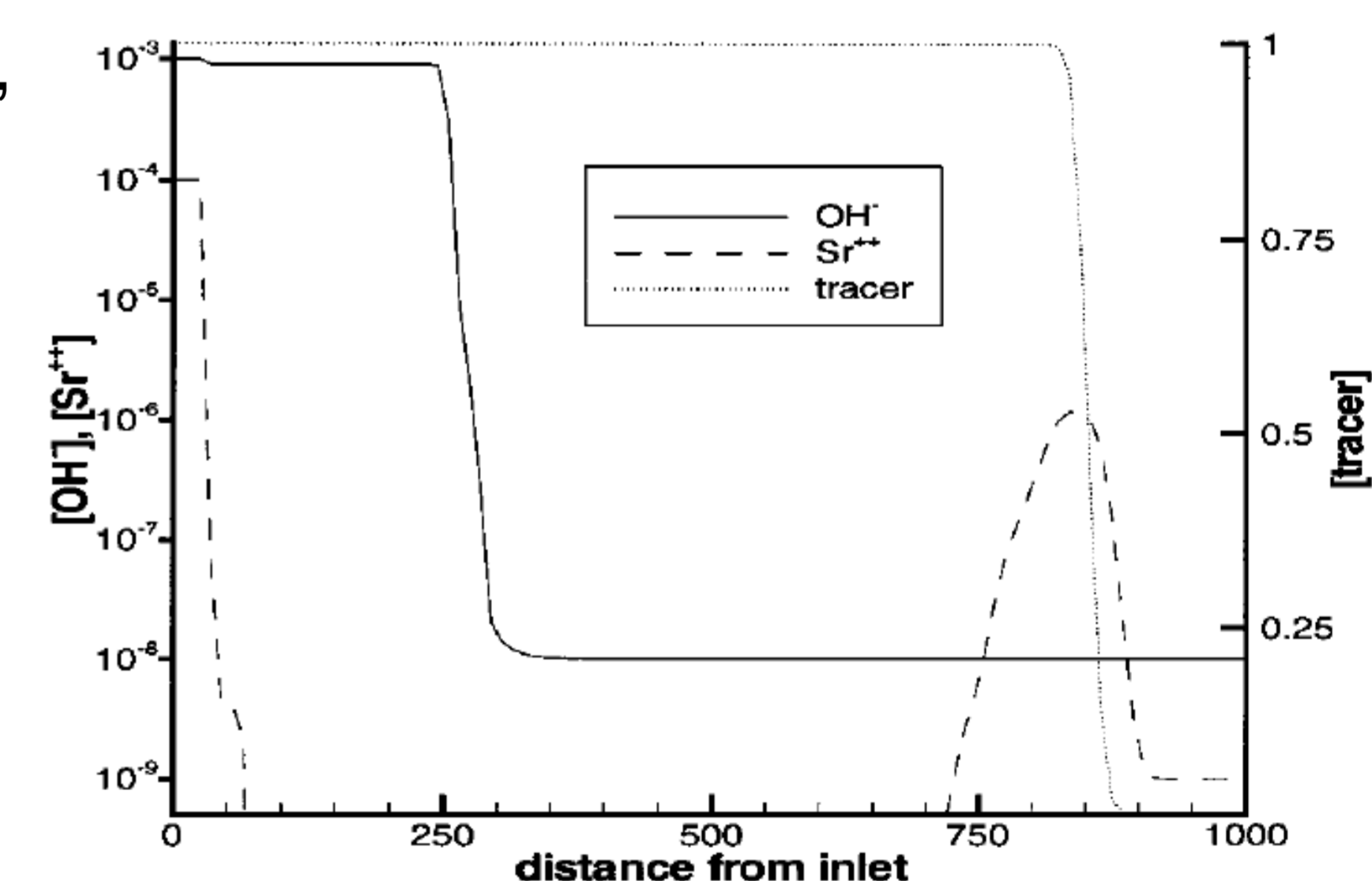
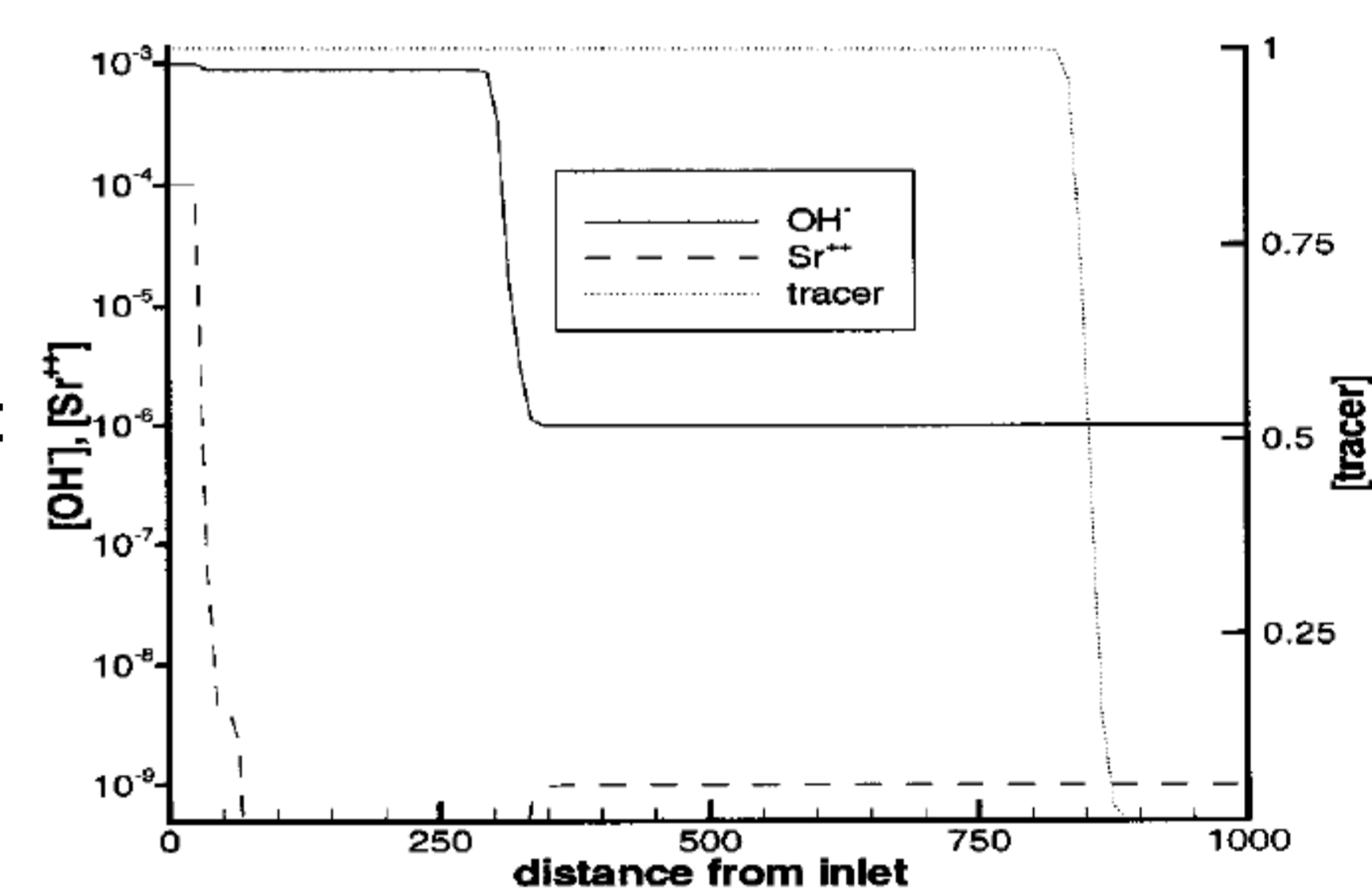


## 4. Numerical results

In **absence of diffusion/dispersion**, the reactive transport model yields two shocks (i.e., of  $\text{OH}^-$  and  $\text{Sr}^{2+}$ ), as predicted from classical theory of chromatography, travelling at velocity:

$$v_{\text{Ci}} = \frac{u / \phi}{1 + \frac{\Delta Z_i}{\Delta C_i}}$$

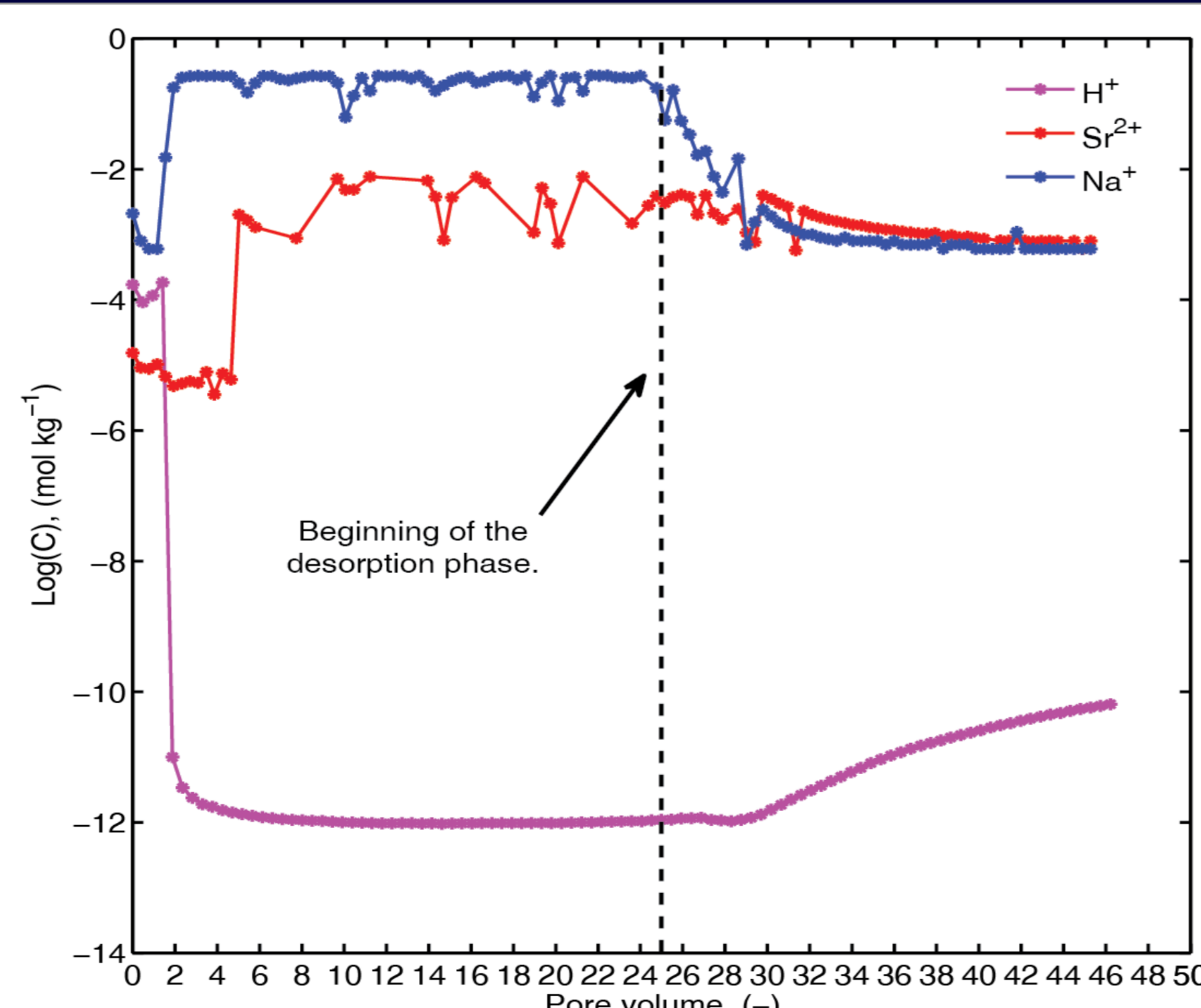
In **presence of diffusion/dispersion**, a pulse of  $\text{Sr}^{2+}$  arises. It travels faster than the  $\text{Sr}^{2+}$  shock. When the two shocks are near each other, diffusion/dispersion yields the formation of a metal flux through the pH shock towards the low-pH region that favors  $\text{Sr}^{2+}$  mobility.



## 5. Experimental results

Using conservative tracers, we estimated the hydrodynamic parameters (porosity ( $\phi$ ) and dispersion coefficient ( $D$ )) of the bed and they correspond to 0.45 and  $1.29 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ , respectively. During the experiment in the figure, the porous media was initially stabilized with a solution of pH 3.64 and then flooded with a solution containing  $10^{-2} \text{ m}$  of  $\text{Sr}^{2+}$  and 0.1 m of  $\text{Na}^+$  at pH 11.95. The flow rate was  $2.66 \text{ ml min}^{-1}$ .

In the **adsorption phase**,  $\text{Sr}^{2+}$  front is the most retarded and arises around 5 pore volumes. In the **desorption phase**, its rarefaction wave appears almost simultaneously with the  $\text{H}^+$  front suggesting a competitive adsorption between these two ions on the same active HFO surface site. Under the applied conditions, no fast wave was observed.



## 6. Conclusions

The anomalous transport of radionuclides was observed in some of the U.S. nuclear waste storage sites. Numerical simulations highlighted the importance of accurate modeling of dispersion and surface complexation to forecast such a anomalous transport behavior. Column-flood experiments were run in a HFO-coated porous media for the  $\text{Sr}^{2+}$ - $\text{H}^+$ - $\text{Na}^+$  system. Under operating conditions favorable for the formation of the fast wave, however, no anomalous phenomena were observed but instead a retarded  $\text{Sr}^{2+}$  front anticipated by the  $\text{H}^+$  and  $\text{Na}^+$  fronts.

### References

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- [3] Sauders, J. A.; Toran, L. E. (1995) Modeling of radionuclide and heavy metal sorption around low- and high-pH waste disposal sites at Oak Ridge, Tennessee. *Applied Geochemistry* **10** 673-684.
- [4] INEEL (2003) INEEL subregional conceptual model. *Report INEEL/EXT-03-01171*.