UT-BATTELLE

Leaching Assessment of Cementitious Rad-Waste Monoliths

Les Dole

Vanderbilt Workshop on Leaching Characterization

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Contact: dolelr@ornl.gov 865-576-4319

Leach Tests with Analysis to Compare and Formulate Better Waste Forms

- **Complex alumina-silicates with fine textured mineral phases and large fraction of amorphous hydrosilicate phase, both of which slowly undergoes diagenesis and contact metamorphism over centuries and millennia**

- **Leaches matrix components at different rates and results in a complex series of solution reactions with groundwater adjacent to the surface that redeposit minerals**

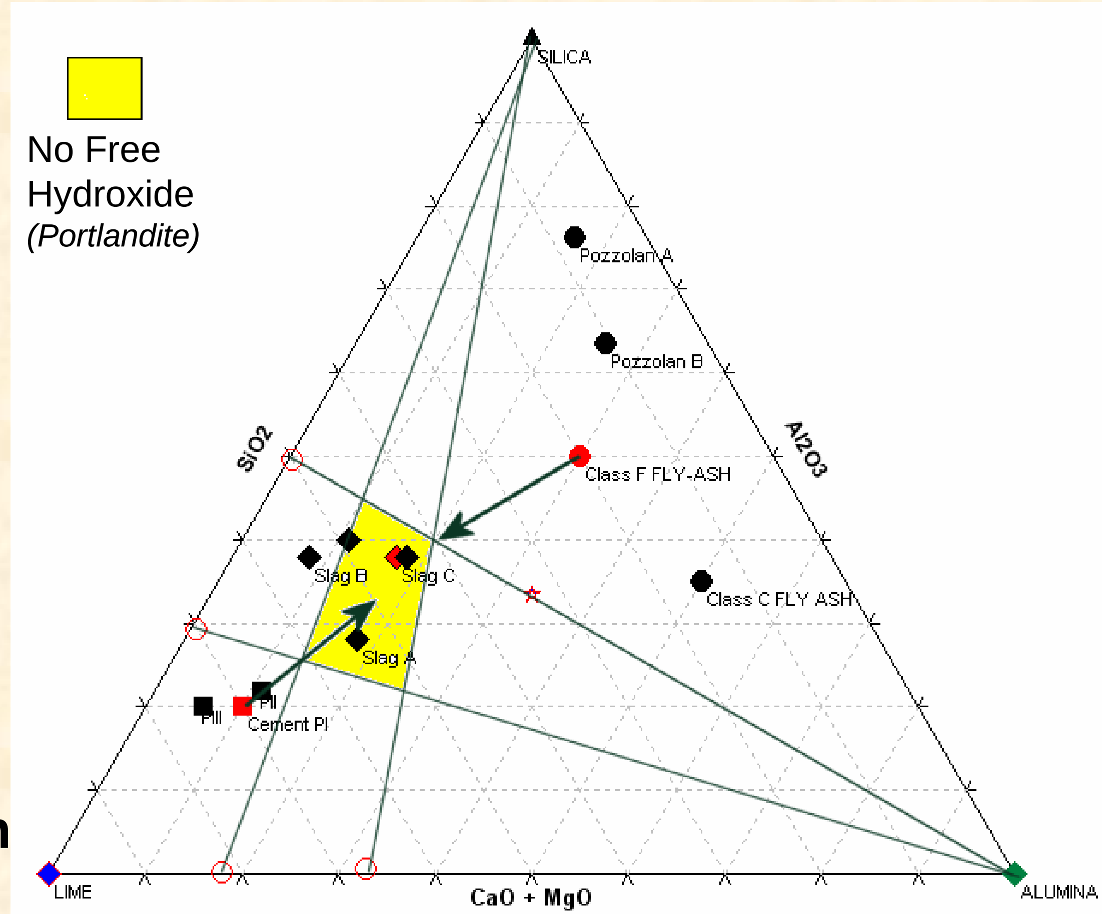
Short-term Leach Testing to Assess impacts of Waste Constituents and Formula Constituents

- **Choices of cement types**
- **Choices of admixtures to change:**
  - **Ca/Si ratios**
  - **Al/Si ratios**
  - **Permeability (H_2O, O_2, $SO_4^{=}$, Cl^-, etc)**
  - **Internal ion exchange capacity**
  - **Reducing conditions (Eh/Ph regime)**

Cementitious Material Compatible with Yucca Mountain Geochemistry

LR Dole, CH Mattus, LR Riciputi, M Fayek, L.M. Anovitz, D Olander, S Ermichev, and VI Shapovalov

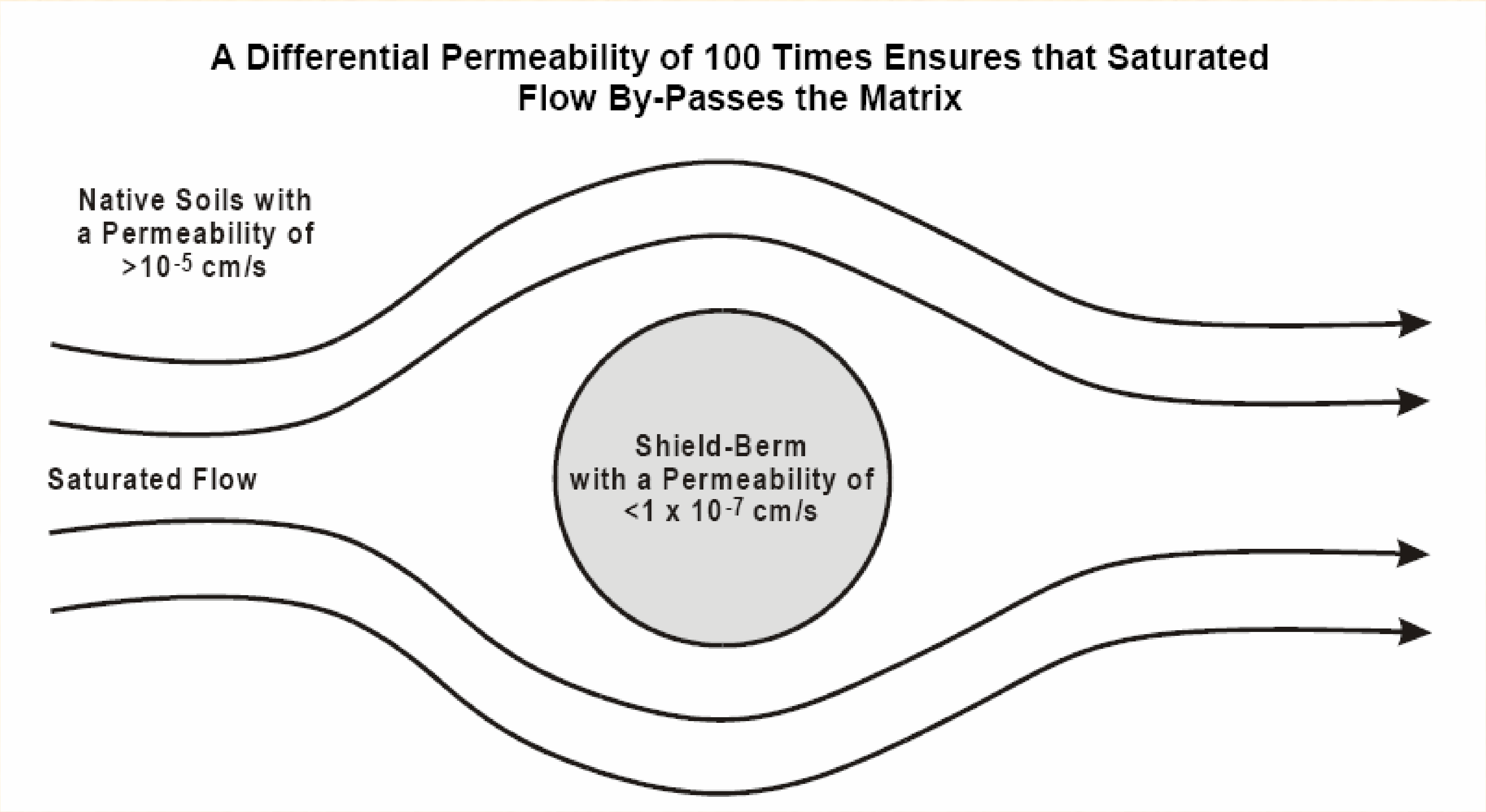
- **Select durable low-pH cement/concrete formulas based on materials science, thermodynamic modeling, and experience**
- **Test mechanical properties and chemical interactions with YMP brines under expected service conditions**
- **Compare results with**
  - **Ancient cements (2 – 6 Ky)**
  - **Natural cements (>100 My)**
- **Calculate impacts on improving YMP construction costs and reducing risks**



Test Performances at Hydraulic Extremes

- **Quasi-static flow (episodic saturation)**
  - **Solubility control**
  - **Ion exchange equilibrium**
  - **Source-term = C_{sat} x Flow**
- **Dynamic (monolith permeability <1/100 soil)**
  - **Advection of saturated groundwater**
  - **Release to groundwater limited by diffusion within the monolith**
  - **Source-term . A_0 {S/V} $(D_{diffusion}/\text{time})^{1/2}$**

A Relatively Impermeable Monolith has no Advection



A Practical Model for the "Effective" Diffusion Coefficient

$$K_{MB} = \left[\frac{\left(\frac{\textit{mole of species}}{\textit{mass of porous solid}} \right)}{\left(\frac{\textit{mole of species}}{\textit{volume of liquid}} \right)} \right].$$

$$D_e = \left[\frac{D_f}{\tau^2 \cdot \left[1 + \rho_b \cdot \left[\frac{(1-\epsilon)}{\epsilon} \right] \cdot K_{MB} \right]} \right],$$

where

τ = tortuosity, *dimensionless* (This study assumed that τ was equal to 1.47 for the compacted berm soils.)

ρ_b = bulk density of porous soil, g/cm^3

ϵ = average *effective* open porosity, *dimensionless*.

500 Year Release Model for Sr-90 Activity from Grouted GAAT Sludge From Gunite Tank W9

Effective diffusion Coefficient:

$$D_e := \left(2.6 \cdot 10^{-13}\right) \cdot \frac{cm^2}{sec}$$

***** Data from similar hydrofracture grouts**

** assumes most activity is Sr-90*

Time iteration

$$i := 0, 10 .. 500$$

$$t_i := i \cdot yr$$

Surface to Volume:

$$\frac{S}{V} = 5.125 cm^{-1}$$

***** Assumes entire surface on the monolith is exposed to flowing ground water. No credit is given for the existing tank walls.**

Infinite slab diffusion model:

$$FI(t) := 2 \cdot \frac{S}{V} \cdot \sqrt{\frac{D_e \cdot t}{\pi}}$$

**** calculates a conservative overestimate of release***

$$t2 := \left(0.2 \cdot \frac{V}{S \cdot 2}\right)^2 \cdot \left(\frac{\pi}{D_e}\right) \qquad t2 = 145.805 yr \qquad FI(t2) = 0.2$$

****On-set of geometry specific effects***

$$t5 := \left(0.5 \cdot \frac{V}{S \cdot 2}\right)^2 \cdot \left(\frac{\pi}{D_e}\right) \qquad t5 = 911.278 yr \qquad FI(t5) = 0.5$$

****Chemical half-life in monolith***

Onset of Geometric Model at FC=0.2

Nestor, C. W., Jr., *Diffusion from Solid Cylinders*, **ORNL/SDTM-84**, Lockheed Martin Energy Research Corp., Oak Ridge National Laboratory, Oak Ridge, Tennessee, January 1980.

$$\alpha_j := \frac{\mathrm{root}(J0(j), j)}{a}$$

De = effective diffusion coefficient, cm2 s-1
a = cylinder radius, cm
j = *j*th positive root of a zero-order Bessel function [*J*0(*m*)]
L = cylinder half-height, cm.

Diffusion from a Cylinder:

$$FC(t) := 1 - \frac{32}{\pi^2 \cdot a^2} \cdot \sum_n \sum_j \frac{e^{-\left[D_e \cdot \left[\left(\alpha_j\right)^2 + (2 \cdot n - 1)^2 \cdot \frac{\pi^2}{4 \cdot L^2}\right] \cdot t\right]}}{(2 \cdot n - 1)^2 \cdot \left(\alpha_j\right)^2}$$

$FC(t2) = 0.223$ $\quad FS(t) := \mathrm{if}(t > t2, FC(t), FI(t))$ $\quad F_i := FS\left(t_i\right)$ $\quad FI_i := FI\left(t_i\right)$

Example: Diffusion Controlled Release of ^{90}Sr from a monolith

Fraction Released

$F_{30} = 0.091$

$F_{300} = 0.303$

$F_{500} = 0.379$

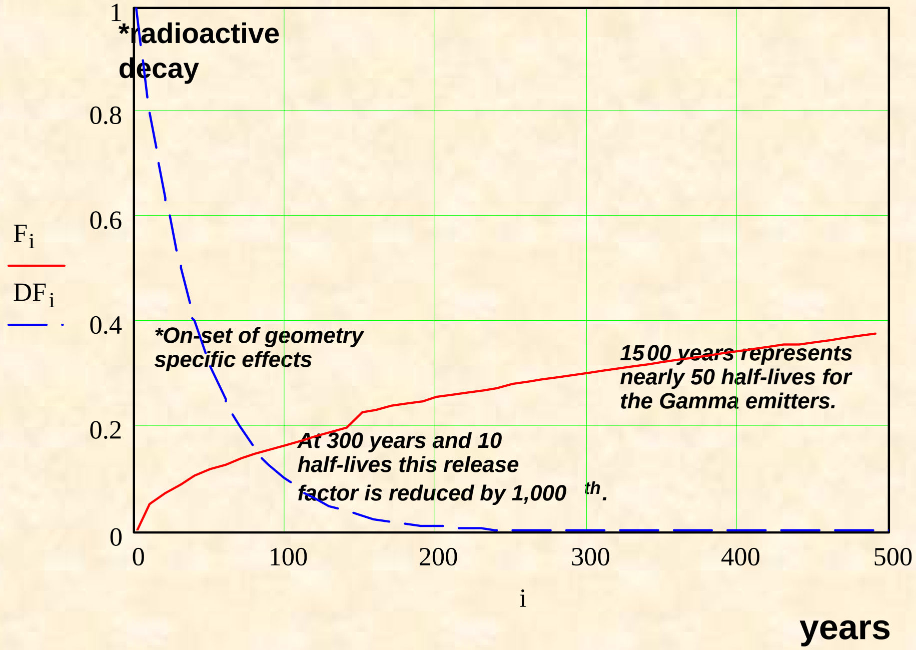
Radioactive Decay Factor

$DF_{30} = 0.5$

$DF_{300} = 9.766 \times 10^{-4}$

$DF_{500} = 9.612 \times 10^{-6}$

CURIE RELEASE FROM W9 MONOLITH as Sr-90



Combination of Decay and Diffusion Controlled Release

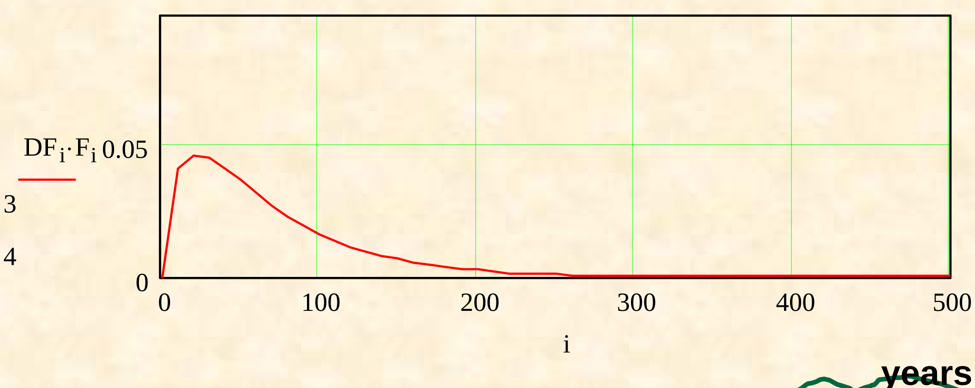
Decay Fraction X Release Fraction

$DF_{30} \cdot F_{30} = 0.045$

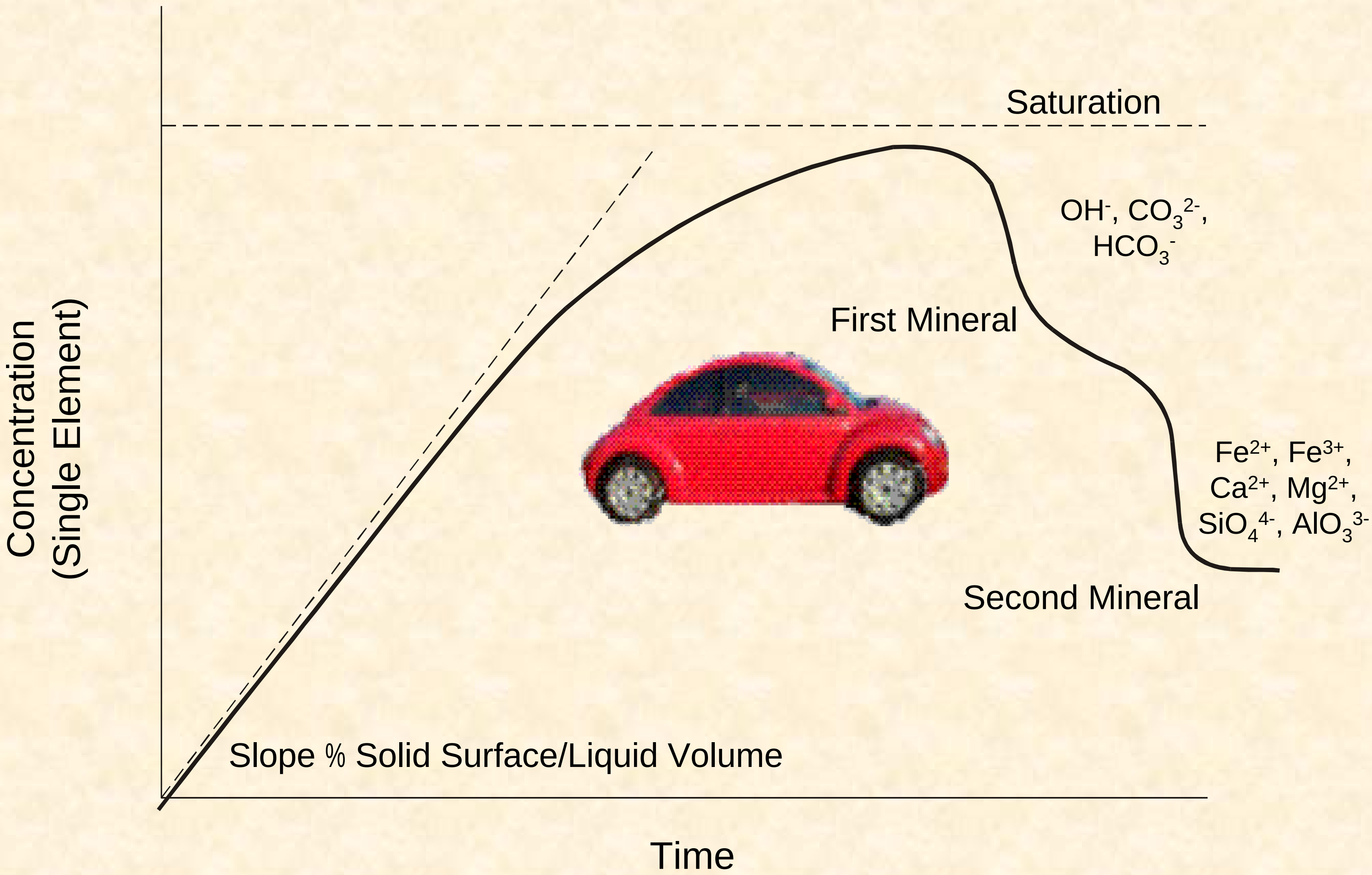
$DF_{90} \cdot F_{90} = 0.02$

$DF_{150} \cdot F_{150} = 7.047 \times 10^{-3}$

$DF_{300} \cdot F_{300} = 2.955 \times 10^{-4}$



Static Leaching with Secondary Mineral Formation



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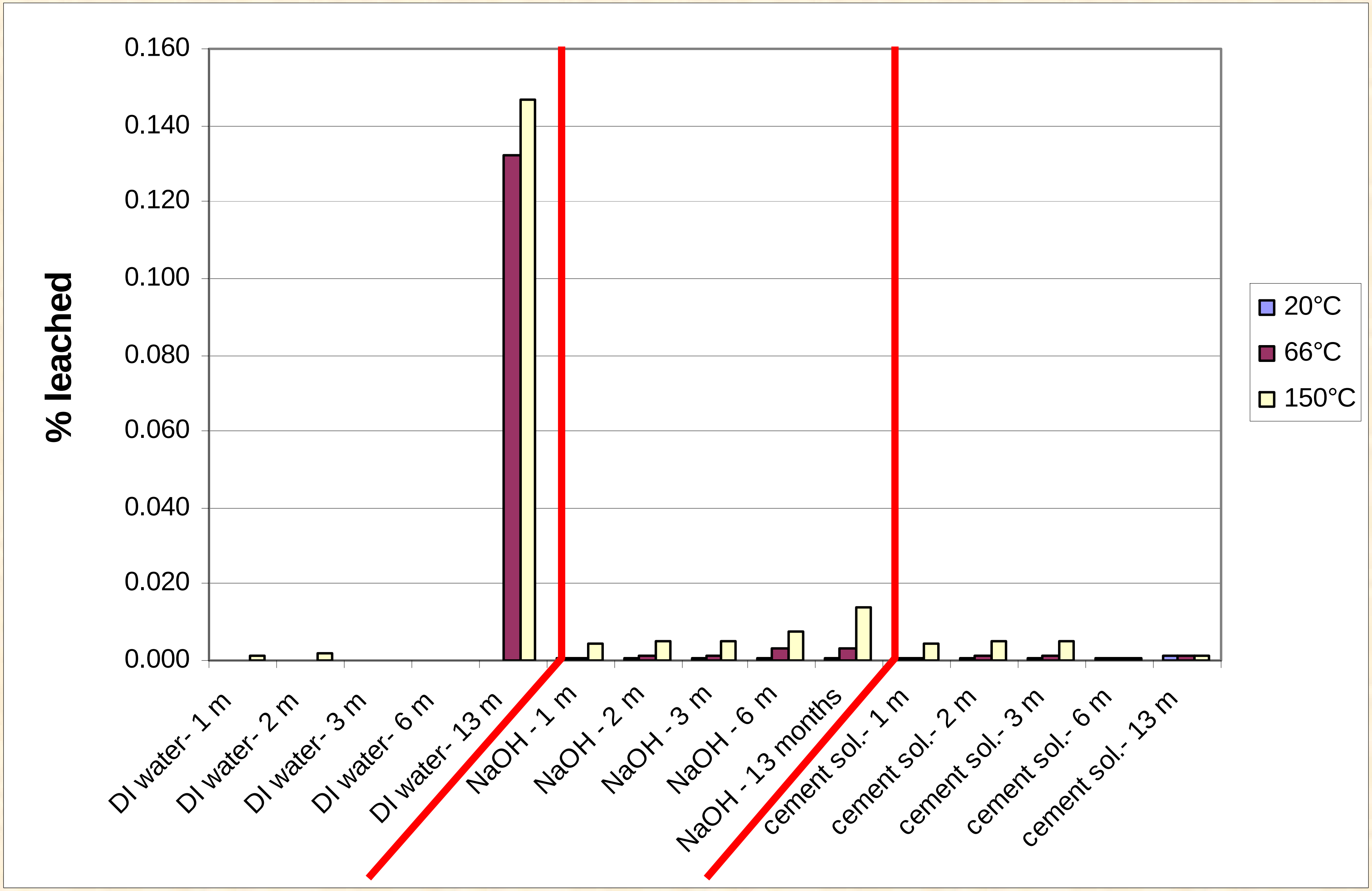
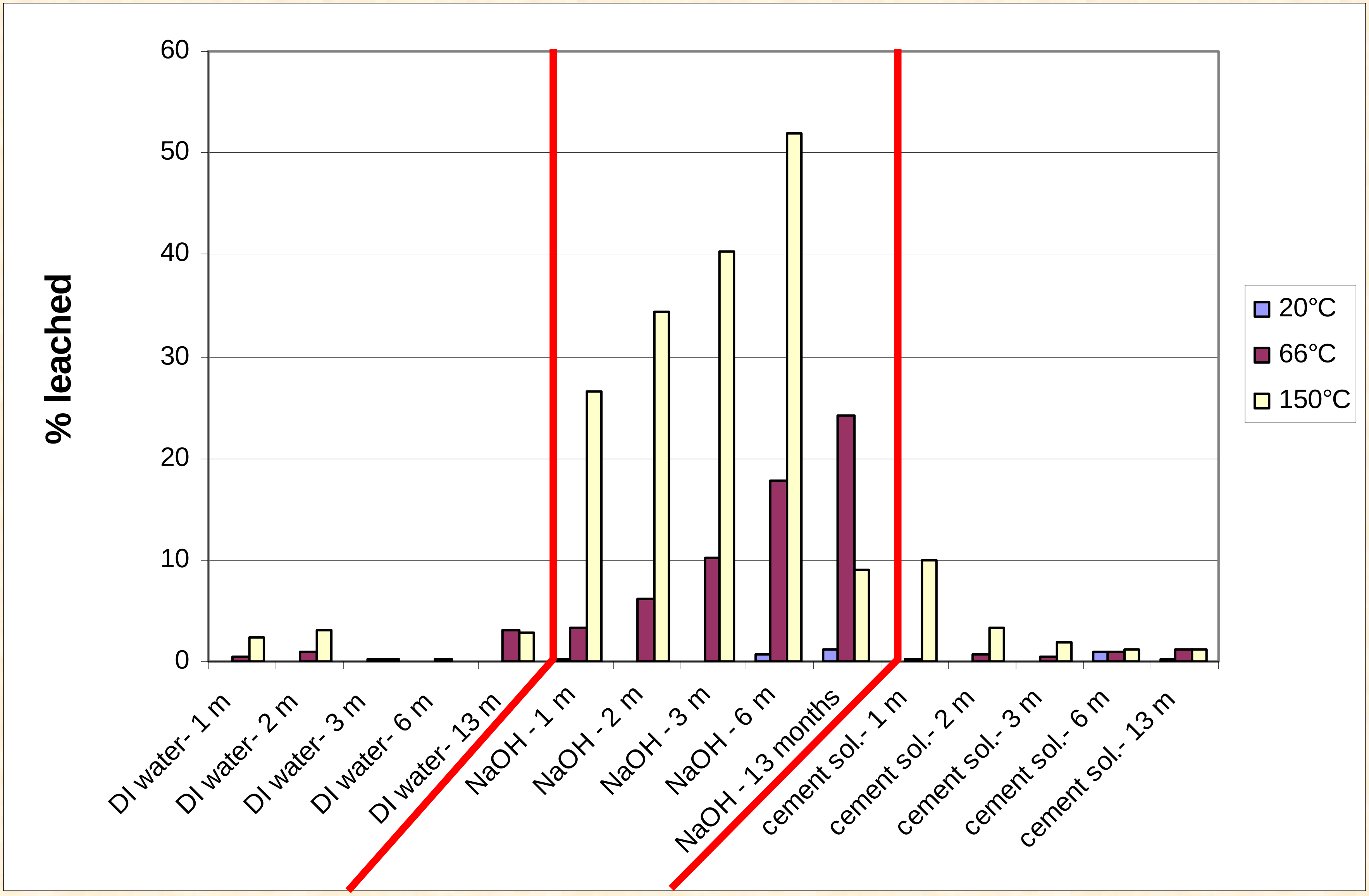
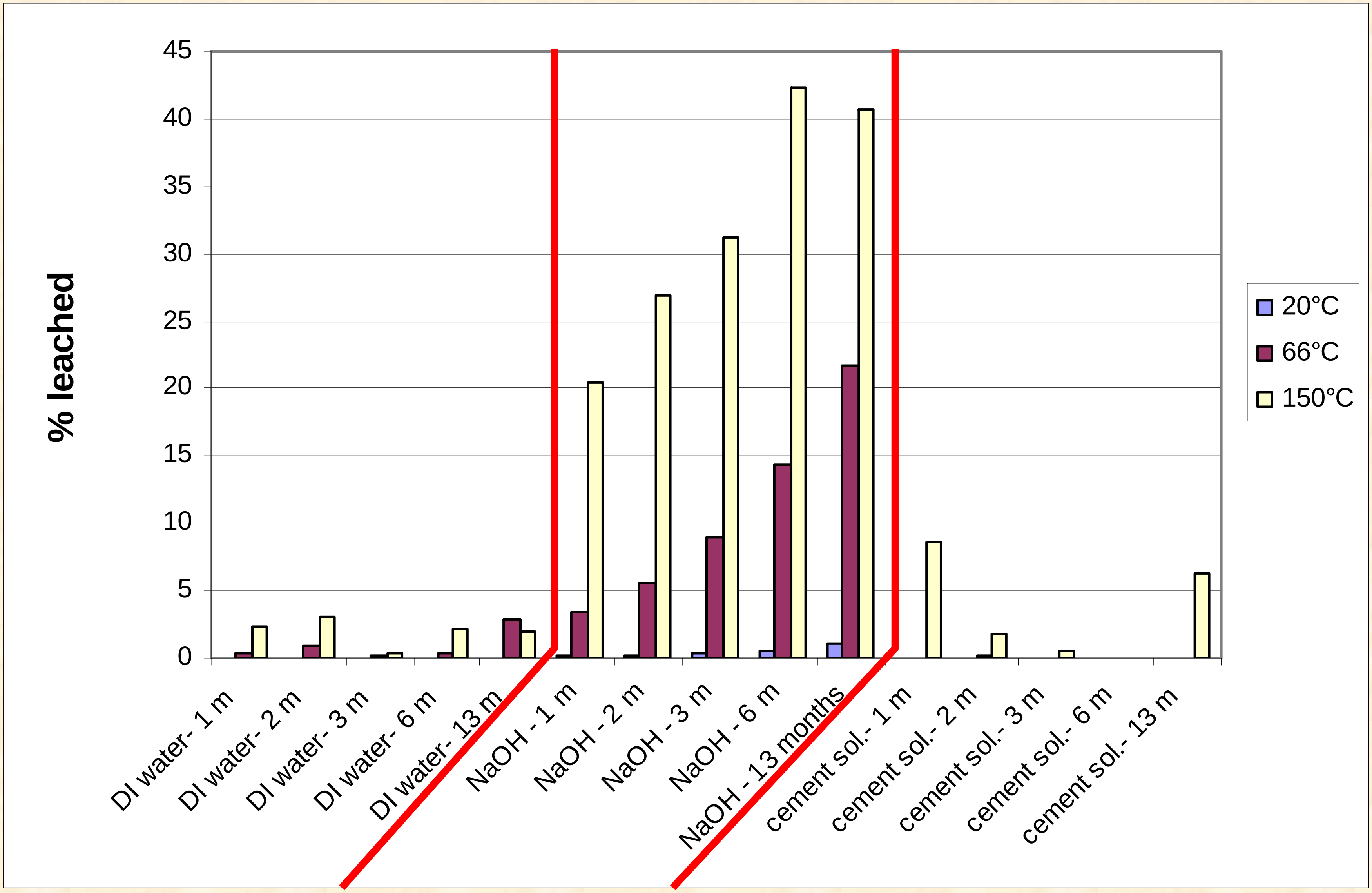
Uranium Leached From DUAGG



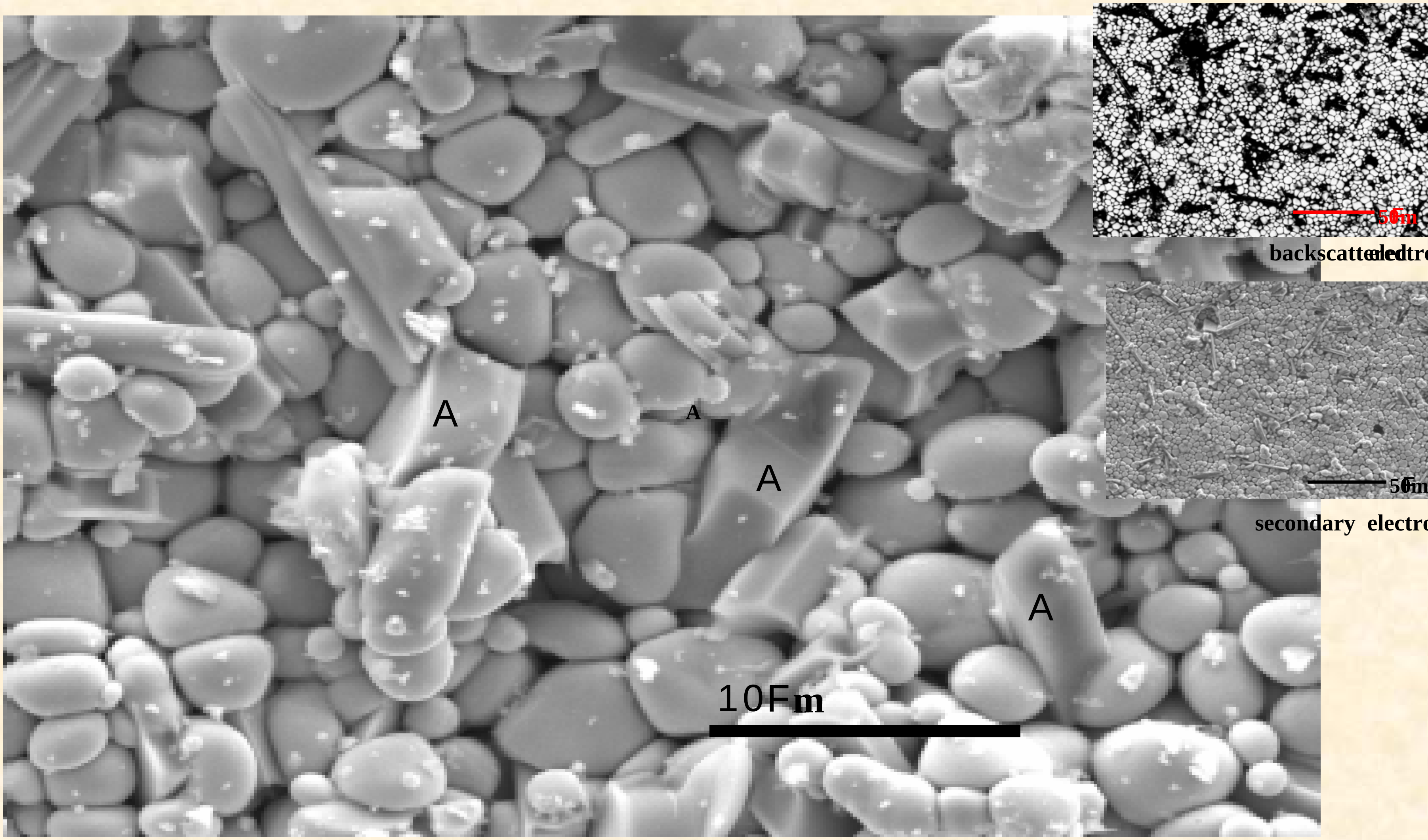
Aluminum Leached From DUAGG



Silicon Leached From DUAGG



DUAGG after 6 months in DI water



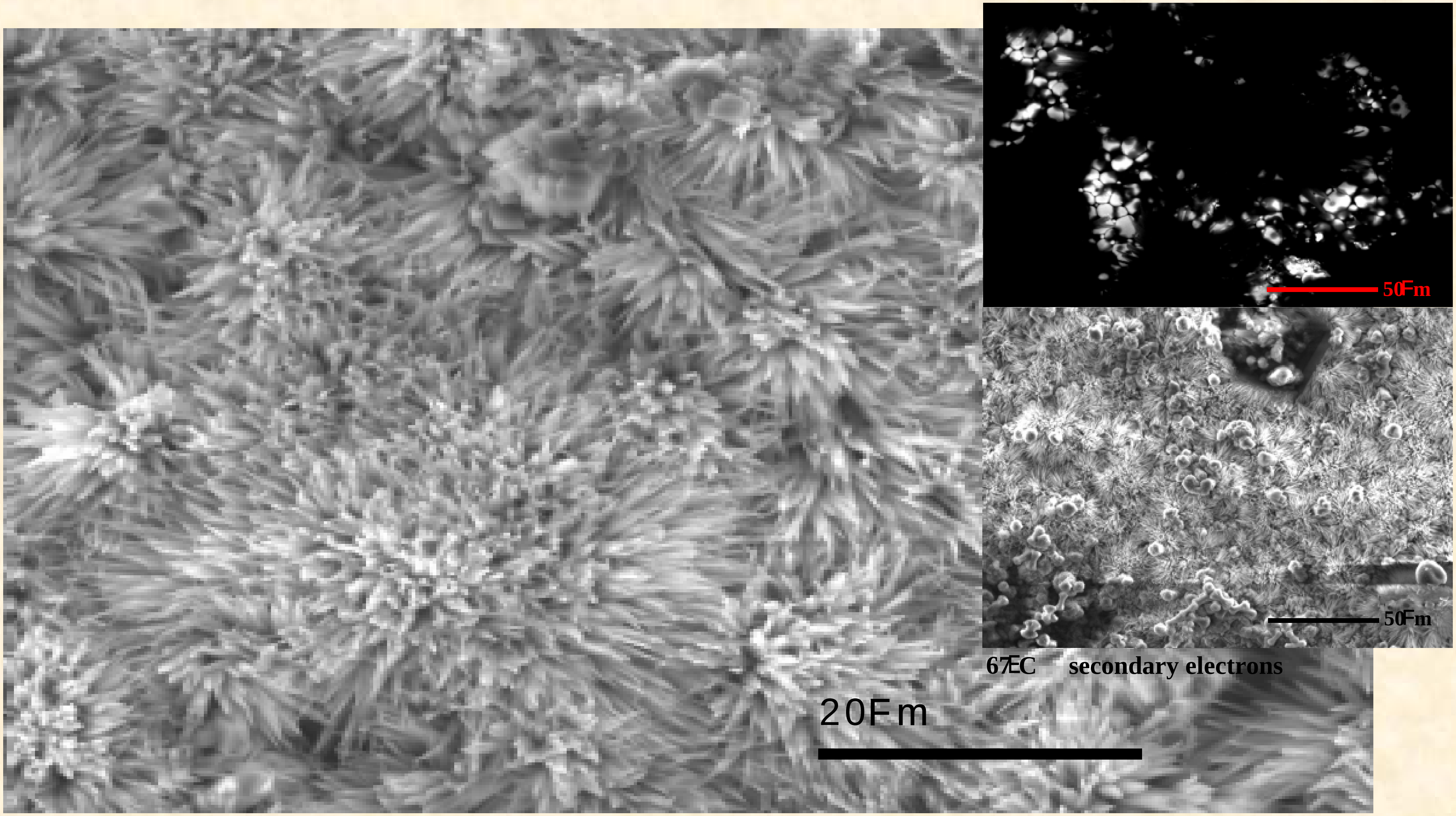
backscattered electrons

secondary electrons

150 C secondary electrons

A contain Ti and some Mg

DUAGG after 6 months in cement pore solution

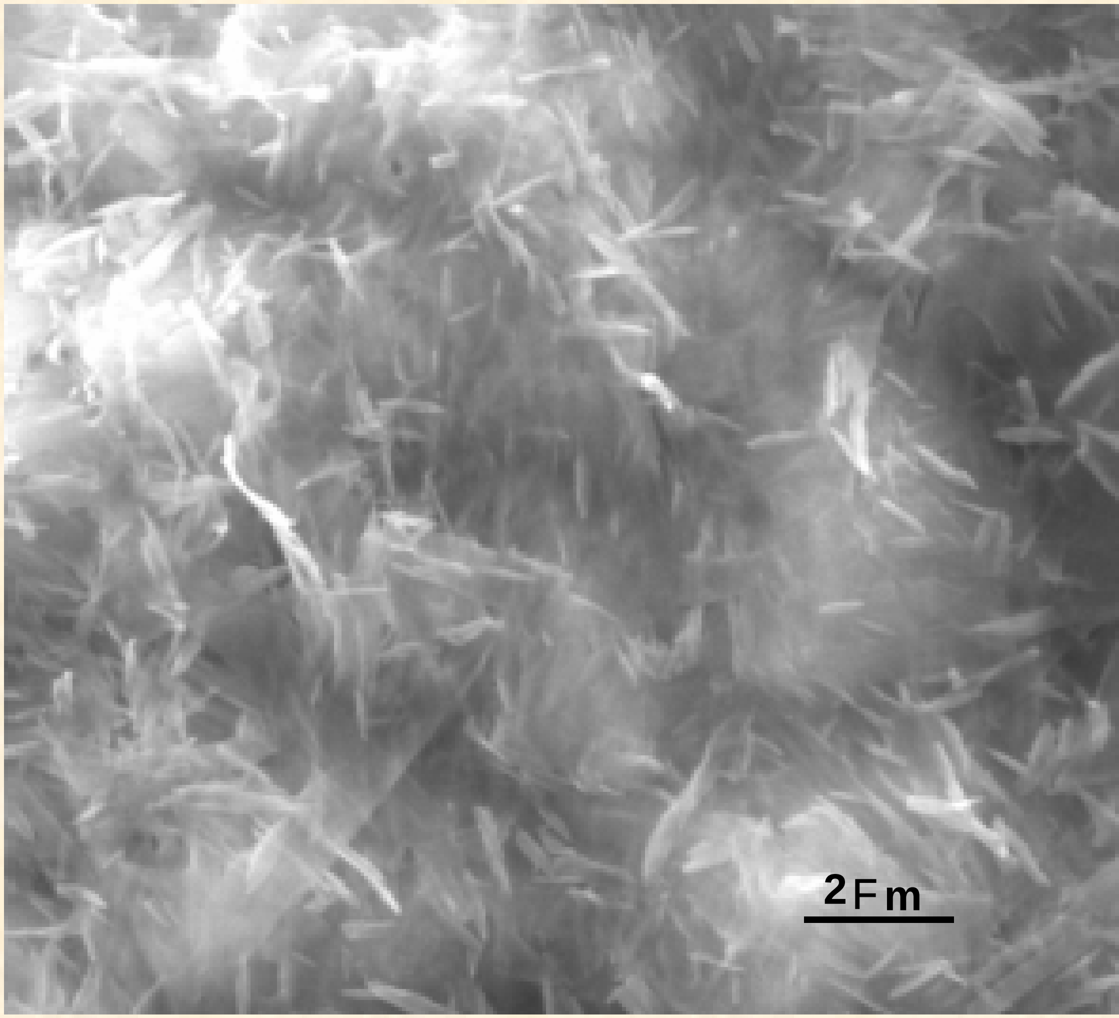


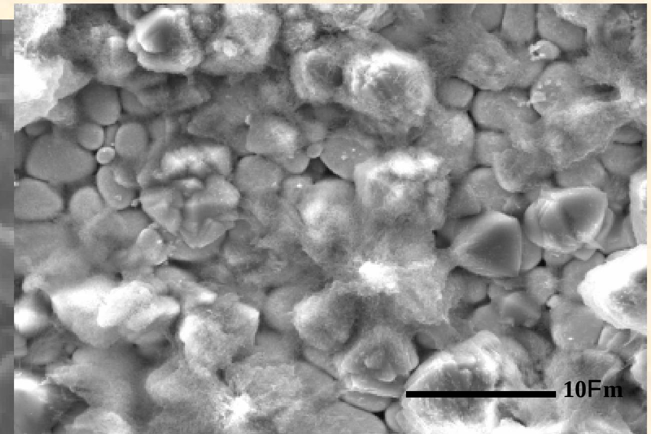
67EC secondary electrons

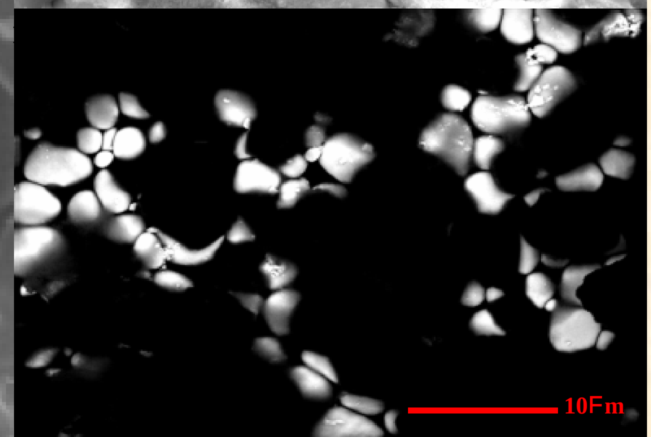
67 C secondary electrons

Covered by $CaCO_3$ and Needle like crystals containing Ca, Si and some Al.

DUAGG after 6 months in cement pore solution







150 C backscattered electrons

150 C secondary electrons

Cement hydration products cover surface with phases with Ca, Si, and Al.

Conclusions?

Short-term leach testing is conservative IF:

- **Test does not allow for the effects of secondary minerals, which are**
  - **Highly selective for contaminant species**
  - **Forms protective diffusion surface-barriers**

- **The monolith matrix is relatively stable in the geochemistry of the disposal horizon**
  - **Shares same regions of the geochemical stability fields**
  - **Has similar SiO_2-Al_2O_3 composition ranges**

- **Ultimate mechanisms of leaching, alterations, and weathering are controlled by solid-diffusion rates**