UT-BATTELLE

Conditions Affecting the Aging Processes of Cementitious Materials and Their Failure

NRC Advisory Committee on Nuclear Waste:

Working Group Meeting on Predicting the Performance of Cementitious Barriers for Near Surface Disposal

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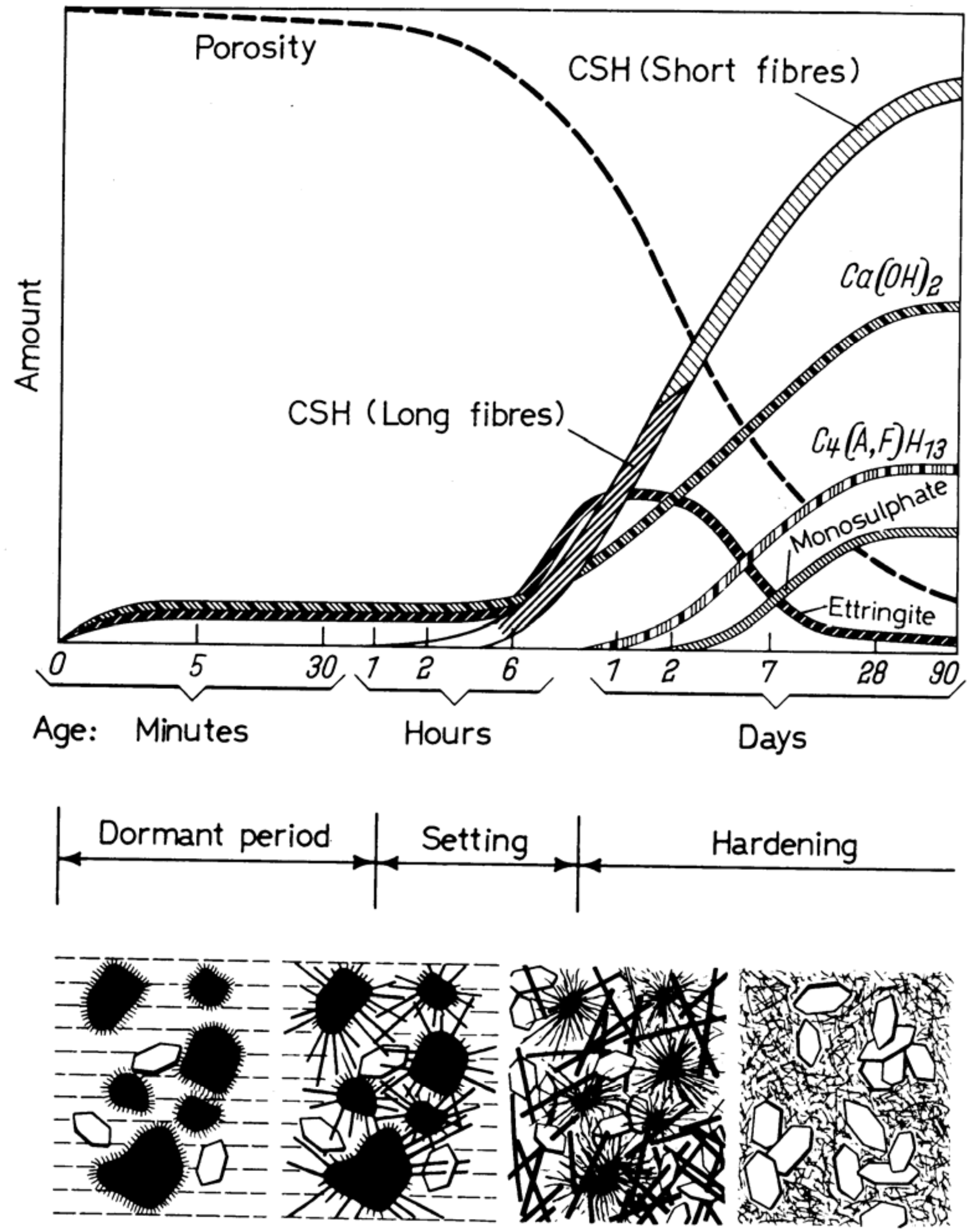
Barrier Roles in a Repository System

- **Mechanical Barrier**
  - Resist external stresses
    - Load capacity/stiffness
    - Compliant with local tectonic displacements
    - Resist or diffuse impacts
  - Permeability and thermal conductivity
- **Geochemical Buffer**
  - Decrease corrosion of waste package components
    - Electrochemical and pH control
    - Suppress aggressive radiolysis products
    - Passivate surfaces
  - Reduce solubility of key nuclides
  - Steer contact metamorphosis to benign phases

Reaction Sequence in Portland Cements

I. Soroka, Portland Cement Paste and Concrete, Chemical Publishing Co., 1979



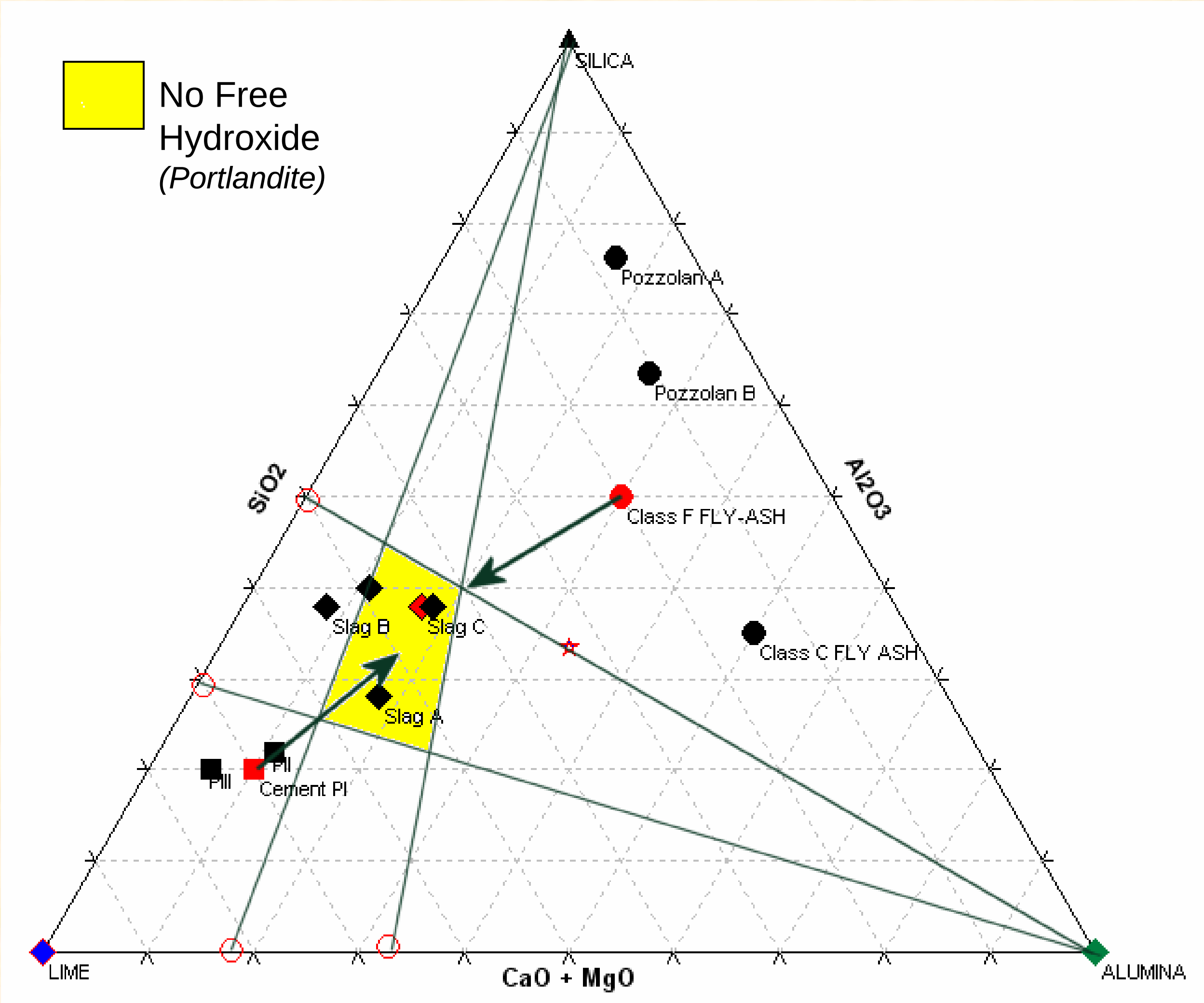
Evolution of the Cement with Time

- **Complex alumina-silicates with fine-textured mineral phases and large fraction of amorphous hydrosilicate phase, both of which slowly undergo diagenesis**
- **Matrix components leach at different rates and results in a complex series of solution reactions with groundwater adjacent to the surface with reprecipitation**

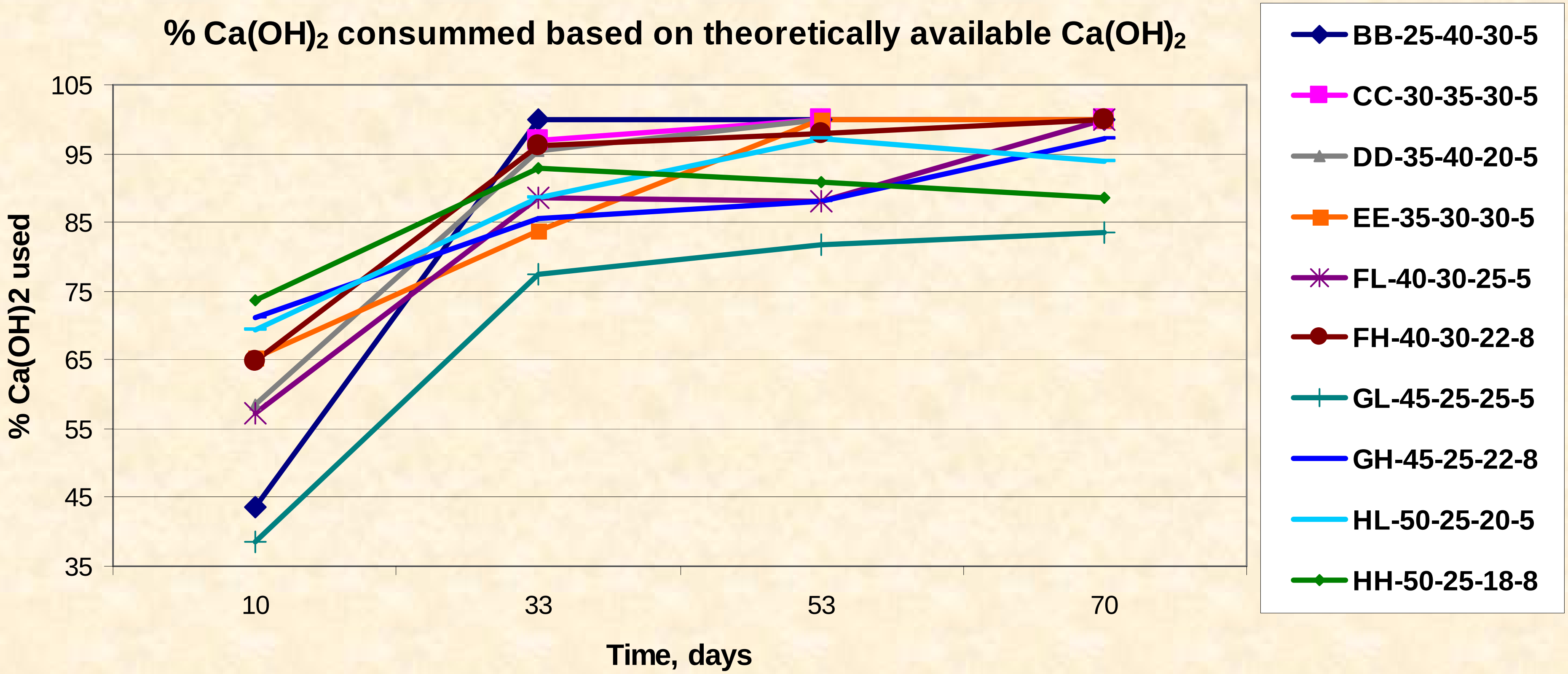
Material Choices to Mitigate Waste Constituents' and Groundwater Impacts on Waste Form Performance

- **Choices of cement types**
- **Choices of admixtures to control waste form physical and chemical properties**
  - **Pozzolanic silicates**
    - **Reduce Ca/Si ratios**
    - **Reduce Al/Si ratios**
    - **Reduce permeability (H_2O, O_2, $SO_4^{=}$, Cl^-, etc.)**
    - **Increase HD-CSH and lower LD-CSH**
  - **Increase internal ion exchange capacity**
  - **Effect reducing conditions (Eh/pH regime)**

Formulation of Grouts to Prevent $Ca(OH)_2$



Results of silica reactivity tests identify formulae that balance the suppression of calcium hydroxide with curing reaction rates



Nomenclature: 30-35-30-5 (30 wt% OPC Type V, 35 wt% BFS, 30 wt% FA and 5 wt% SF)

Dewatering and Changes in CSH Packing Density

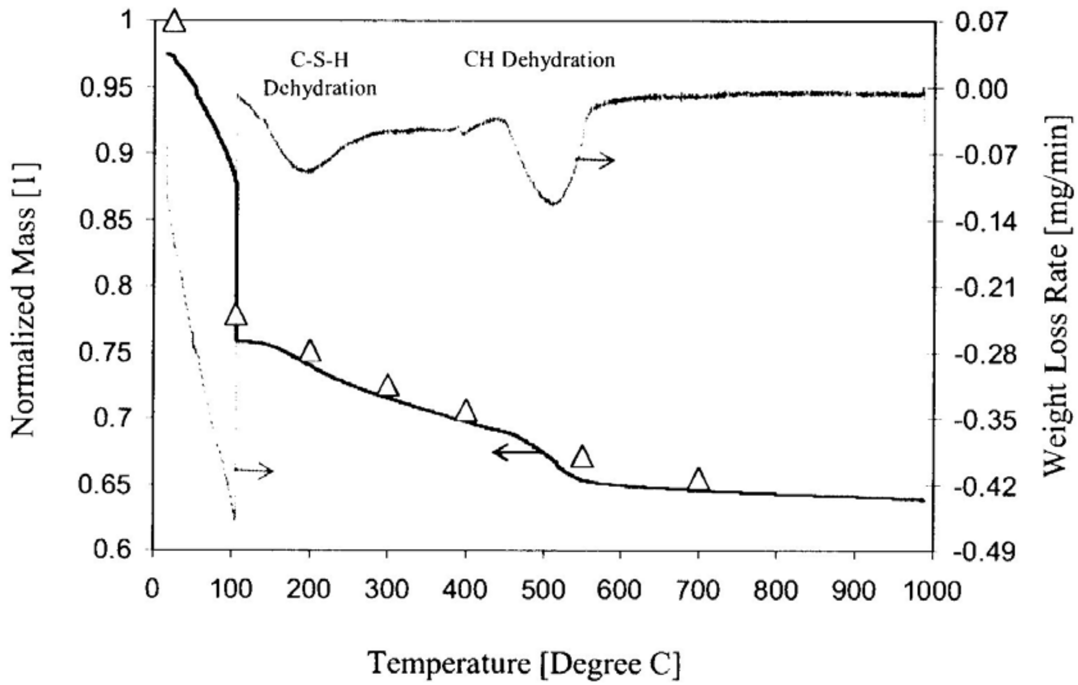


Figure 1: Results of thermogravimetric analysis (TG) on $w/c = 0.5$ cement paste: The normalized mass determined by TG (continuous line) is in excellent agreement with manual mass loss measurements of the specimens used for indentation (discrete points). The derivative of the weight loss (labeled 'weight loss rate') shows the characteristic C-S-H and CH dehydration.

M.J. DeJong and F-J Ulm, "The Nanogranular Behavior of C-S-H at Elevated Temperatures (Up to 700C)," Massachusetts Institute of Technology, Cambridge MA, February 14, 2006.

Dewatering and Changes in CSH Packing Density (*Continued*)

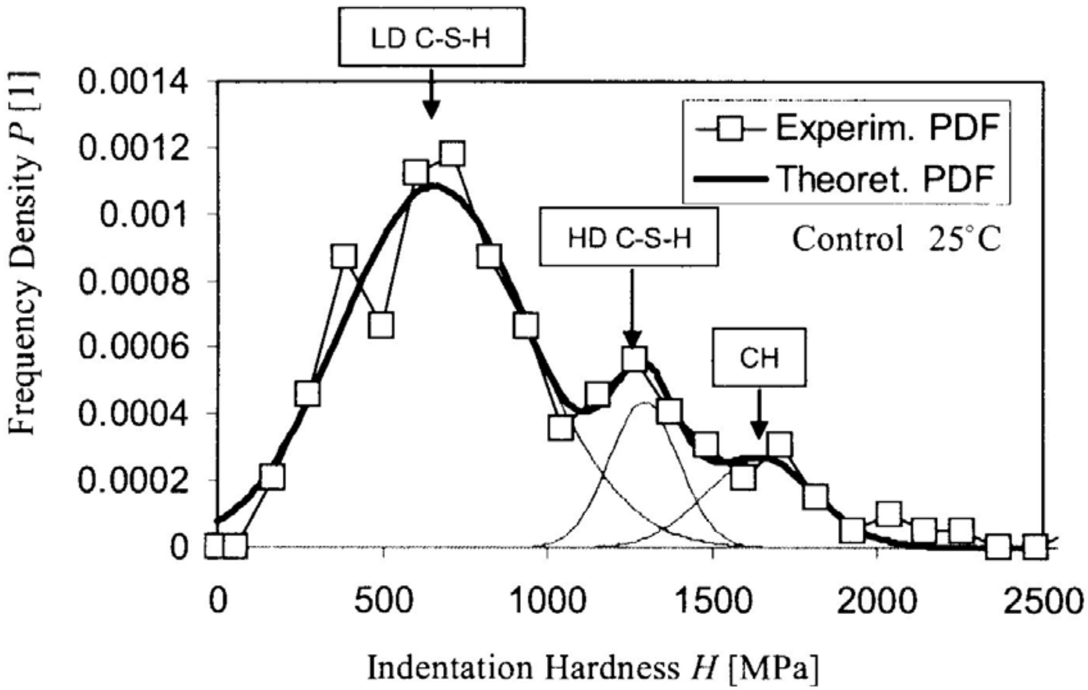


Figure 3: Frequency plots of indentation modulus and indentation hardness with fitted Gaussian curves for low-density (LD) C-S-H, high-density (HD) C-S-H, and Portlandite (CH). The deconvolution was carried out for a bin size of $\Delta M = 2.5$ GPa and $\Delta H = 110$ MPa.

Dewatering and Changes in CSH Packing Density (*Continued*)

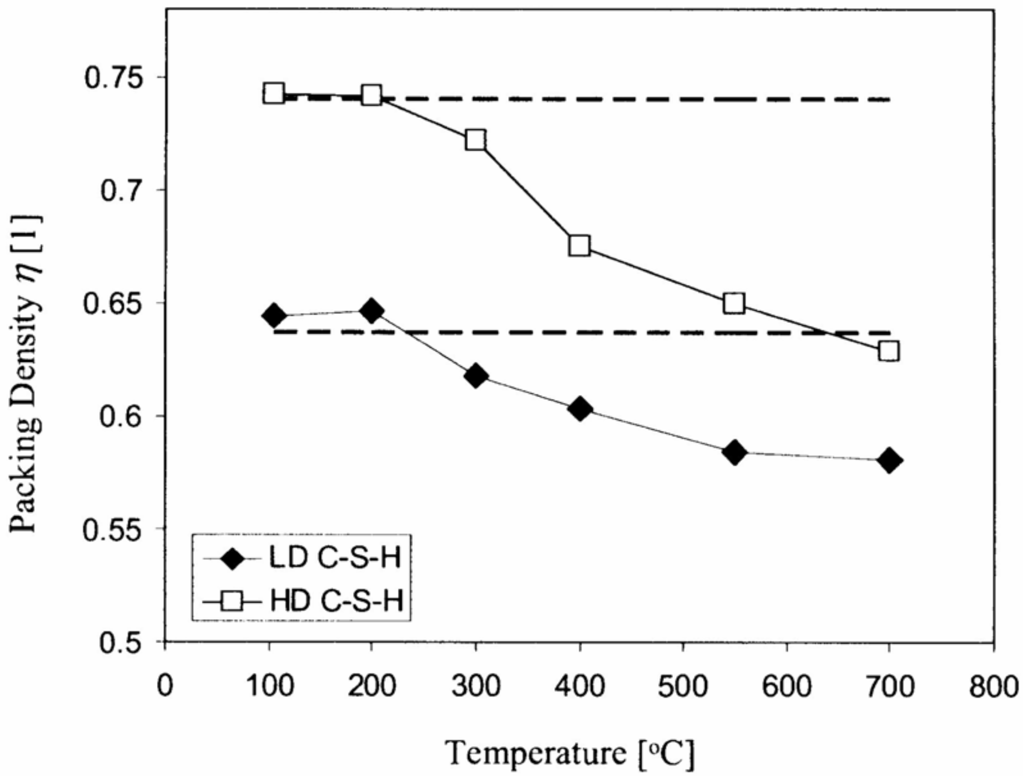
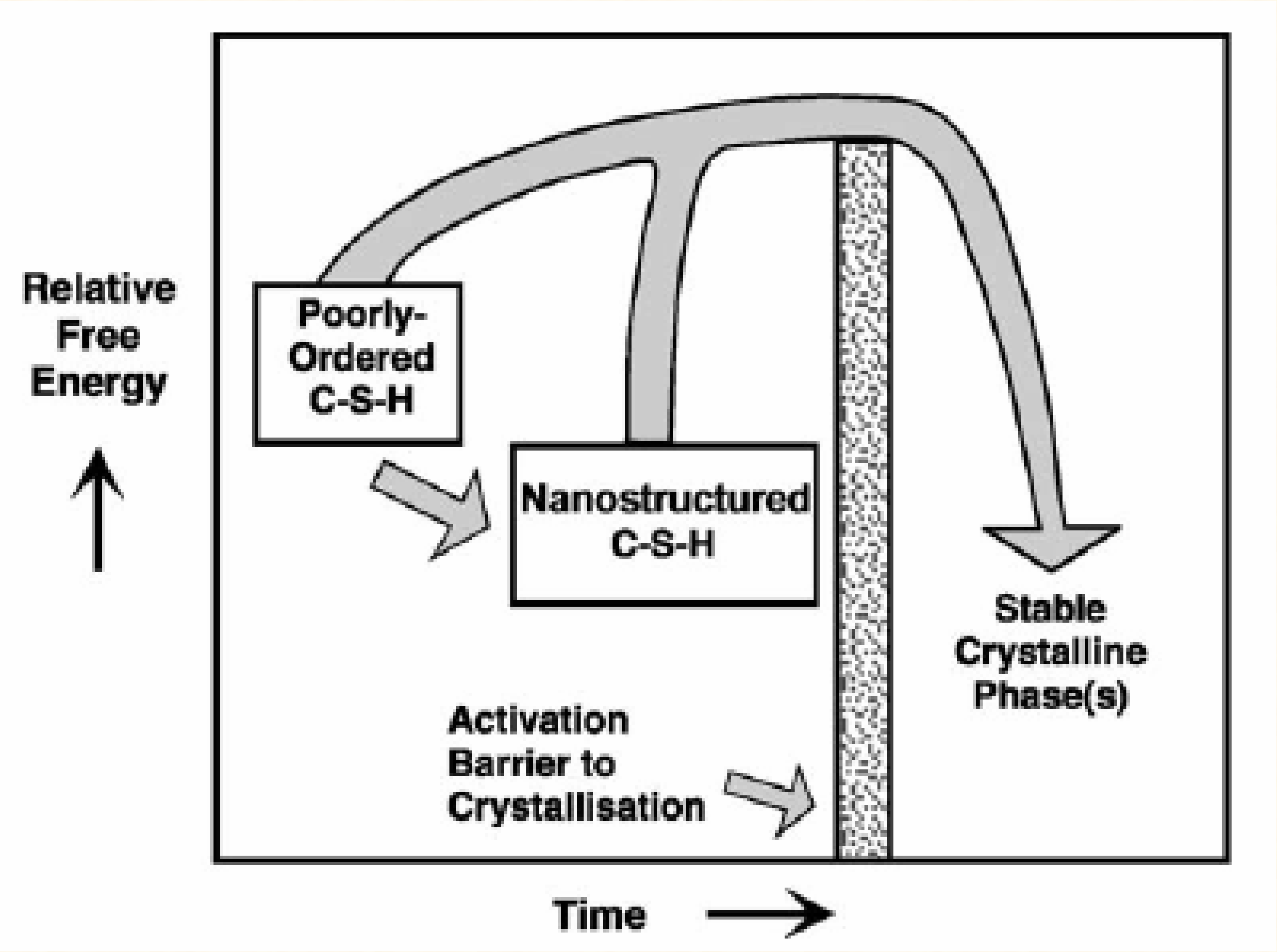


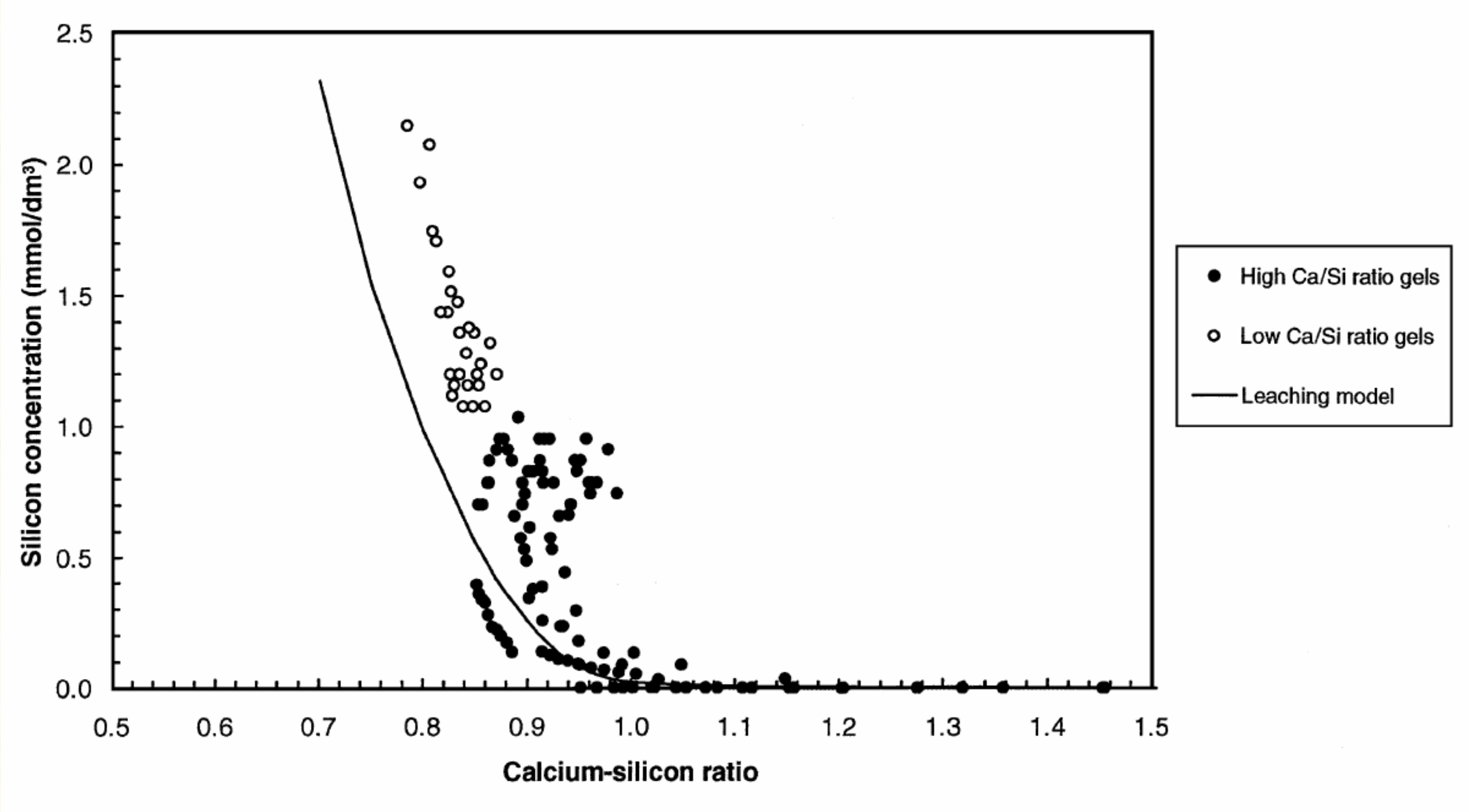
Figure 11: Packing density as a function of the exposure temperature determined from a reverse analysis of the micromechanics model (for $\nu_s = 0$). The broken lines represent the *limit* packing density values: $\eta_{LD} \approx 0.64$ and $\eta_{HD} \approx 0.74$.

Cured High-Silica Cements prevent Alterations and Water Loss from Concretes



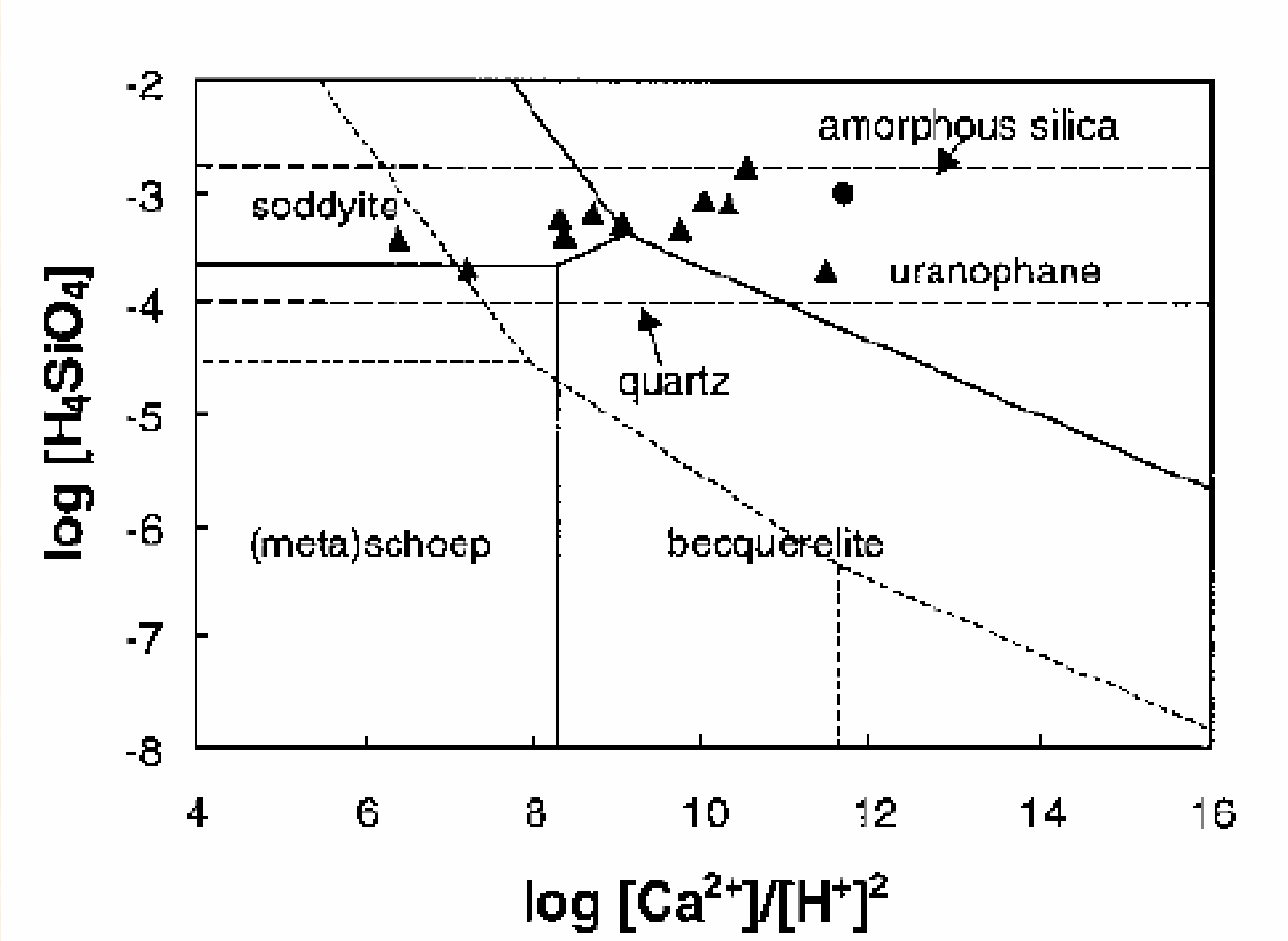
F.P. Glasser, S.-Y. Hong,
Cement and Concrete
Research 33 (2003) 271–279

Increasing Silica in Cement Increases Silica in Leachates

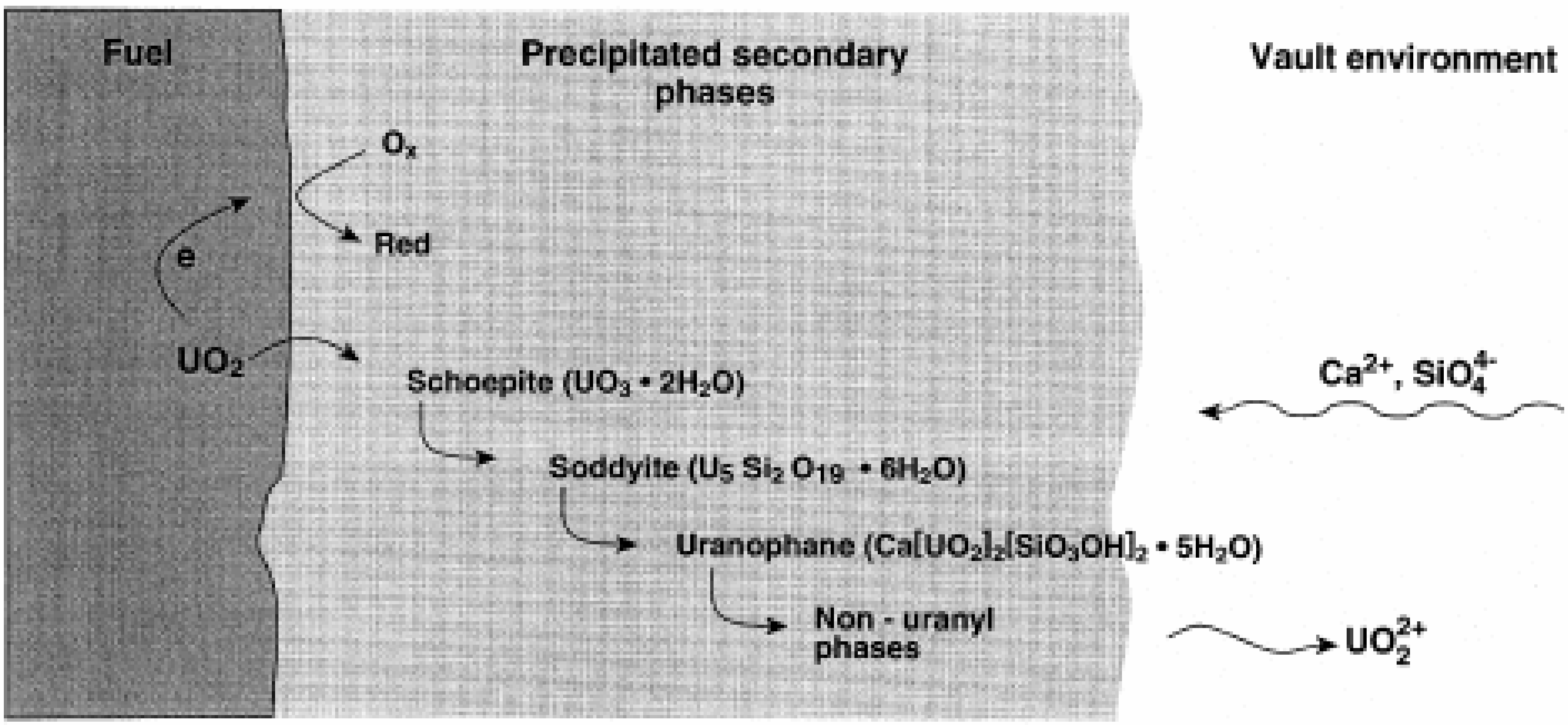


Harris, A.W., M.C. Manning, W.M. Tearle, and C.J. Tweed, Testing of models of the Dissolution of cements—leaching of synthetic CSH gels, Cement and Concrete Research, 32, pp 731–746, 2002.

High-Silica Forces Formation of Insoluble Uranium Silicates



Silicates Form a Dense Diffusion Layer on the Surface of UO_2 even under Oxidizing Conditions



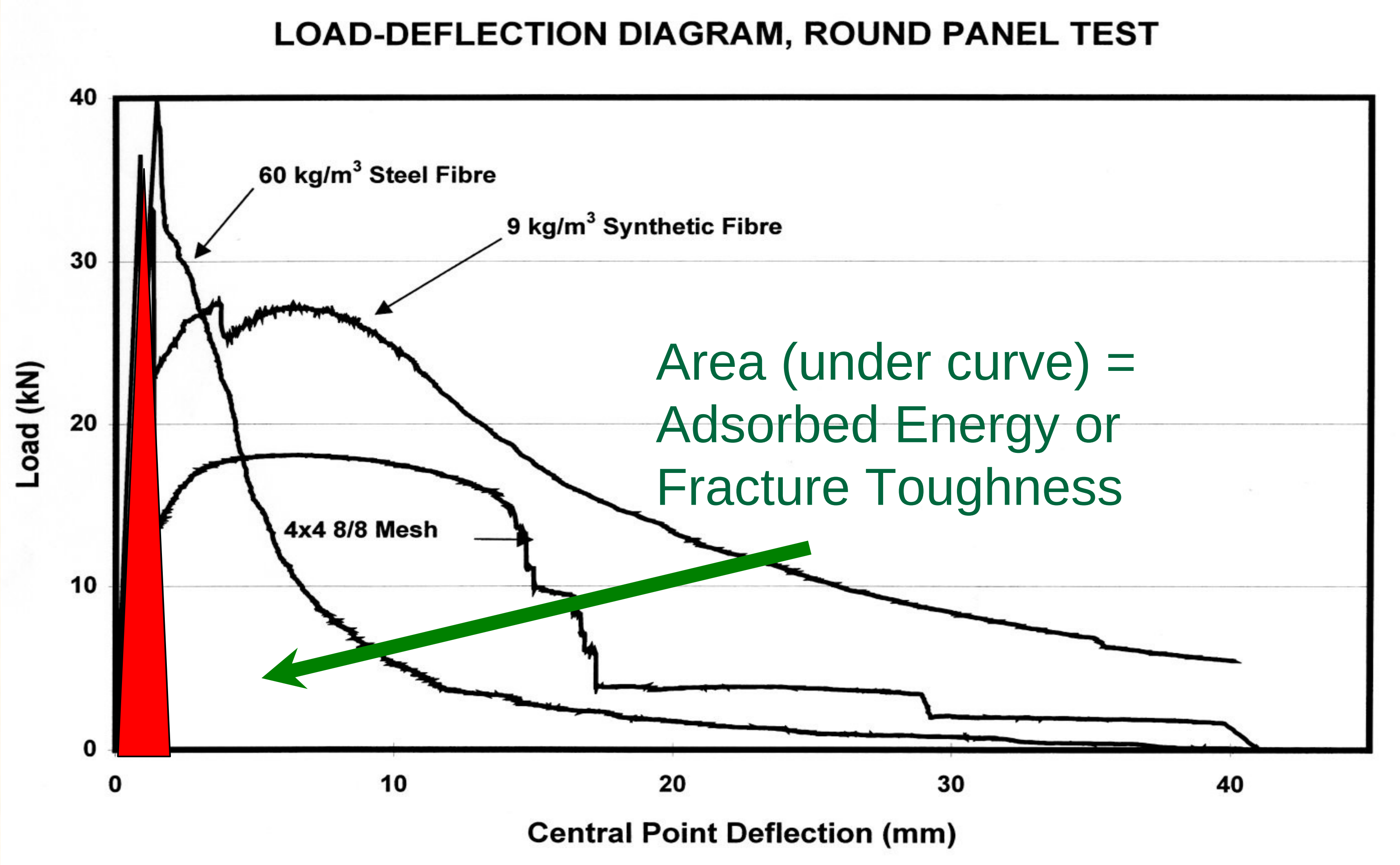
Principal U(VI) Compounds

Values of $\Delta G^{\circ}_{f,298}$ for the U(VI) minerals used in the construction of Fig. 7 (Chen 1999)

Uranyl phases	Formula	kJoule/mol[a]	kJoule/mol[b]
Metaschoepite	$[(UO_2)_8O_2(OH)_{12}]*(H_2O)_{10}$	–13,092.0	–13,092.0
Becquerelite	$Ca[(UO_2)_6O_4(OH)_6]*(H_2O)_8$	–10,324.7	–10,305.8
Rutherfordine	UO_2CO_3	–1,563.0	–1,563.0
Urancalcarite	$Ca_2[(UO_2)_3(CO_3)(OH)_6]*(H_2O)_3$	–6,036.7	–6,037.0
Sharpite	$Ca[(UO_2)_6(CO_3)_5(OH)_4]*(H_2O)_6$	–11,607.6	–11,601.1
Fontanite	$Ca[(UO_2)_3(CO_3)_4]*(H_2O)_3$	–6,524.7	–6,523.1
Liebigite	$Ca_2[(UO_2)(CO_3)_3]*(H_2O)_{11}$	–6,446.4	–6,468.6
Haiweeite	$Ca[(UO_2)_2(Si_2O_5)_3]*(H_2O)_5$	–9,367.2	–9,431.4
Ursilite	$Ca_4[(UO_2)_4(Si_2O_5)_5(OH)_6]*(H_2O)_{15}$	–20,377.4	–20,504.6
Soddyite	$[(UO_2)_2\ SiO_4]*(H_2O)_2$	–3,653.0	–3,658.0
Uranophane	$Ca[(UO_2)(SiO_3OH)]_2*(H_2O)_5$	–6,192.3	–6,210.6

[a] Chen 1999 [b] Finch 1997

ASTM C 1550 Round Panel Test



Issues with Accelerated Aging at Elevated Temperatures to Test Long-Term Durability when Reaction Paths Change

Conditions	Result
100°C for 10 minutes	Boiled egg
25°C for 28 days	Chicken
15°C for 60 days	Rotten egg

Formation Energies of Phases That Can Form in Aging Cement Pastes

Product	At 25°C	At 100°C
Hillebrandite $Ca_6Si_3O_9(OH)_6$	-2.42	-1.60
Afwillite $Ca_3Si_2O_4(OH)_6$	+3.94	+6.82
Xonotlite $Ca_6Si_6O^{17}(O_2H)$	-0.42	+0.49
Tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4(H2O)$	-1.38	+0.18

Missing Links Between Studies of Ancient Cements and Laboratory Tests

- Mass transfer coupled thermodynamic model
  - Thermodynamic data missing
  - Need for models for metastable intermediates trapped by diffusion-controlled metamorphisms
- Microprobe analytical tools to see start of phase transitions

Future Studies Anthropogenic and Natural Analogs to Address Durability

- **Anthropogenic for 2000 to 6000 years**
  - **Gallo – Roman**
  - **Nabateans (6,000 years)**
- **Natural for over 10,000's to 1,000,000's year**
  - **Million-year-old natural samples from sanidinite-facies metamorphic rocks in Marble Canyon, Texas.**
  - **Hatrurim formation in Israel. These formations contain many of the same phases that form in high-silica cements. For example, the minerals are natural analogs for the common cement-clinker phases "alite" (Ca_3SiO_5, C3S) and "belite" (Ca_2SiO_4, C2S).**
  - **Scawt Hill, Northern Ireland, occurs in a region with high precipitation.**

  These cementitious analogs and their alteration products provide the opportunity to study transport processes and mineral metamorphisms on geologic time scales.

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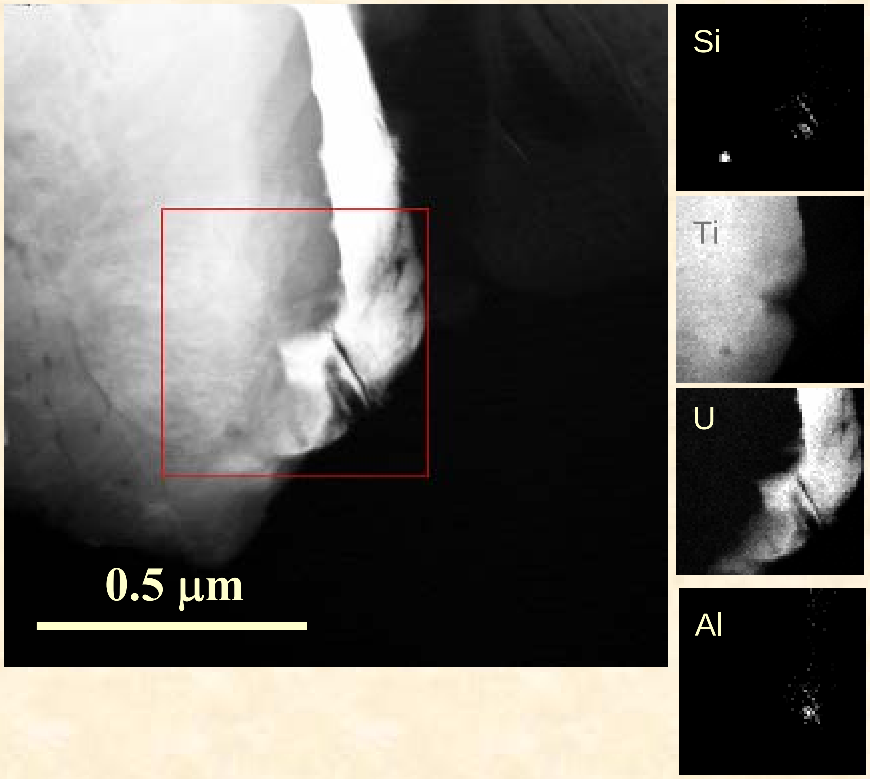
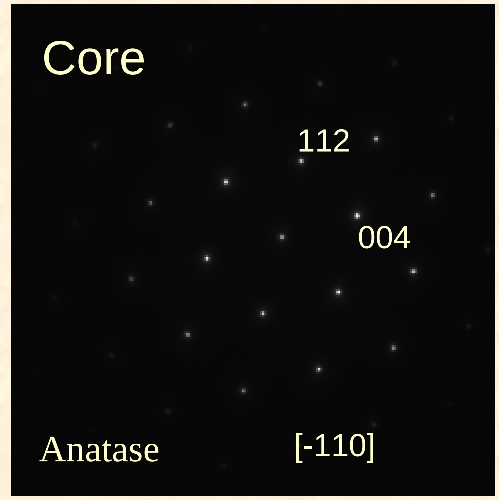
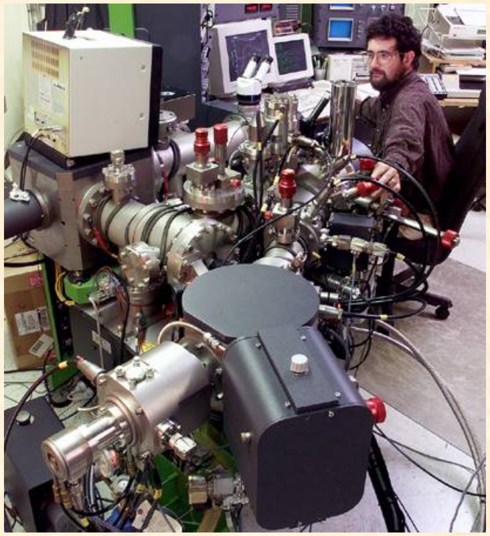
Transmission Electron Microscopy





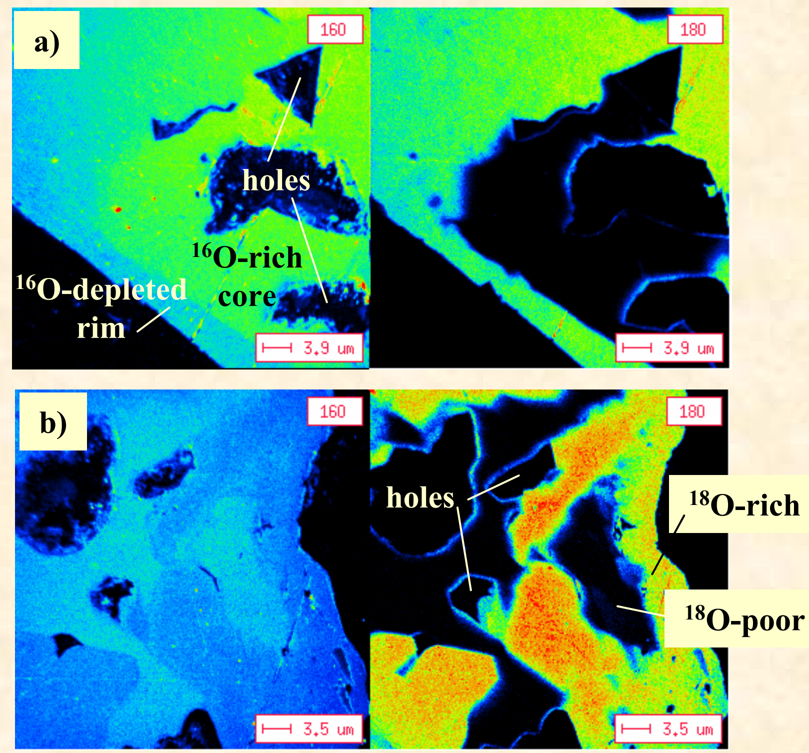
Scanning transmission electron microscope (STEM) images of U and Ti minerals

Secondary Ion Mass Spectrometry

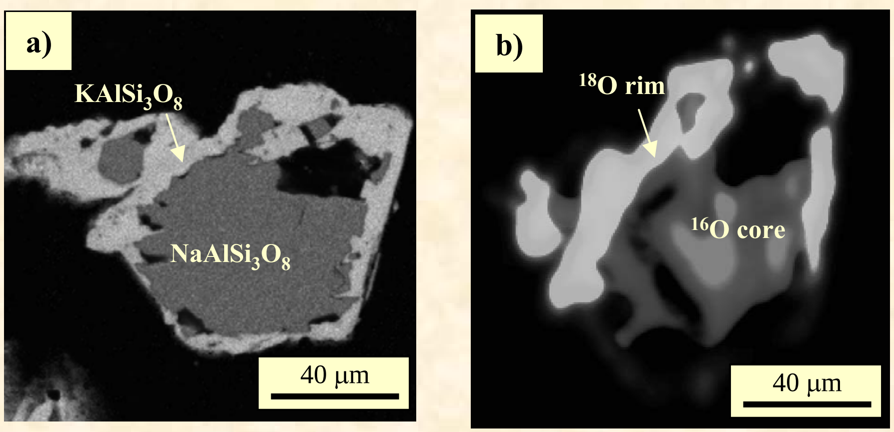


Secondary ion mass spectrometry is one of very few methods that provides highly spatially resolved (a few microns), *in situ* chemical and isotopic analysis of solid materials.

Na-feldspar reacted with ^{18}O rich 2 *m* KCl at 600°C, 200 MPa for 6 d; note ^{18}O rich halo penetrating solid.



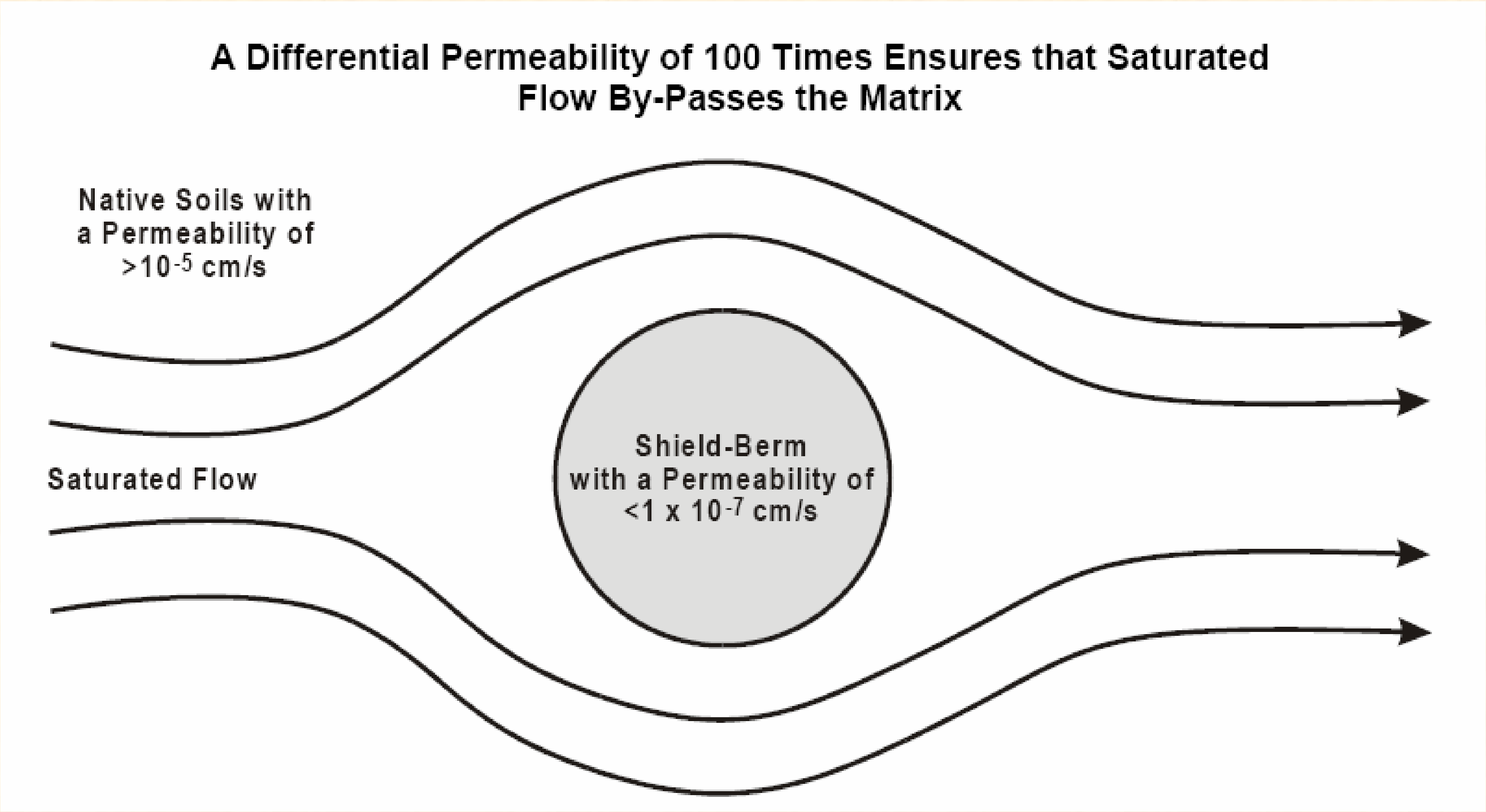
Ion imaging can provide details on the chemical modification of solids interacted with water.



Assessing Leach Performance 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** $A_0 \{S/V\} (D_{diffusion}/time)^{1/2}$

A Relatively Impermeable Monolith Has no Advection



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.

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

D_e = effective diffusion coefficient, $cm^2\ s^{-1}$
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

$F_{30} = 0.091$

$F_{300} = 0.303$

$F_{500} = 0.379$

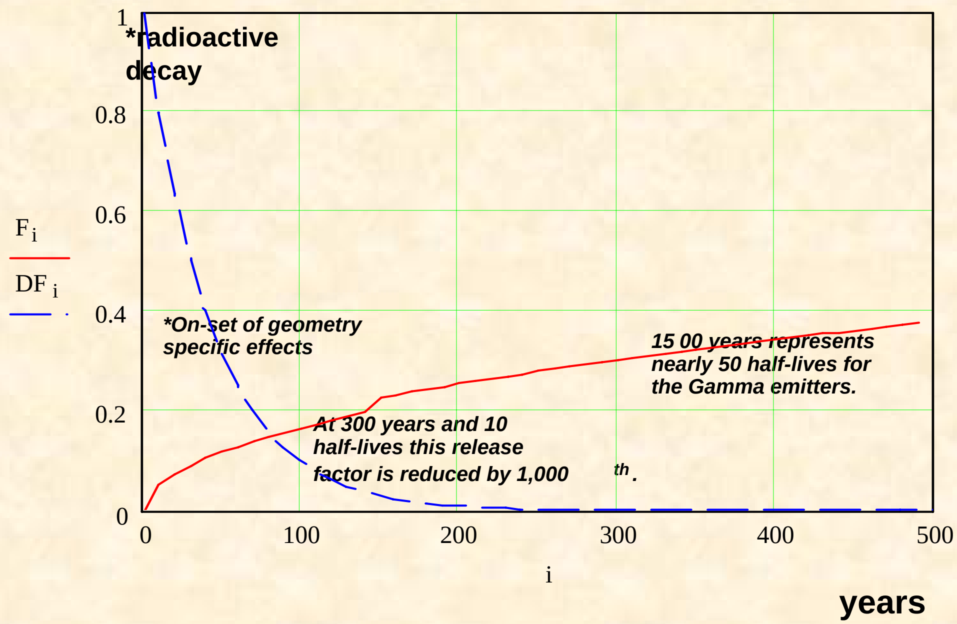
Radioactive Decay Factor

$DF_{30} = 0.5$

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

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

CURIE RELEASE FROM W9 MONOLITH as Sr-90



Combination of Decay and Diffusion Controlled Release

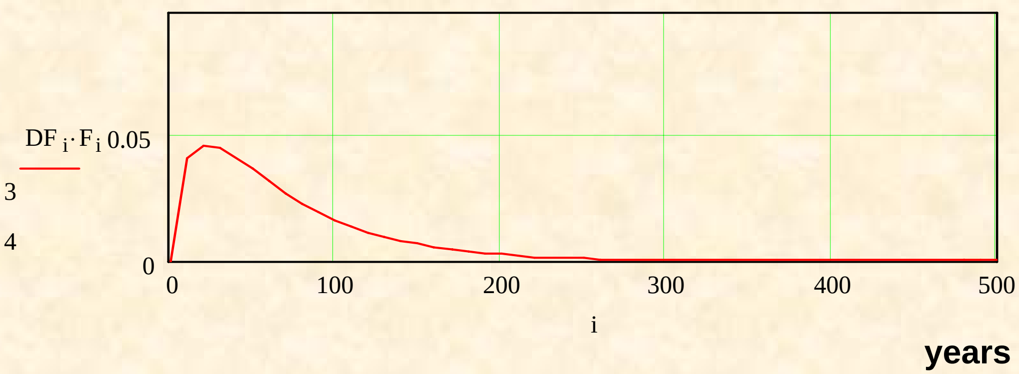
Decay Fraction X Release Fraction

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

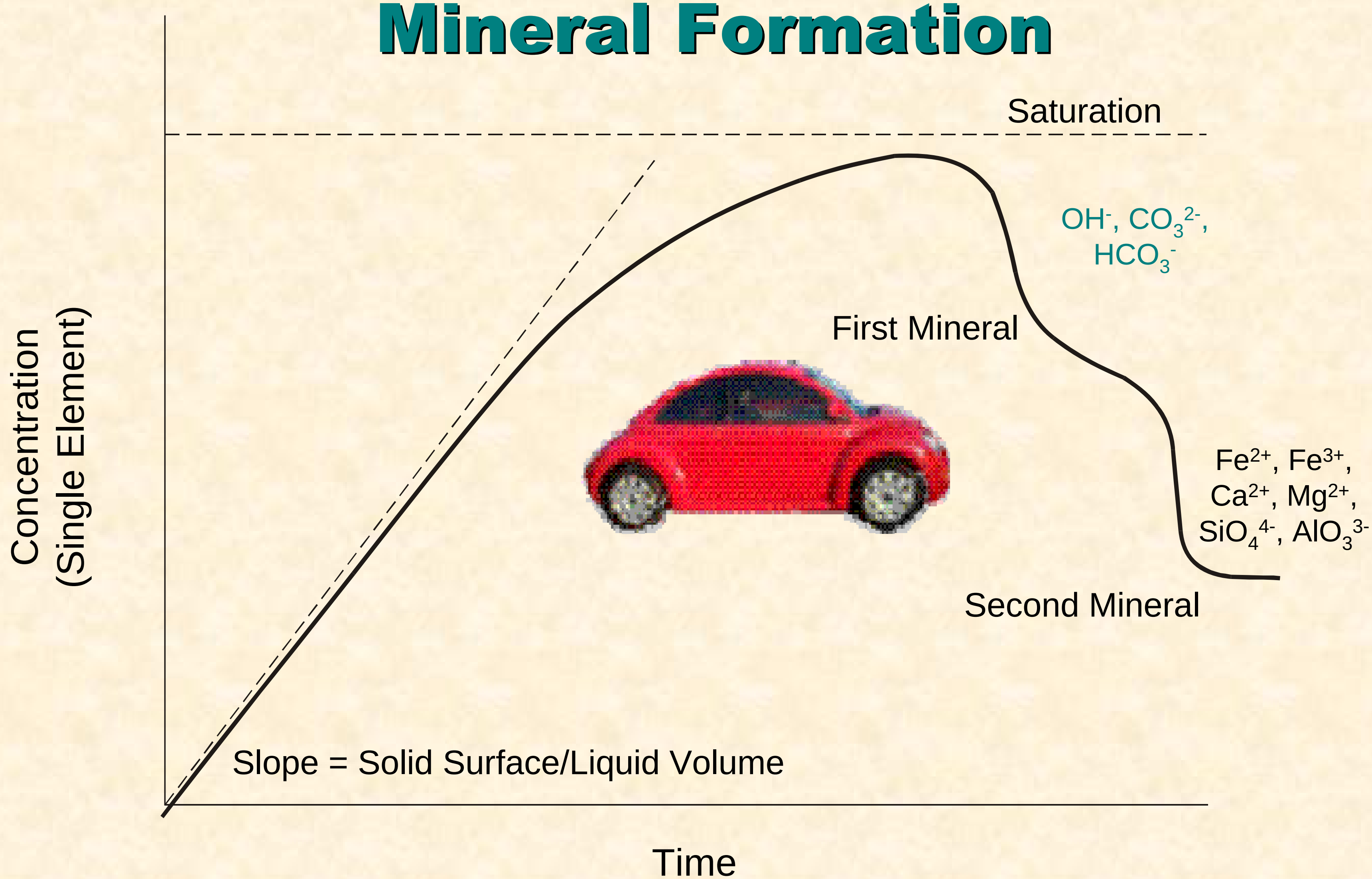
$DF_{90} \cdot F_{90} = 0.02$

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

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



Static Leaching with Secondary Mineral Formation



Conclusions About Leach Testing

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

General Conclusions

- **There is a great body of knowledge on how to formulate cementitious waste forms to process and solidify radwastes from across the DOE complex.**
- **There is disagreement on how to measure and model source-terms for the leaching for nuclides into the near-field transport models.**
- **There is no coordinated effort to reconcile measured waste form performances with accelerated testing and natural/anthropomorphic analogs.**

Modeling Long-Term Durability of Cementitious Materials (LBNL)

- **Tasks**
  - **Critically evaluate thermodynamic and kinetic data relevant to silica-rich cements**
  - **Develop meso-scale models to describe competing carbonation and hydrothermal alteration in the matrix and fine aggregate of cementitious materials as a function of T, relative humidity and P_{CO2}.**
  - **Model repository-scale alteration of emplaced cementitious materials following closure for periods up to 10,000 years**

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Modeling Long-Term Durability of Cementitious Materials (LBNL)

- **Near-Term Plans**
  - Modify TOUGHREACT to model cement aging at elevated temperature.
  - Build a meso-scale model to simulate cement carbonation, and calibrate model against reported field observations

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LBNL and ORNL to Examine YMP Heater Drift Specimens

- Obtain a sub-set of cores and achieved specimens from YMP Heater drift to be split between LBNL and ORNL
- Microscopic examinations to benchmark phase modeling and laboratory observations.
- LBNL has submitted testing plan