U.S NUCLEAR REGULATORY COMMISSION

Presentation by

F.P.Glasser

"State of the Art in Long-Term Prediction of Cementitious Material Performance"

July 2006

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OUTLINE

- Role of cement in nuclear waste disposal
- Resistance to degradation: mechanisms and processes
- Synergies with civil engineering
- Attributes of "performance"
- Solubility studies: impacts of NaCl, CO_2,...
- Towards a new paradigan
- Testing and test methods
- Special hazards in nuclear applications
- Cements and the source term
- Remediation activities
- Summary

USE OF CEMENT AND CONCRETE IN NUCLEAR WASTE DISPOSAL -1

- By "cement" I mean an alkaline cement, either Portland cement (PC) or PC modified by reactive mineral admixtures (blended cement).
- Cement is a standard product the properties of which are governed by specification, e.g. ASTM.
- Codes of practice govern blended cement specifications.

USE OF CEMENT AND CONCRETE IN NUCLEAR WASTE DISPOSAL -2

- As matrix material, for solidification/ stabilisation of liquids, sludges, particulates etc.
- As shielding and outer containers for storage, transport, etc.
- In repository construction, sealing etc., in both operational and post-closure phase: access to permit retrieval.
- Special uses may require special formulations.

USE OF CEMENT AND CONCRETE IN NUCLEAR WASTE DISPOSAL -3

- Cement as a primary matrix material has physical and chemical activity. It is thus not directly comparable with other barriers, e.g. metals, that have a mainly physical role.
- The chemical conditioning role is always present and has both positive and negative implications for performance.

  Example: degradation of glass at high pH.

USE OF CEMENT AND CONCRETE IN NUCLEAR WASTE DISPOSAL -4

- Cement is thermodynamically unstable in most repository environments. Time-dependent changes affecting performance will occur.
- A purpose of this meeting is to define and, if possible, quantify these changes.

RESISTANCE TO DEGRADATION -1

- Comparing metals and cement:
  - metallic corrosion is essentially an oxidation-reduction process requiring electron transport whereas cement corrosion does not generally involve oxidation-reduction,
  - but certain features are common to both, for example, formation of both soluble and insoluble reaction products.

RESISTANCE TO DEGRADATION -2

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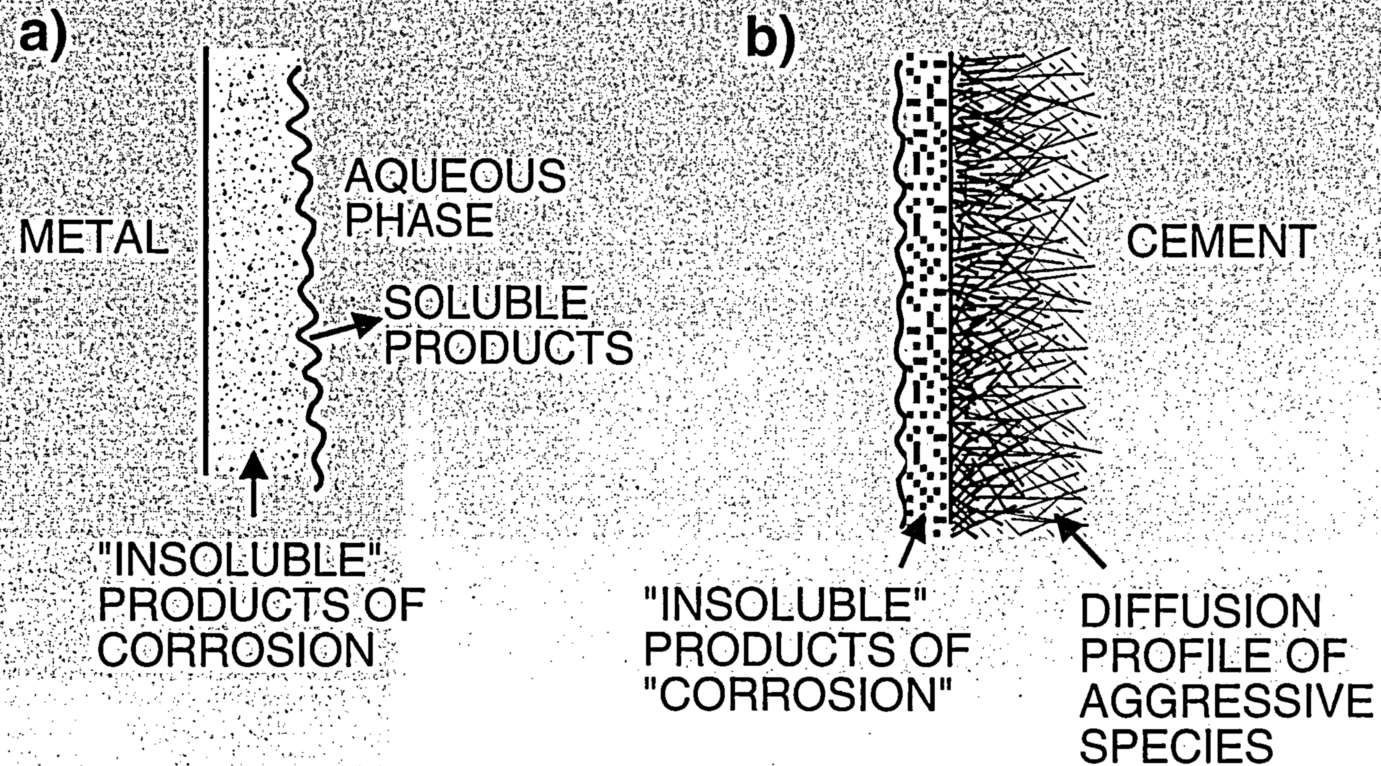


RESISTANCE TO DEGRADATION -3

- Note that for cements
  - diffusion of attacking species into the matrix is an important mechanism.
  - the strength of interaction of diffusing species with cement solids varies greatly.
  - need to preserve local electrostatic change balances; measured diffusions give "apparent" numerical values.

RESISTANCE TO DEGRADATION -4

- It follows that matrix diffusions are subject to a "quality factor". This is a complex function of matrix formulation, ageing and thermal history, etc.
- This "quality factor" has been much studied by engineers. Many empirical relationships have developed, but as yet have not led to true predictive capability.

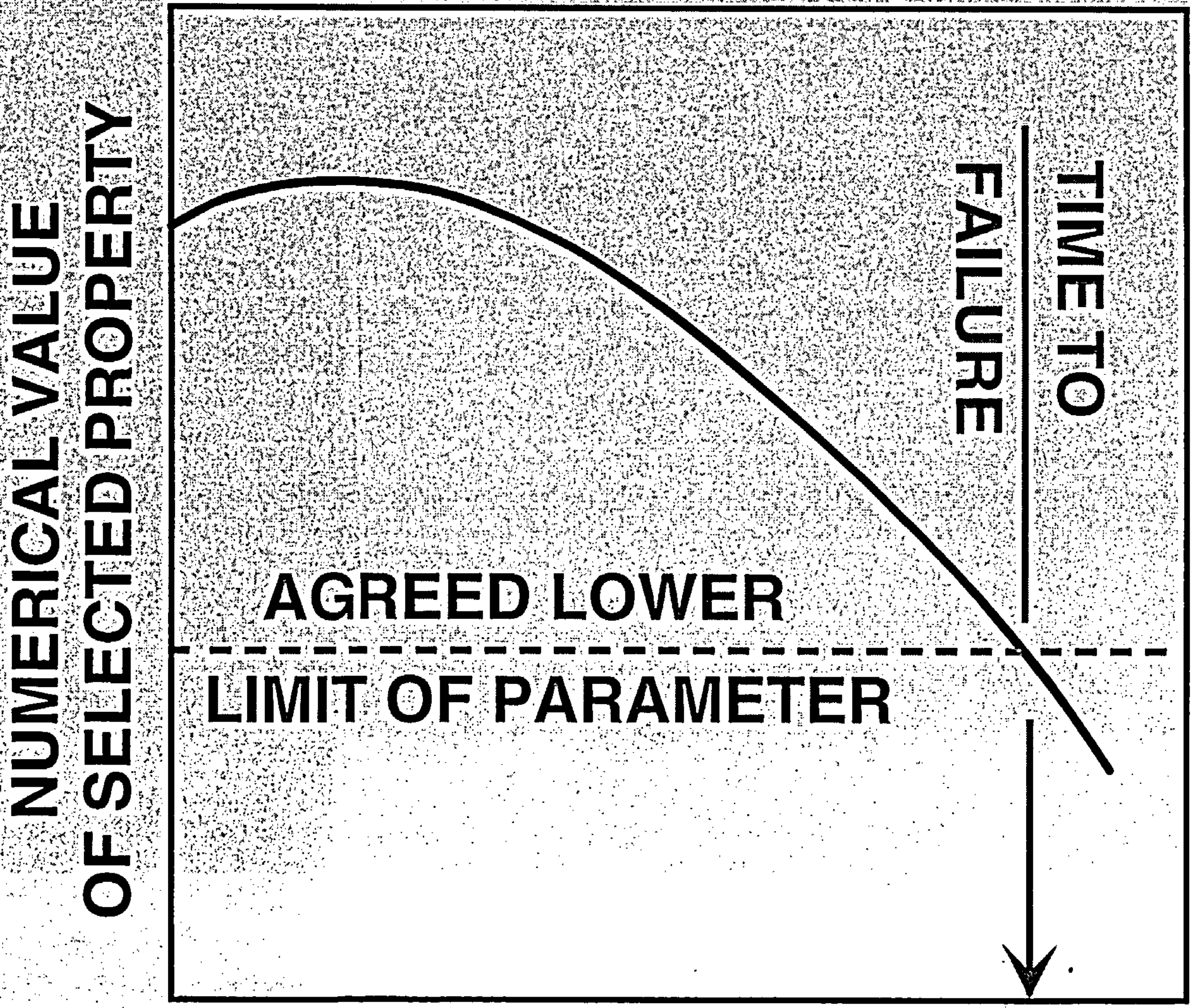
RESISTANCE TO DEGRADATION -5

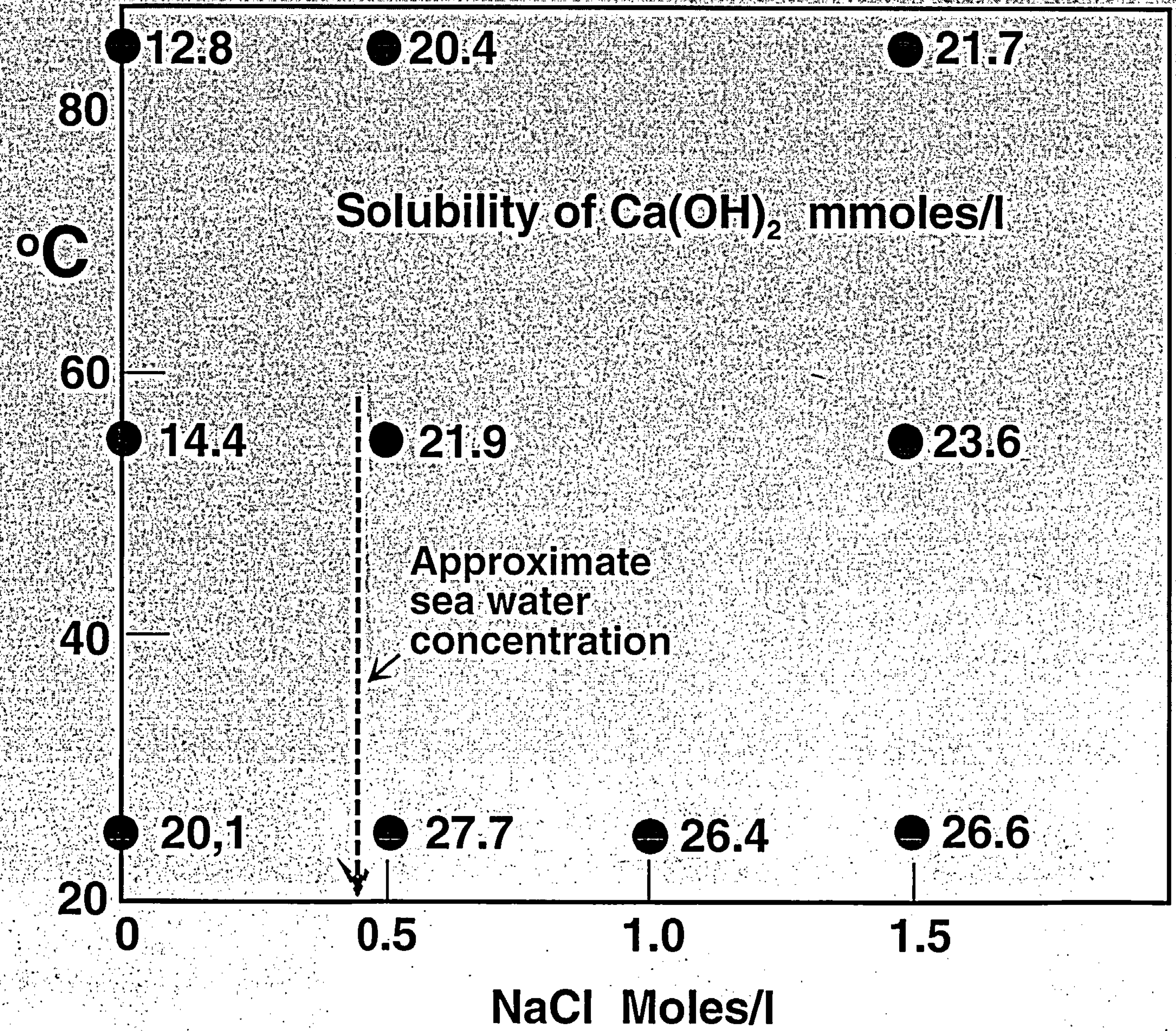
- Given the long history of civil engineering, it might be expected that quantitative models existed.
- But this is not so – for a variety of reasons, some valid but others less so.

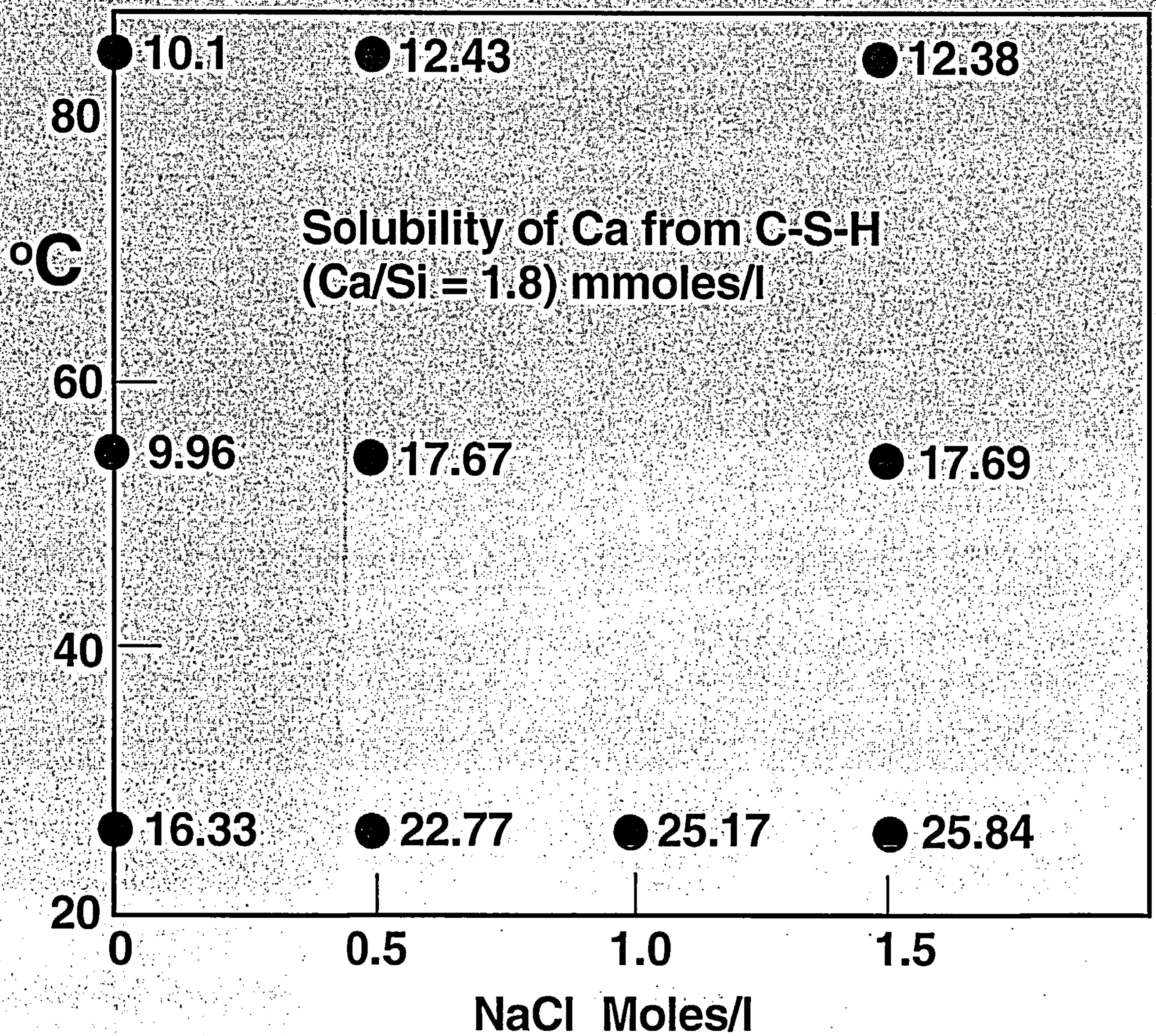
DURABILITY STANDARDS IN CIVIL ENGINEERING

- Rest on experience, tests and standards (themselves often products of experience).
- Partly, cements and concretes are often made on the job and not necessarily subject to rigorous QA.
- The complexities of natural environments coupled with physical processes, e.g. freeze-thaw, create a virtually infinite spectrum of service conditions requiring to be tested.
- Excessive reliance on compressive strength as a performance indicator.

Attributes of Performance




Solubility of Ca(OH)2 mmoles/l
°C
80
60
40
20
12.8
20.4
21.7
14.4
21.9
23.6
20,1
27.7
26.4
26.6
Approximate
sea water
concentration
0
0.5
1.0
1.5
NaCl Moles/l



Solubility of Ca from C-S-H
(Ca/Si = 1.8) mmoles/l
°C
80
60
40
20
10.1
12.43
12.38
9.96
17.67
17.69
16.33
22.77
25.17
25.84
0
0.5
1.0
1.5
NaCl Moles/l

ROLE OF CO_2 -1

- Most natural waters contain CO_2; rain is saturated to $P_{CO2} \simeq 10^{-3.5}$ atm at sea level.
- Moist atmospheres carbonate cement. All cement phases react forming calcite, silica gel alumina and ferric oxide hydrates.
- Rate of carbonation is dependent on relative humidity.

ROLE OF CO_2-2

- A rough rate of carbonation is 0.2-2mm/year depending on cement quality, exposure, etc.
- Strength is not impared but by decreasing the internal pH, embedded steel (if present) is depassivated and corrodes.
- Corrosion leads to volume expansion which cracks the matrix and reaction becomes self-accelerating.

CO_2 REACTIONS -3

- $CaCO_3$ is several orders of magnitude less soluble than $Ca(OH)_2$ or C-S-H so, on balance, it forms a protective carbonate skin in the near-surface.
- The protective quality varies, depending in part on cement quality. But in general, models relying on solubility in initially pure water much overpredict the importance of dissolution.

CO_2 REACTIONS -4

- The above principle is well illustrated by historic examples of construction made with slaked lime ($Ca(OH)_2$) cements. The solubility of "lime" is high, ca 1.1g/l at 18°C , indicating poor resistance to water.
- Rapid carbonation of the near-surface layers result in about a 2 order-of-magnitude decrease in solubility with the result that "lime" is successful whereas gypsum, of about the same solubility, is not.

ROLE OF CO_2 -4

- BUT
- Certain natural waters said to contain "aggressive CO_2" attack cement strongly.
- Qualitative classifications of "aggressiveness" based on water analysis are (i) often inaccurate and (ii) do not account for the speciation of CO_2 (as CO_2 (dissolved), H_2CO_3, HCO_3^- and CO_3^{2-}). The balance is crucial to "aggressiveness": see Cowie and Glasser, Adv. Cement Res. 4, 119-134 (1992).
- Computer-based interactions handle calculations well.

TOWARDS A NEW PARADIGM

- It is apparent that existing test methods for determining the long-term durability of cements are, to varying degrees, inaccurate or inadequate.
- Examples will be given in support of this, using standards of sulfate resistance of cements, e.g. ASTM and Canadian standards.

THE PRESENT SITUATION -1

- Sulfate resistance is measured by immersion of mortar prisms/cylinders of known composition in dilute sodium sulfate.
- Changes in length and compressive strength monitored as a function of time, typically up to 1 year, at fixed temperature.
- Due to destructive nature of the compression test and inherent variability of response, large numbers of specimens are required for statistical reproducibility.

FEATURES & PROCESSES OCCURING IN SULFATE TESTING -1

- In the sodium sulfate test, the sulfate concentration of the aqueous solution depletes with time.

  (What is the effective sulfate concentration?)

- Sodium is not, however, depleted. To maintain change balance, the cement contributes OH ions and the pH rises.

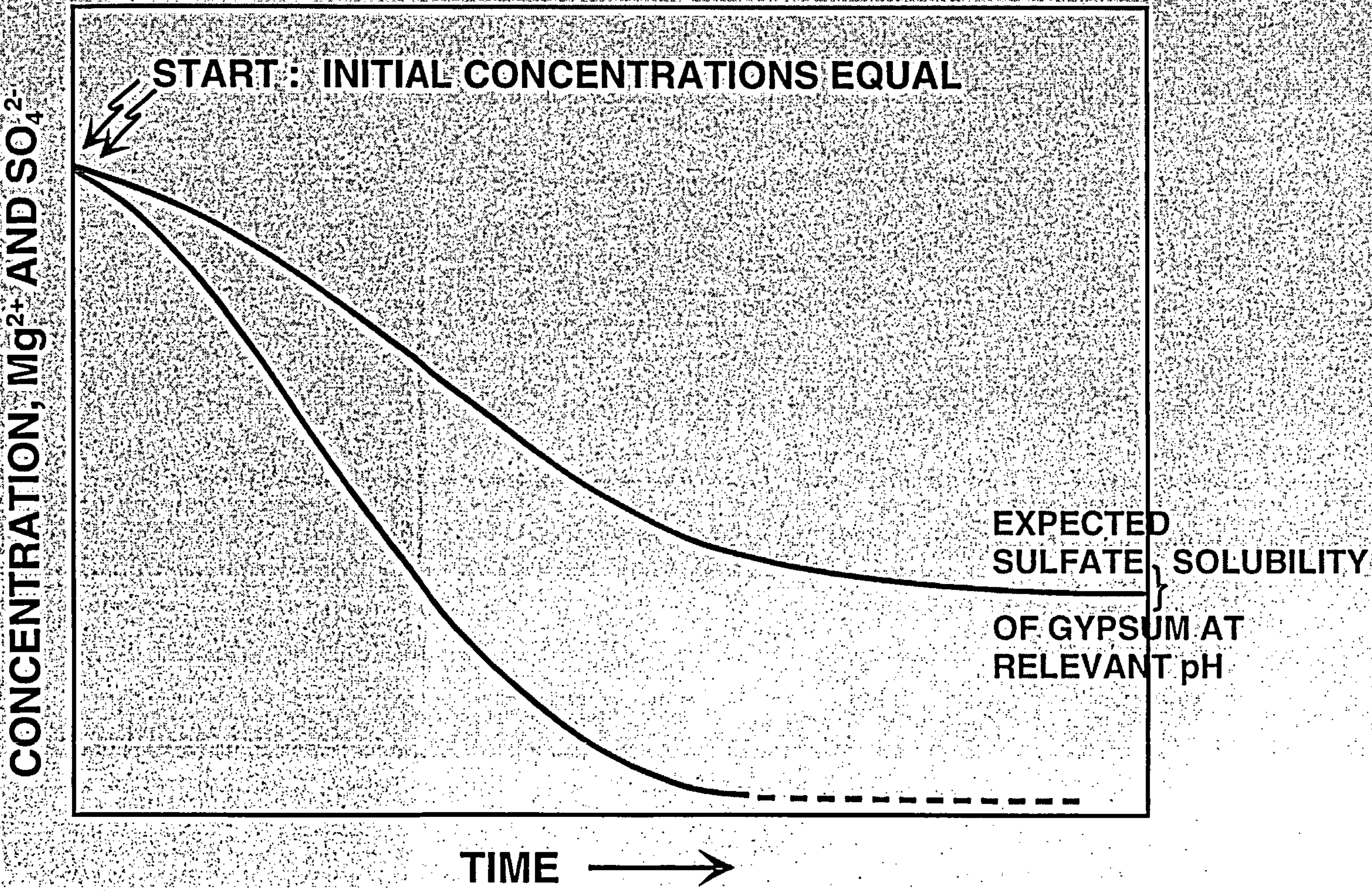
  (The solution gradually converts to an $NaOH/Na_2SO_4$ composition. Is this realistic?)

FEATURES & PROCESSES OCCURING IN SULFATE TESTING -2

- The alkaline test solution, if in contact with air, sorbs CO_2 which in turn, precipitates calcium carbonate.

  Is this process – not specified in tests – desirable or not? What is the position about CO_2 access? If it is to be controlled, how can this be done in a reproducible manner?

  (We are presently reporting results of calculations to RILEM).


START : INITIAL CONCENTRATIONS EQUAL
CONCENTRATION, Mg^{2+} AND SO_4^{2-}
EXPECTED SULFATE SOLUBILITY OF GYPSUM AT RELEVANT pH
TIME

$MgSO_4$ Testing

- Note that the shape of curves is not generic – depends on geometry, relative mass of test solution/cement, etc.
- Also, that renewal of attacking solution does not really help; aqueous concentration profiles develop a “sawtooth” shape.

SUMMARY – STANDARD TESTS -1

- I hope enough has been given to convince you that standard tests and test methods do not provide a reliable and quantitative guide to future performance.
- On the one hand, this body of knowledge cannot be ignored; it represents experience in its identification of destructive agents and is legally binding but on the other hand it does not measure reliably and quantitatively what it purports to do – a paradox indeed!

SUMMARY – STANDARD TESTS -2

- I do not suggest that standard tests be abandoned, only that:
  - tests need supplementary calculations in support of analytical data.
  - tests should be more carefully analysed from a physiochemical point of view.
  - additional data may need to be collected and test procedures better focussed.

HAZARDS TO CEMENT IN WASTE TREATMENT/DISPOSAL -1

1. THERMAL HAZARD

- <u>Initial exothermic heat release (short-term)</u>

  Affects large masses. Cooling in the post-hardening stage results in thermal contraction and cracking.

- Must be managed by attention to formulation and design, including sequential emplacement, forced cooling etc. Importance of cracking to transport properties is a neglected area of study.

HAZARDS TO CEMENT IN WASTE TREATMENT/DISPOSAL -2

1. THERMAL HAZARD

- Radiogenic heating (long-term)

  Scenario development depends on moisture state. Hazards include (i) crystallization, (ii) reaction with aggregate (if used), (iii) impacts resulting from other materials interactions.

- In part, can be managed by choice of aggregate (if used). But holistic analysis of repository performance needed to conduct a systematic evaluation.

THE THERMAL HAZARD

- Cement is used in a notional situation where it is subject to a prolonged thermal excursion.
- What are the consequences to
  - mineralogy
  - pH conditioning ability
  - resistance to dissolution
  - physical coherence/strength, permeability and dimensional stability?

THE THERMAL HAZARD: MINERALOGY -1

- Cement contains ~90 of two solids: $Ca(OH)_2$ and C-S-H.
- The latter is (nearly) X-ray amorphous and in coexistence with $Ca(OH)_2$ has a Ca/Si (mole) ratio 1.8-2.0.
- Experience of autoclaving at ~100-150°C shows that C-S-H crystallises, mainly to α dicalcium silicate monohydrate with decrease in specific volume $\simeq$ increased permeability and reduced strength.

THE THERMAL HAZARD: MINERALOGY -2

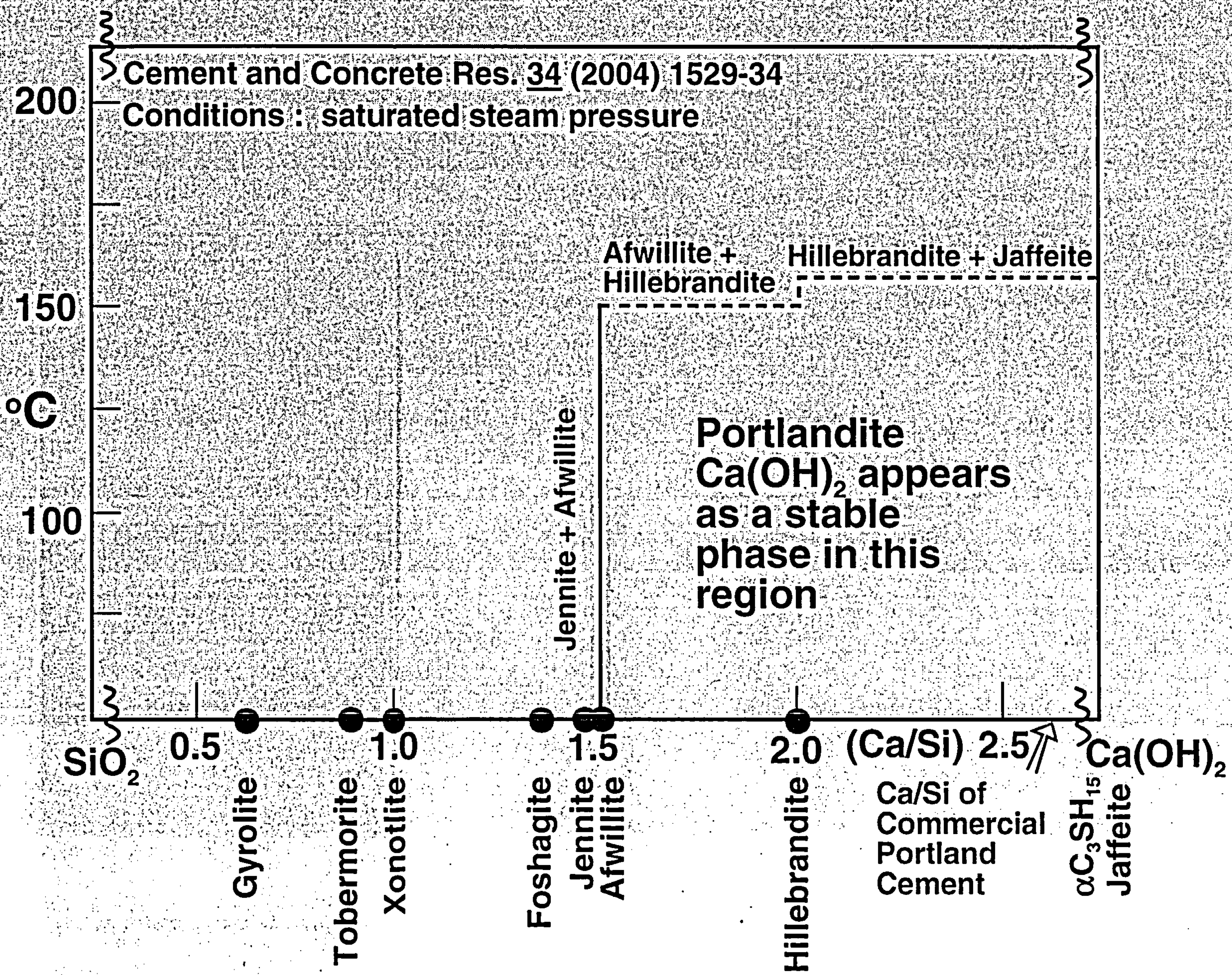
Al (and to a lesser extent Fe(III) and Mg) react to form siliceous hydrogarnet, $Ca_3\ Al_2\ (OH)_{12-4x}\ (SiO_4)_x$. Its high density, (~3g/cm^{3}), relative to precursors, increases porosity and permeability and reduces strength.

Reaction forming hydrogarnet observed in commercial Portland cement in 7 years, 85°C.

THE THERMAL HAZARD: MINERALOGY -3

A potentially greater problem is the reaction with mineral aggregates in grouts, mortars, etc. Normally considered to be inert, quartz reacts increasingly rapidly with cement above ~100°C.

Reaction depends on mass balances, but in general the reaction products have lower Ca/Si ratios than cement. For example, tobermorite (Ca/Si ~0.87) is a favoured product.


Cement and Concrete Res. 34 (2004) 1529-34
Conditions : saturated steam pressure
200
150
°C
100
Afwillite + Hillebrandite
Hillebrandite + Jaffeite
Jennite + Afwillite
Portlandite $Ca(OH)_2$ appears as a stable phase in this region
SiO_2
0.5
1.0
1.5
2.0
(Ca/Si)
2.5
$Ca(OH)_2$
Gyrolite
Tobermorite
Xonotlite
Foshagite
Jennite
Afwillite
Hillebrandite
Ca/Si of Commercial Portland Cement
$\alpha C_3SH_{1.5}$
Jaffeite

PORTLANDITE - ITS SIGNIFICANCE

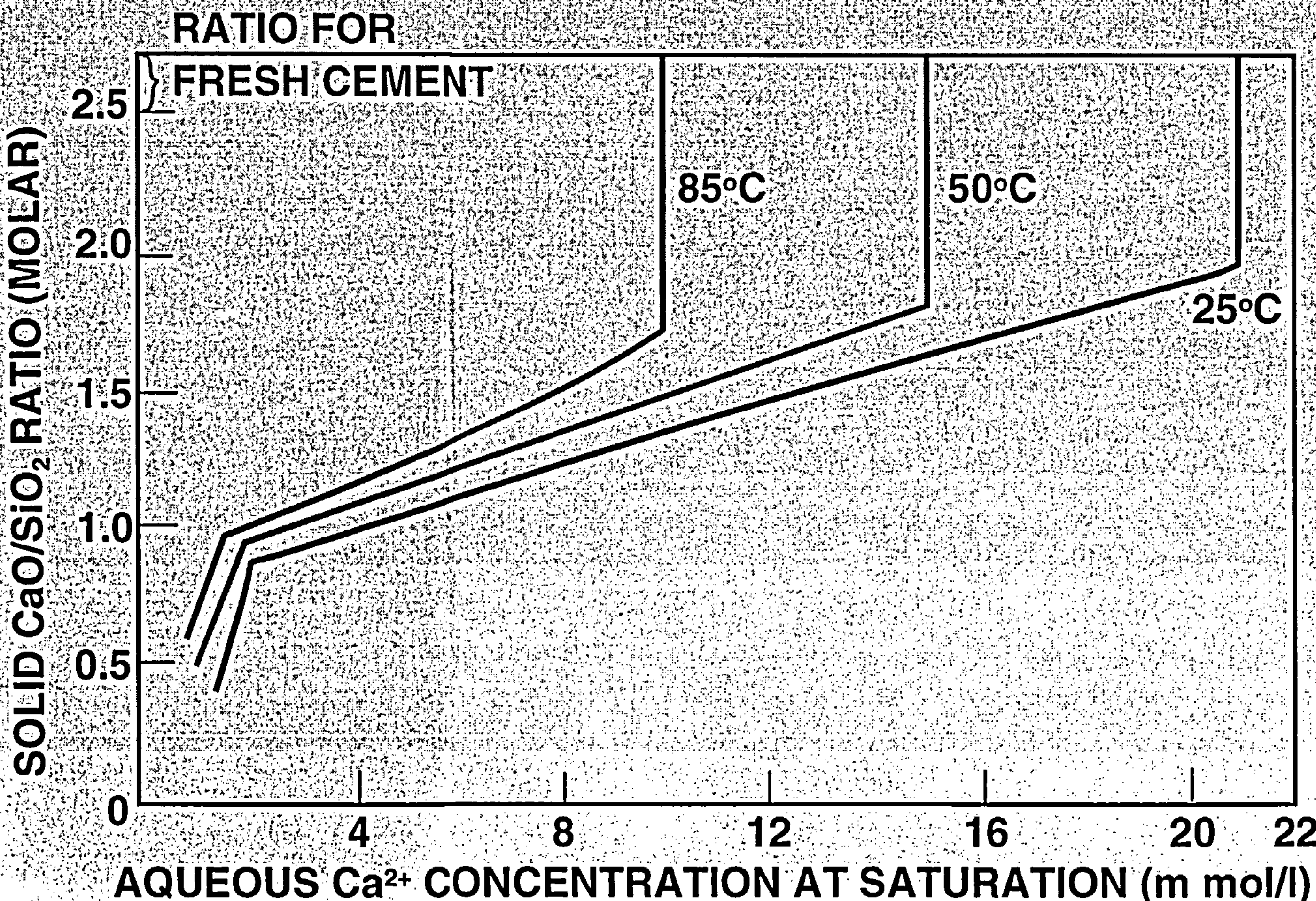
- Congruently soluble, well-known properties (solubility *decreases* with rising temperatures at least to 180°C).
- Therefore it "anchors" predictions about pH conditioning and pH buffering reserves. A robust case can be made for retention of high pH if portlandite, $Ca(OH)_2$, can be shown to persist.

DISSOLUTION OF CEMENT AND CEMENT COMPONENTS

Chemical modelling of the solubility of cements is relatively well advanced.

Most models concentrate on dissolution into initially pure water.

While this case, of dissolution into pure water, is required for benchmarking, studies of more complex systems are are advancing only slowly.


RATIO FOR
FRESH CEMENT
85°C
50°C
25°C
SOLID CaO/SiO2 RATIO (MOLAR)
0
0.5
1.0
1.5
2.0
2.5
4
8
12
16
20
22
AQUEOUS Ca2+ CONCENTRATION AT SATURATION (m mol/l)

CEMENTS AND THE "SOURCE TERM" -1

During the 1980's and 1990's, the binding mechanism between specific radionuclides and cement substances was much explored. Where specific compounds were formed, these were made in pure form and solubilities determined. In some cases, stability was also measured, at least semi-quantitatively.

CEMENTS AND THE "SOURCE TERM" -2

Cationic species were found to

- replace Ca
- replace Mg (in slag cements)
- replace Al, Fe and/or Si in cement minerals
- form independent compounds; hydrous oxides, calcium salts etc.

Anionic species were found to

- replace OH
- replace SO_4 in cement minerals

CEMENTS AND THE "SOURCE TERM" -3

C-S-H, the gel-like phase also showed non-specific sorption for both cations and anions. This was related to Ca/Si ratio and the extent of Al for Si substitution.

CEMENTS AND THE "SOURCE TERM" -4

Progress could be seen : specific radionuclide solubility mechanisms could be defined and order-of-magnitude solubilities used to implement deterministic models.

But progress seems to have slowed or stopped. Just as the methodology had been perfected, and with many unsolved problems remaining, work virtually ceased. Why?

CEMENTS AND THE "SOURCE TERM" -5

<u>Example: Ni and Co</u>

These are strongly fractionated into the layer double hydroxides (LDH's), e.g hydrotalcite. Hydrotalcite –like phases are also a permanent and stable constituent of slag-based cements. Moreover, in nature the LDH's extend their stability by substitution in part of CO_3^{2-} for OH^- and persist in weathering, often appearing in soils.

REMEDIATION ACTIVITIES -1

- Cement much favoured because it is cheap, "formable" i.e., delivered as a fluid grout, compatible with a wide range of materials, has a physical and chemical potential for immobilisation is not itself toxic and is stable in the natural environment.

REMEDIATION ACTIVITIES -2

- Remediation is often planned and accomplished in a series of microdecisions, often dominated by short term criteria: for example, properties of the fluid grout for emplacement are reflected in formulation without evaluation of longer-term consequences.

REMEDIATION ACTIVITIES -3

- This often leads to conflict: for example, can organic plasticisers be used to fluidise grouts?

  (Designers favour plasticised systems but regulatory concerns exist that prasticisers or their hydrolysis products will solubilise and complex radionuclides).

REMEDIATION ACTIVITIES -4

Once a plan has been agreed, trials may be done. These often suffer from:

- adequate QA in the course of the trial.
- adequate testing of the product to ensure targets are achieved.
- lack of feedback to design and implementation stages if targets are not achieved.

REMEDIATION ACTIVITIES -5

RECTIFICATION OF THESE PROBLEMS IS IN SOME CASES OBVIOUS, BUT AMONGST THE RESEARCH NEEDS I IDENTIFY

- need for better non-destructive tests to QA simulate and real remediation.
- better understanding of all those involved of the goals of remediation – short and long term.
- development of a "Plan B" for out-of-specification remediations.
- long term, automatic indicators of failure.

SUMMARY -1

It appears frustrating that we cannot, at present, predict the lifetime performance of cement barriers, either as a matrix or a barrier.

In fact, the demands placed on cements are often unreasonable in terms of ability to predict and uncertainties about cements are comparable to those for other materials *under the same circumstances*.

SUMMARY -2

Cements are required in many applications to perform

- in non-steady state conditions, e.g. wet/dry, oxidizing-reducing, changing mass fluxes….
- by maintaining physical integrity and dimensional stability *as well as* a chemical potential – achieving the latter by chemical reaction, e.g. sacrificial dissolution.

SUMMARY -3

In fact, purely chemical models of cement performance are well advanced, albeit simplistic in terms of being able to cope with chemically complex environments.

SUMMARY -4

Weak areas, additionally to those highlighted, are

- in linking chemical/mineralogical changes with mechanical properties.
- a basis for accelerated testing which does not also alter the mechanisms involved.
- reluctance to rely more on computer based models predictions from which are *subject to experimental verification*.
- better integration of data into deterministic performance models: identification of "missing" data.

SUMMARY -5

- Cement formulations are often selected on the basis of short term properties, e.g. of fresh grouts, and with little regard to the holistic scenario.
- Quality of cement-based formulations rests heavily on site practice. Research may prove performance but poor/inadequate QA can undermine its recommendations.

SUMMARY – FINAL THOUGHTS

Present knowledge is not fully adequate but it should be recognised that

- material performance in non-steady state conditions is always difficult to quantify.
- "performance" is a qualitative term: it has to be quantified by a subset of parameters that can be determined.
- quantitative models of cement performance need to be matched by holistic whole-of-repository performance models.

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

Les Dole,

Oak Ridge National Laboratory

July, 2006

Washington, DC

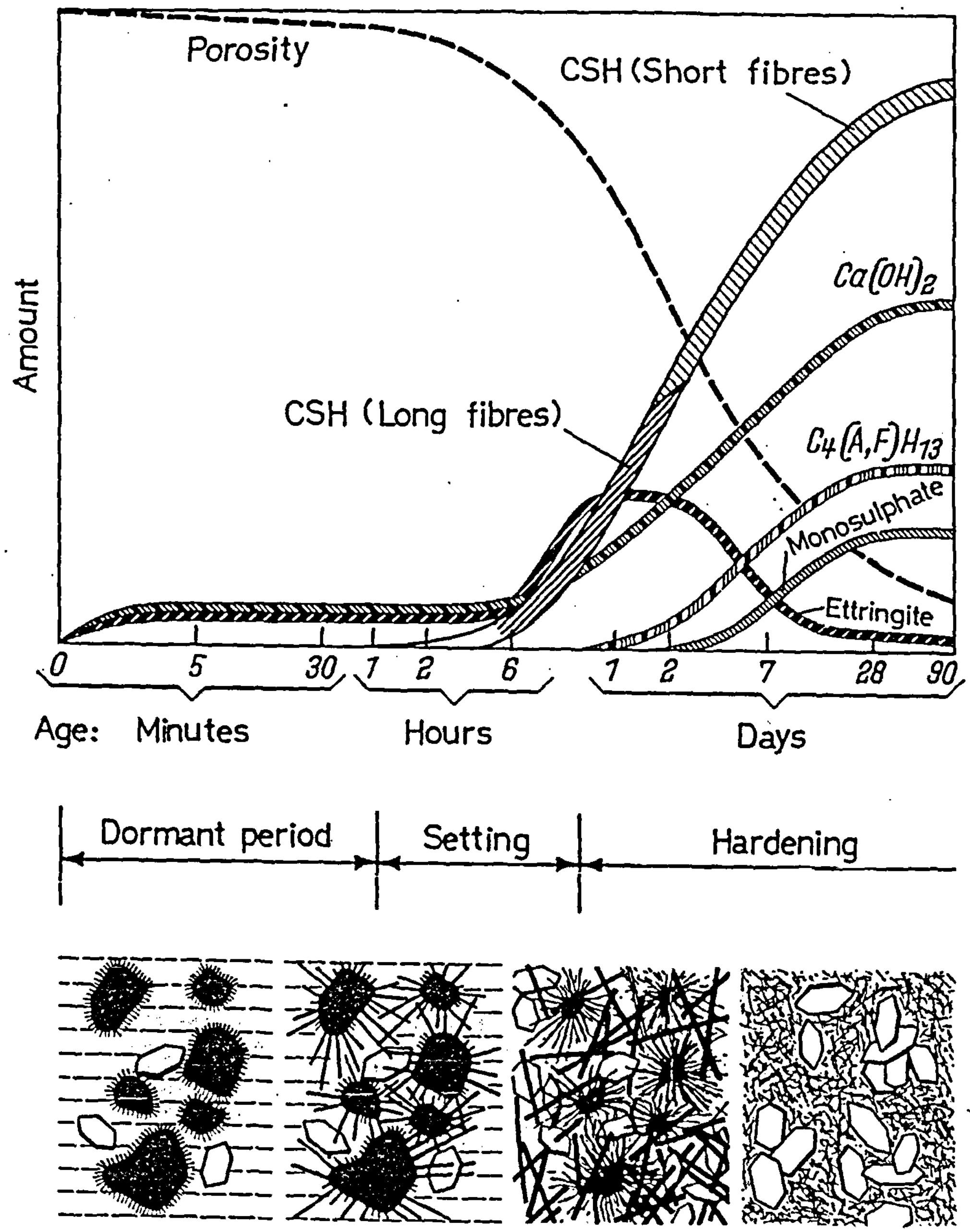
contact: dolelr@ornl.gov 865-576-4319

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

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

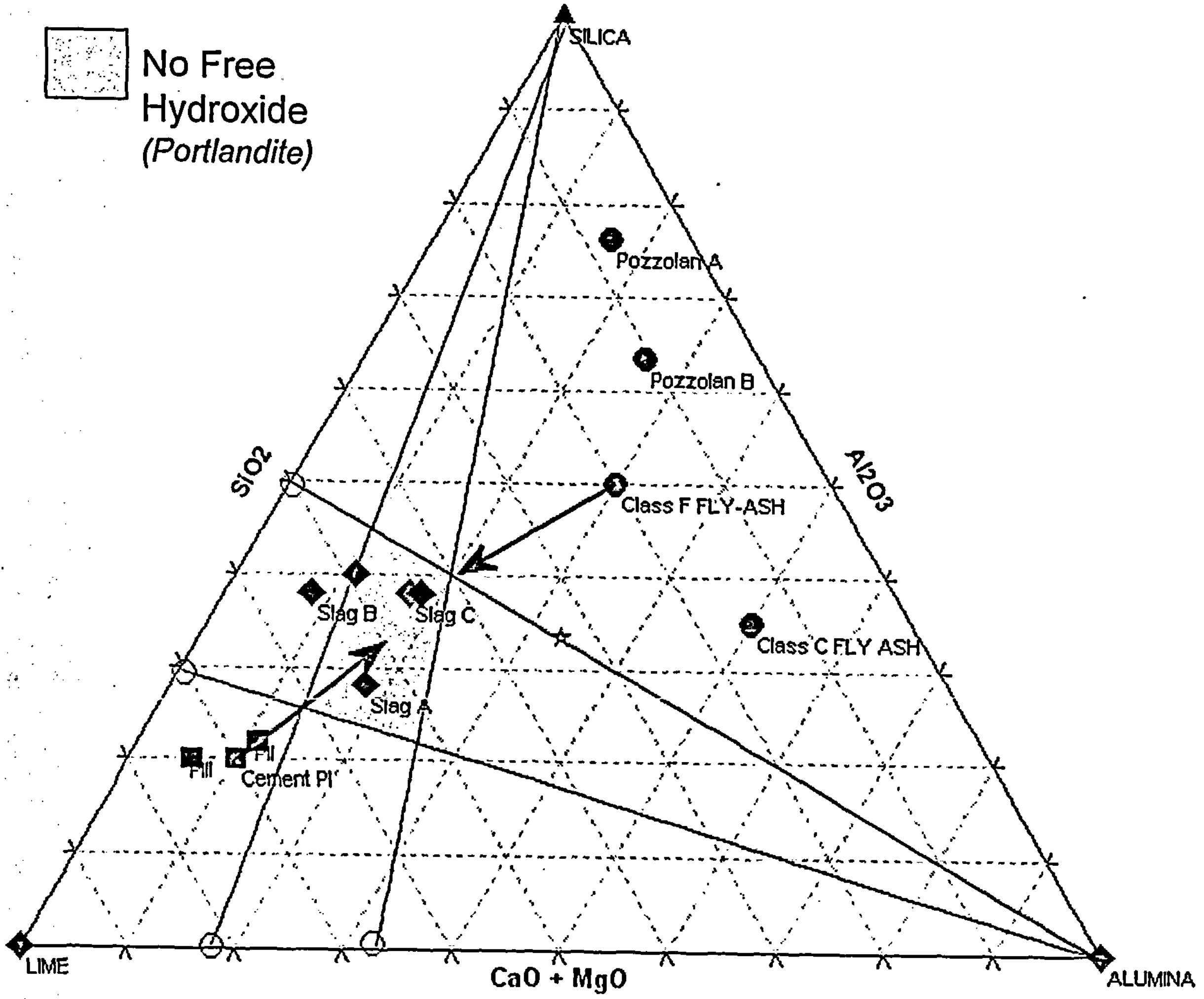
Evolution of the Cement with Time

- 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

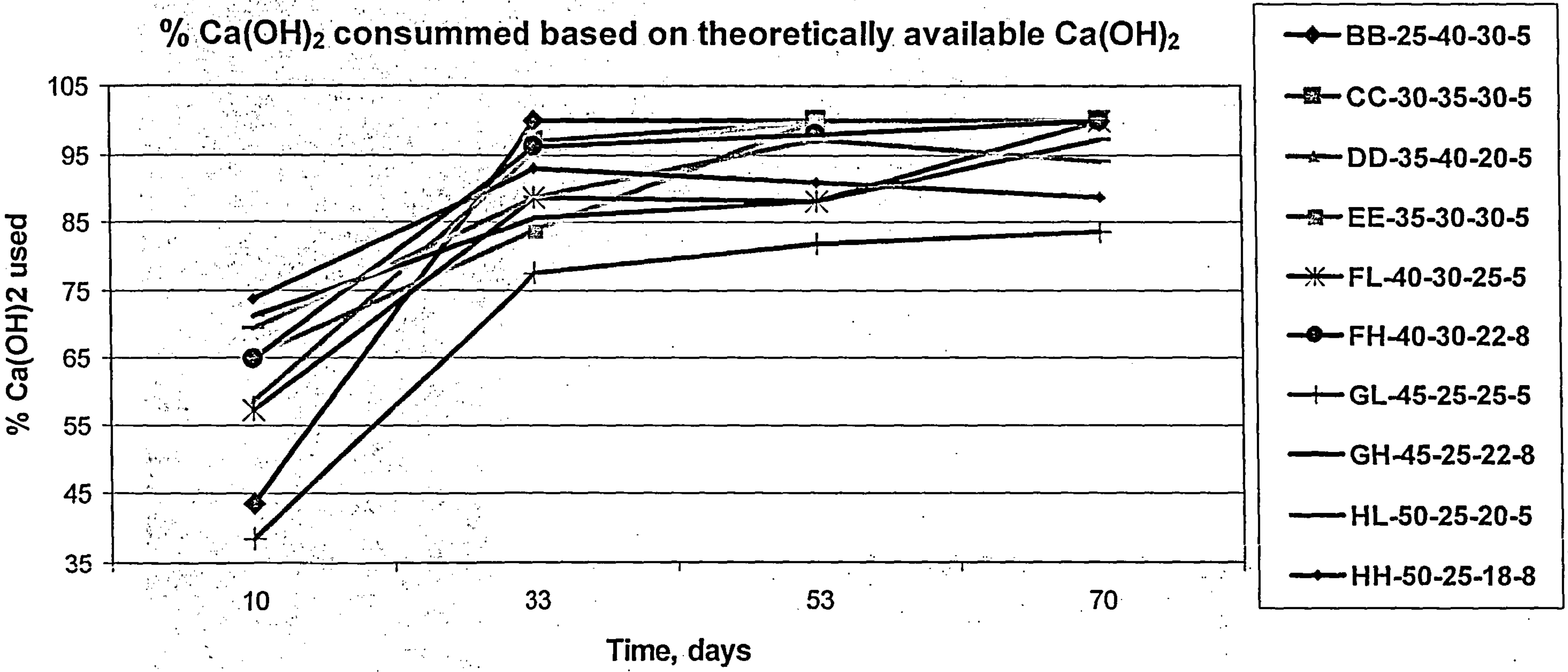
Material Choices to Mitigate Waste Constituents' and Groundwater Impacts on Waste Form Performance

- 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

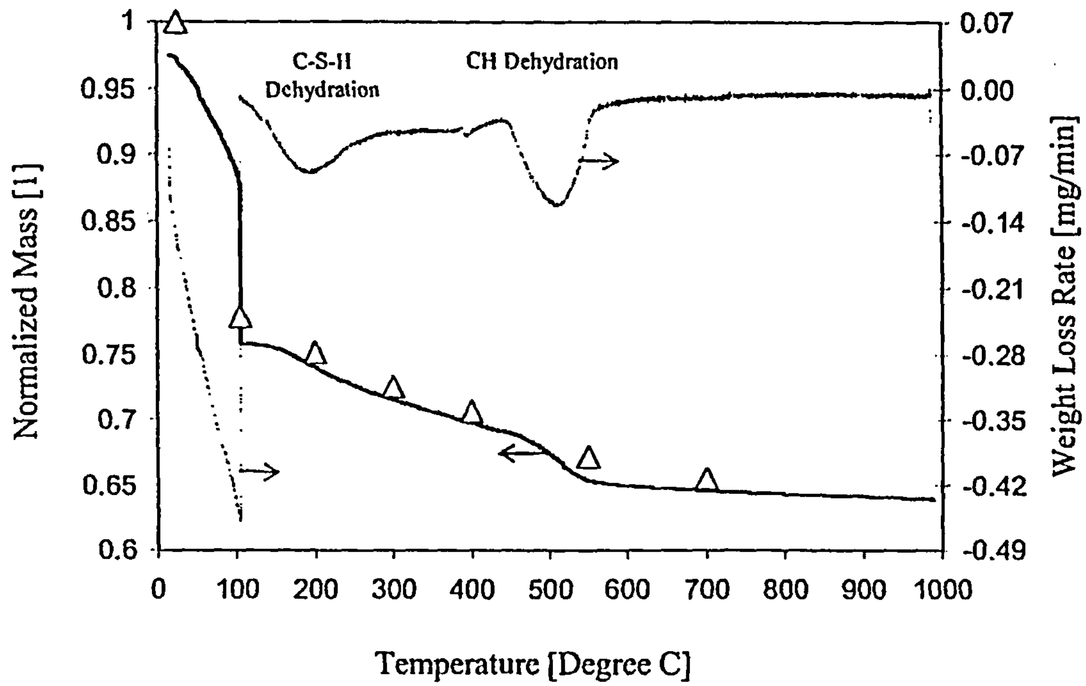


Figure 1: Results of thermogravimetric analysis (TG) on $w/c = 0.5$ cement paste: The normalized mass determined by TG (continuous line) is in excellent agreement with manual mass loss measurements of the specimens used for indentation (discrete points). The derivative of the weight loss (labeled 'weight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

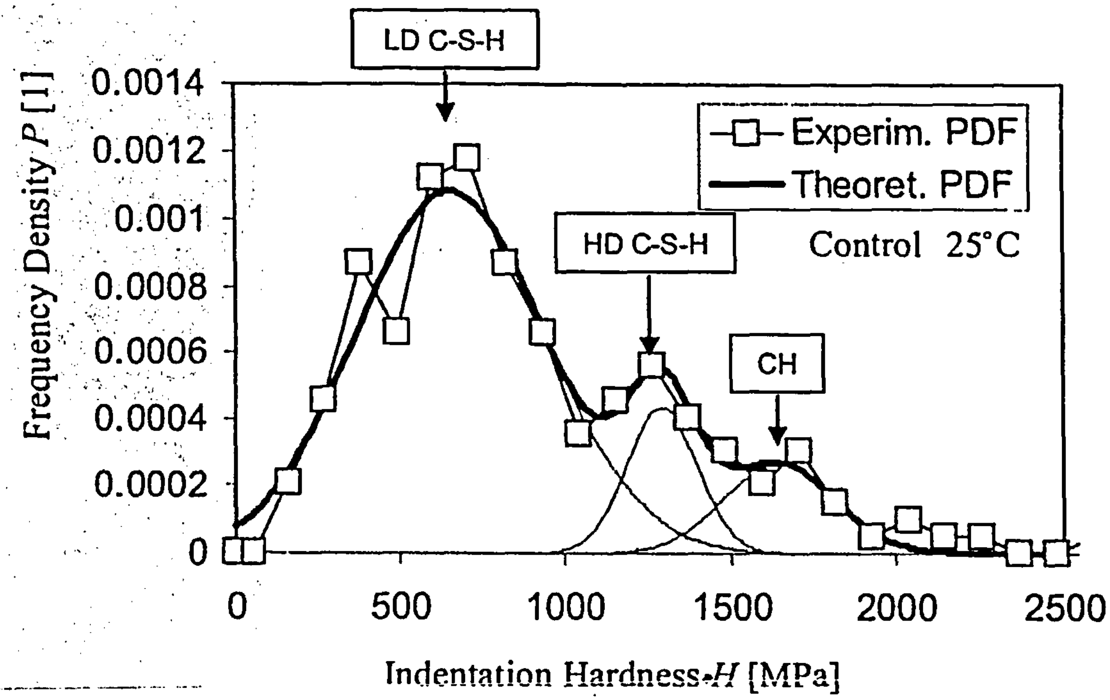


Figure 3: Frequency plots of indentation modulus and indentation hardness with fitted Gaussian curves for low-density (LD) C-S-H, high-density (HD) C-S-H, and Portlandite (CH). The deconvolution was carried out for a bin size of $\Delta M = 2.5$ GPa and $\Delta H = 110$ MPa.

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

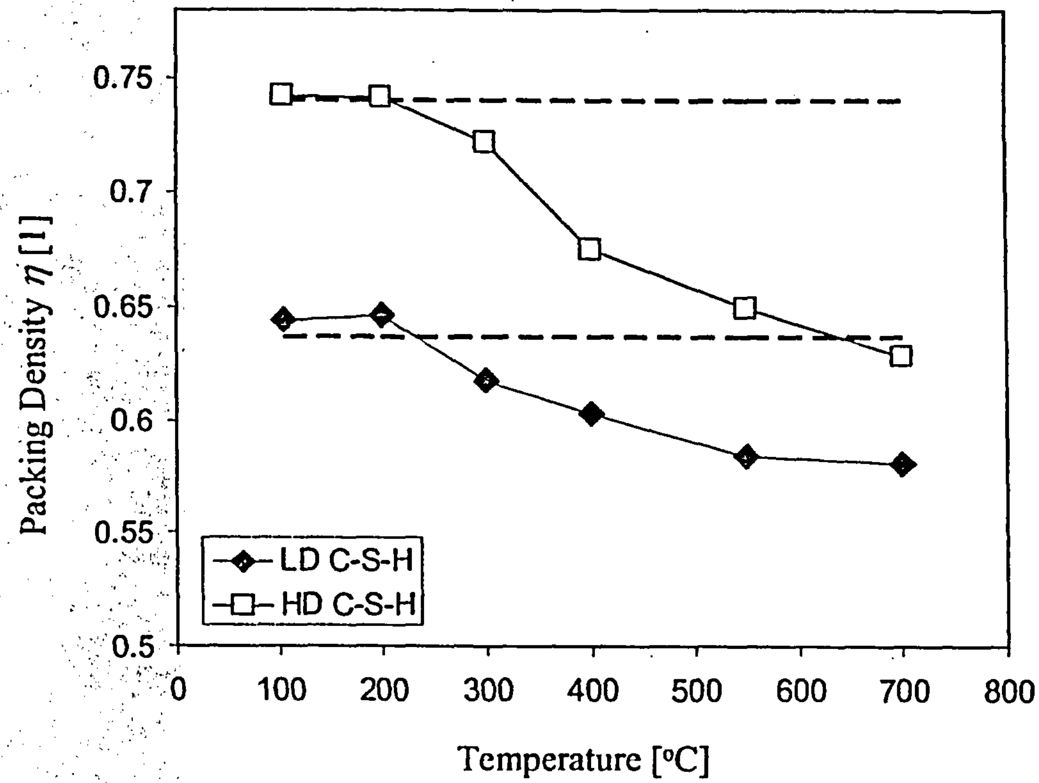
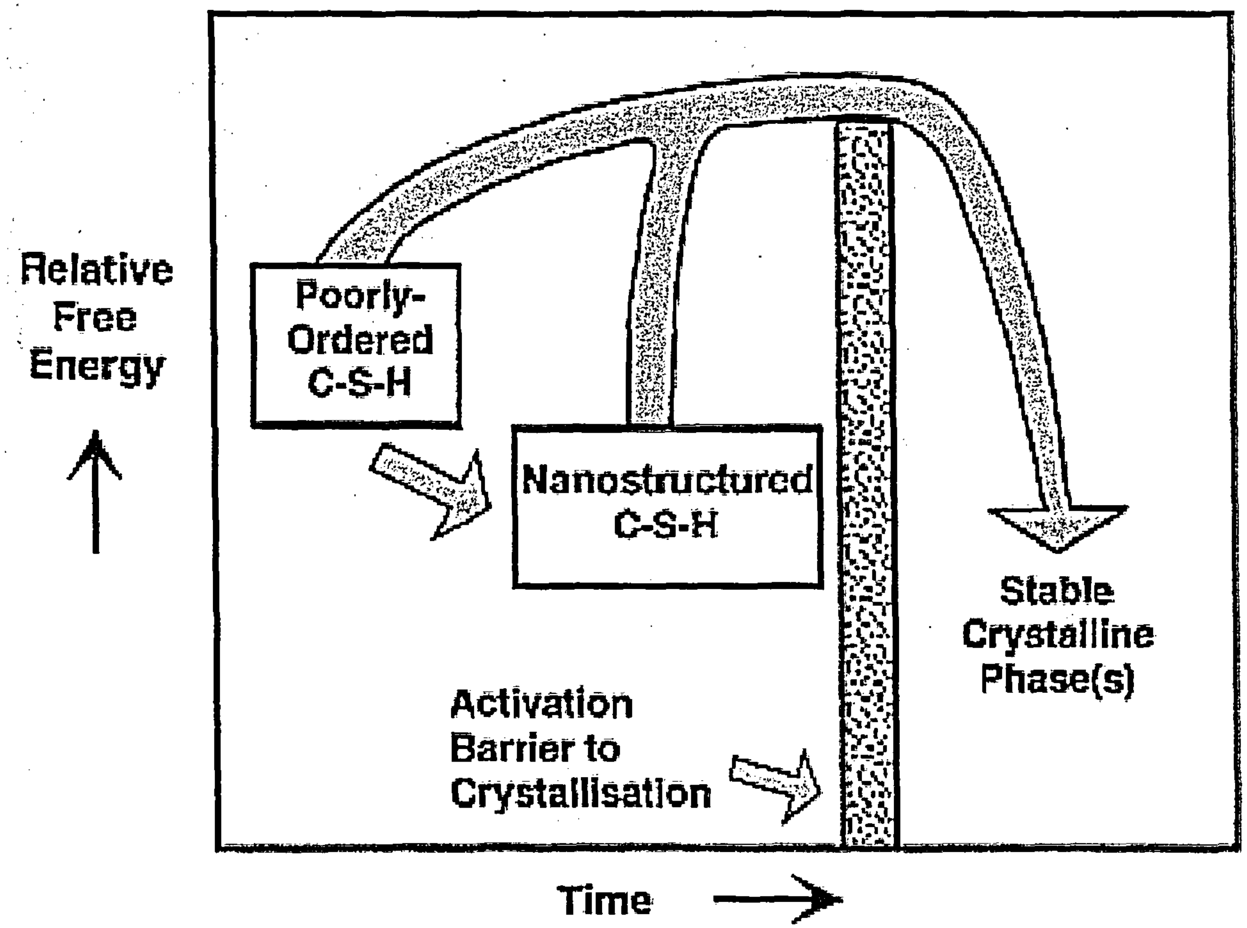


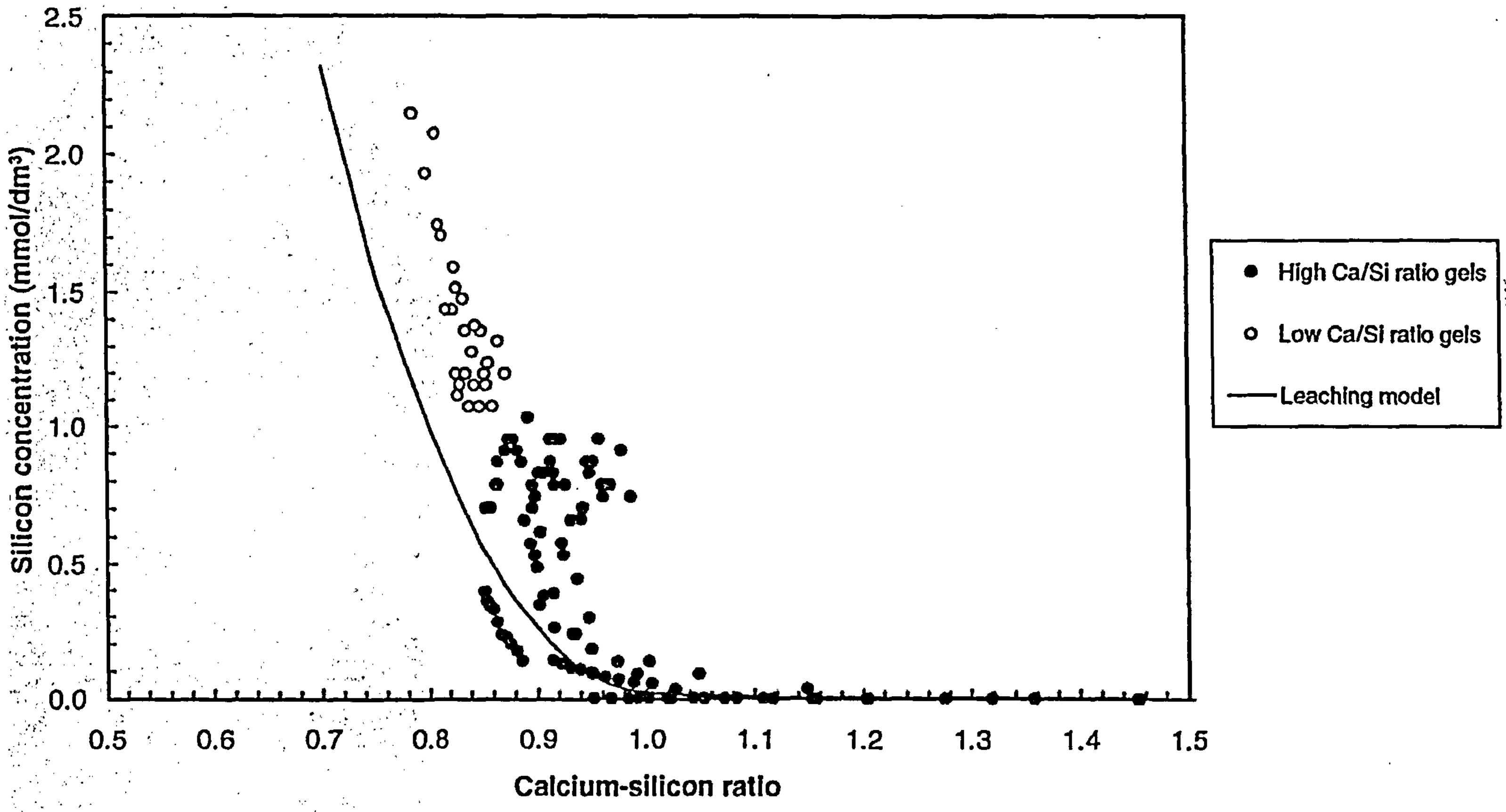
Figure 11: Packing density as a function of the exposure temperature determined from a reverse analysis of the micromechanics model (for $\nu_s = 0$). The broken lines represent the *limit* packing density values: $\eta_{LD} \approx 0.64$ and $\eta_{HD} \approx 0.74$.

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



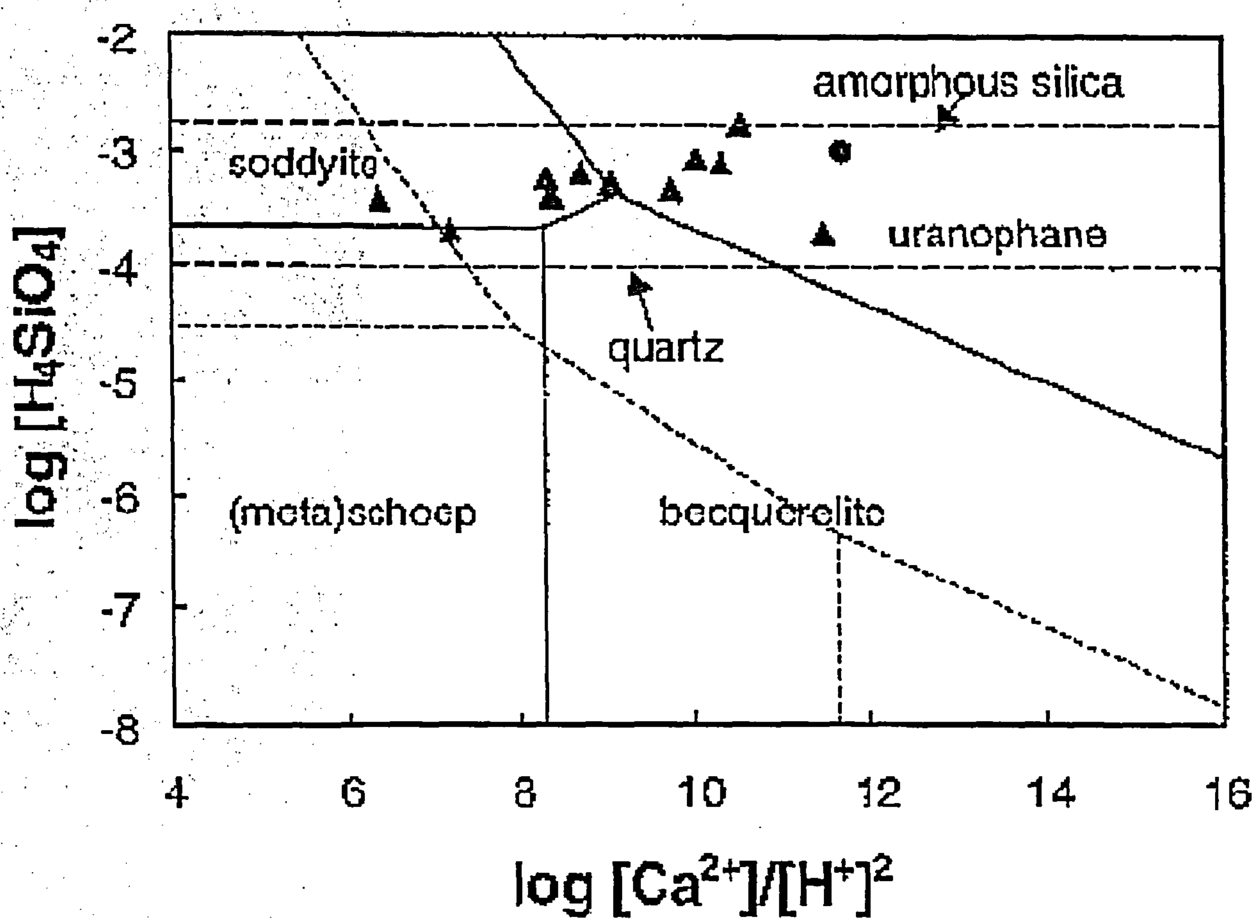
F.P. Glasser, S.-Y. Hong, Cement and Concrete Research 33 (2003) 271–279

Increasing Silica in Cement Increases Silica in Leachates

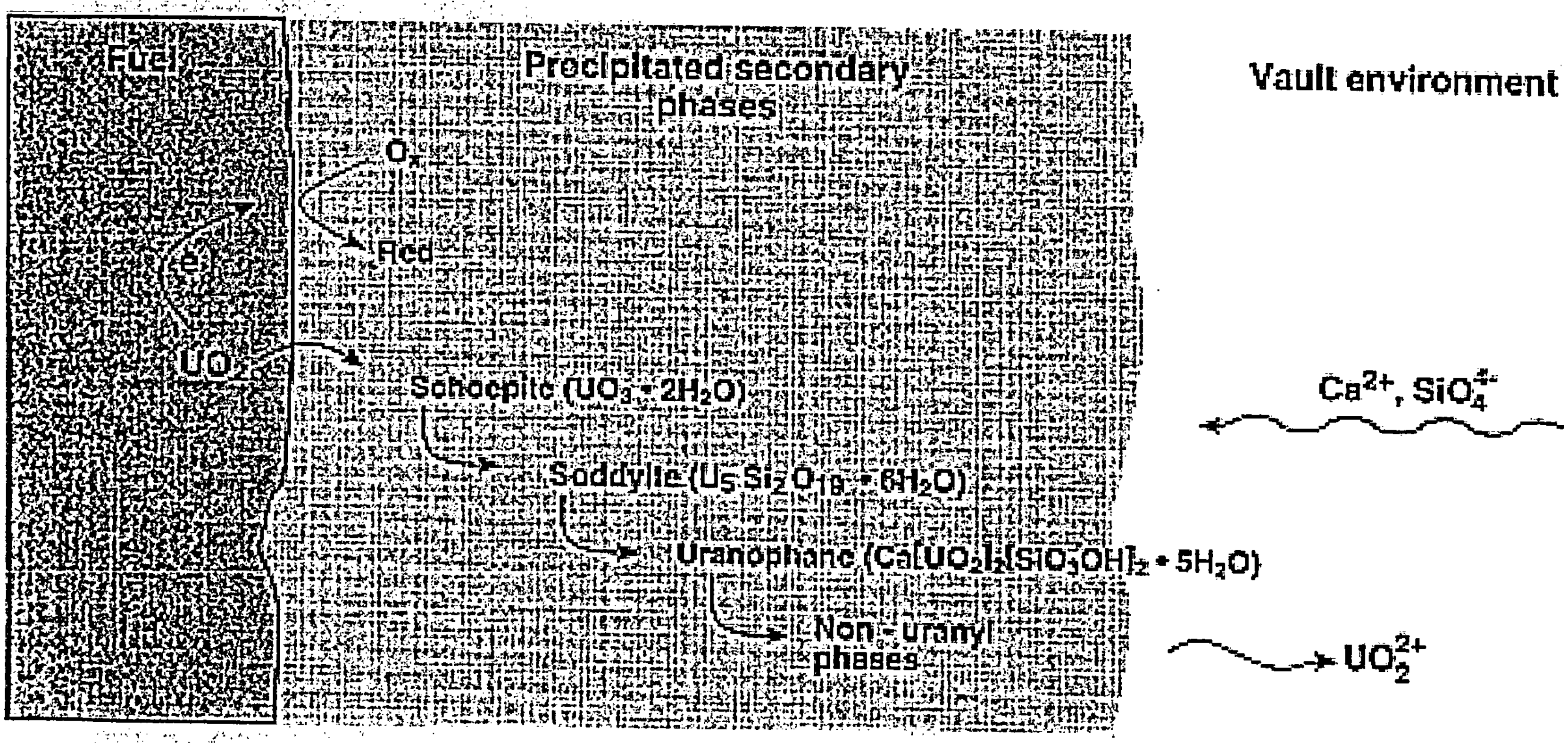


Harris, A.W., M.C. Manning, W.M. Tearle, and C.J. Tweed, Testing of models of the Dissolution of cements—leaching of synthetic CSH gels, Cement and Concrete Research, 32, pp 731–746, 2002.

High-Silica Forces Formation of Insoluble Uranium Silicates



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



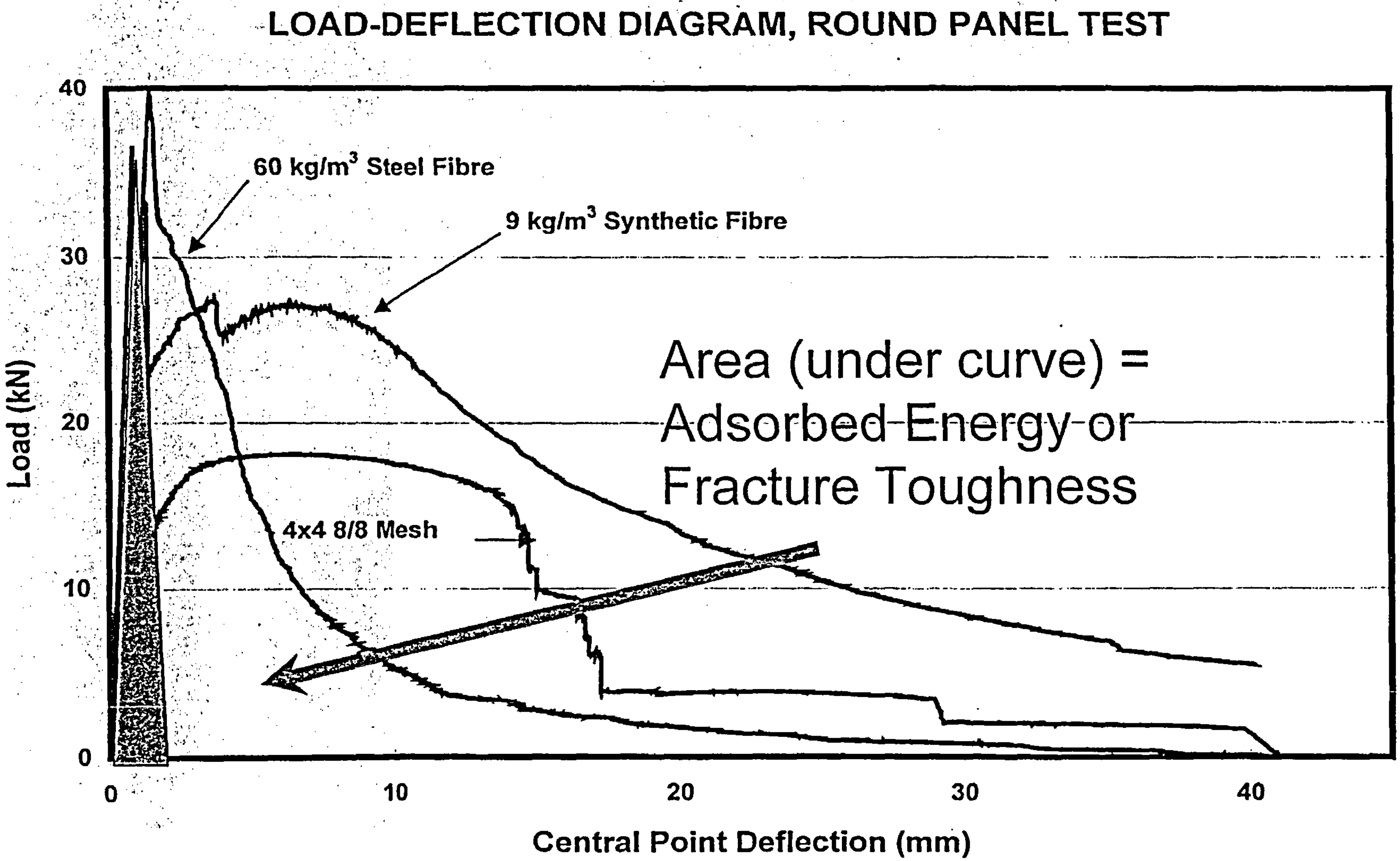
Principal U(VI) Compounds

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.

C C C

Missing Links Between Studies of Ancient Cements and Laboratory Tests

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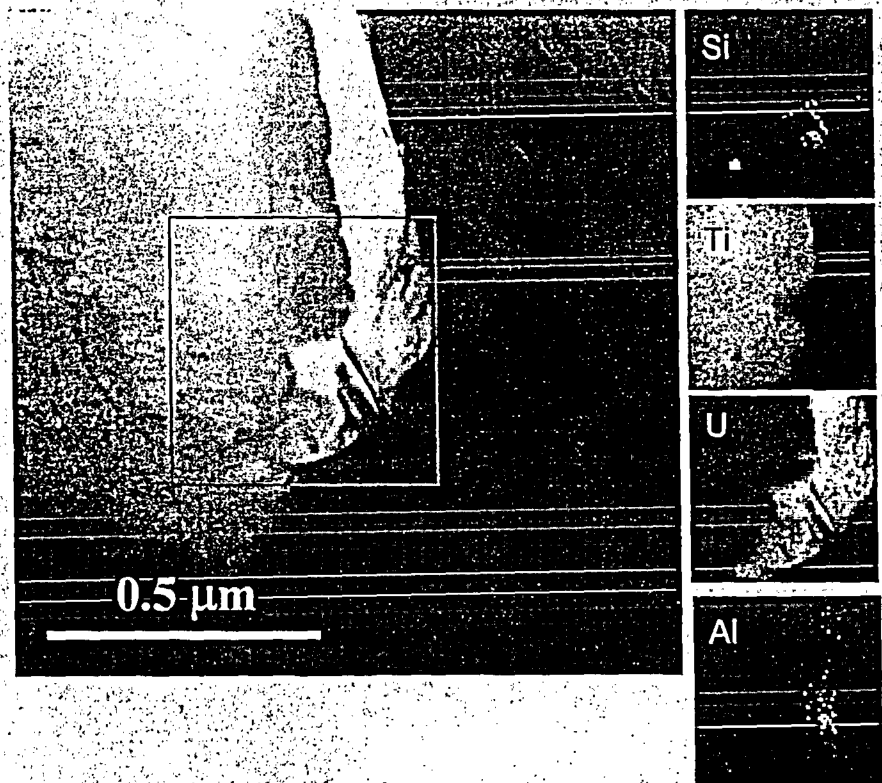
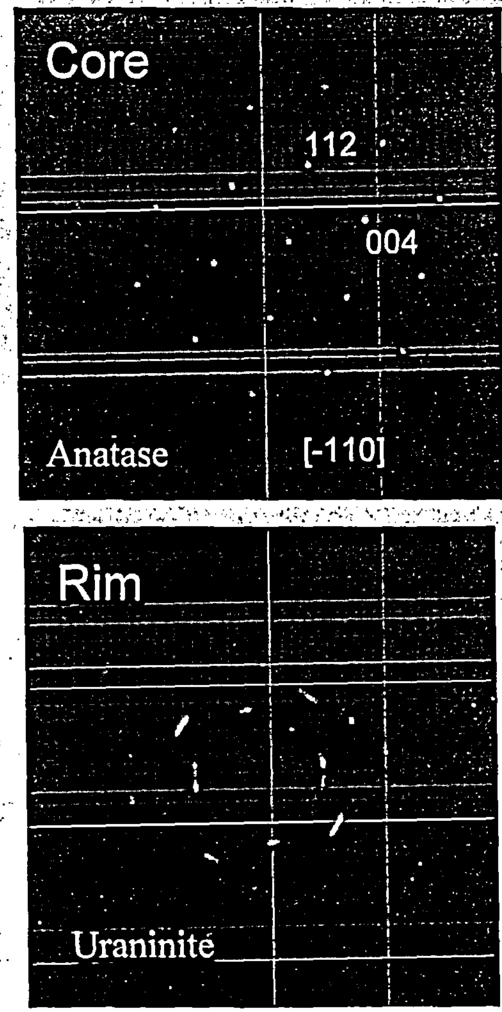
  - Need for models for metastable intermediates trapped by diffusion-controlled metamorphisms
- Microprobe analytical tools to see start of phase transitions

Transmission Electron Microscopy



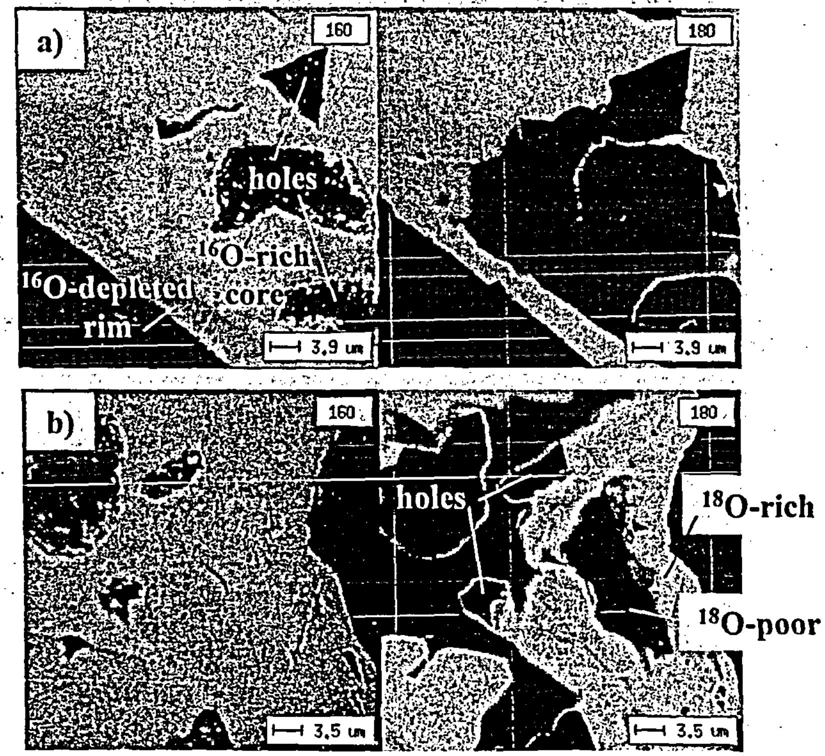


Scanning transmission electron microscope (STEM) images of U and Ti minerals

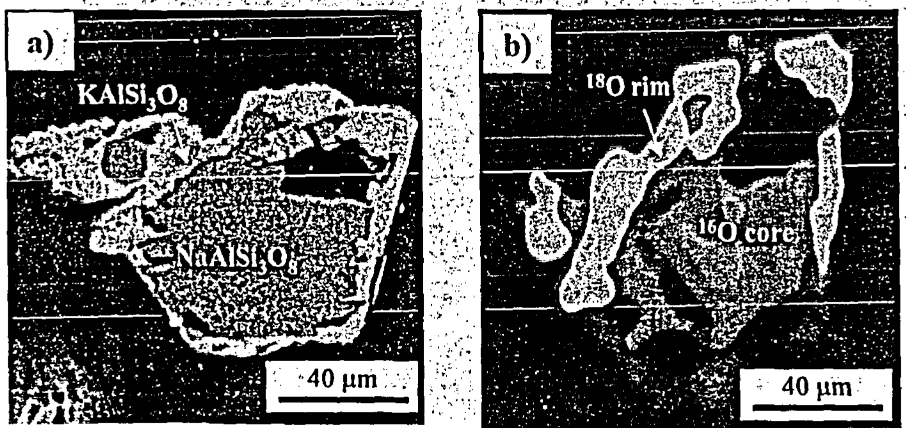
Secondary Ion Mass Spectrometry

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.

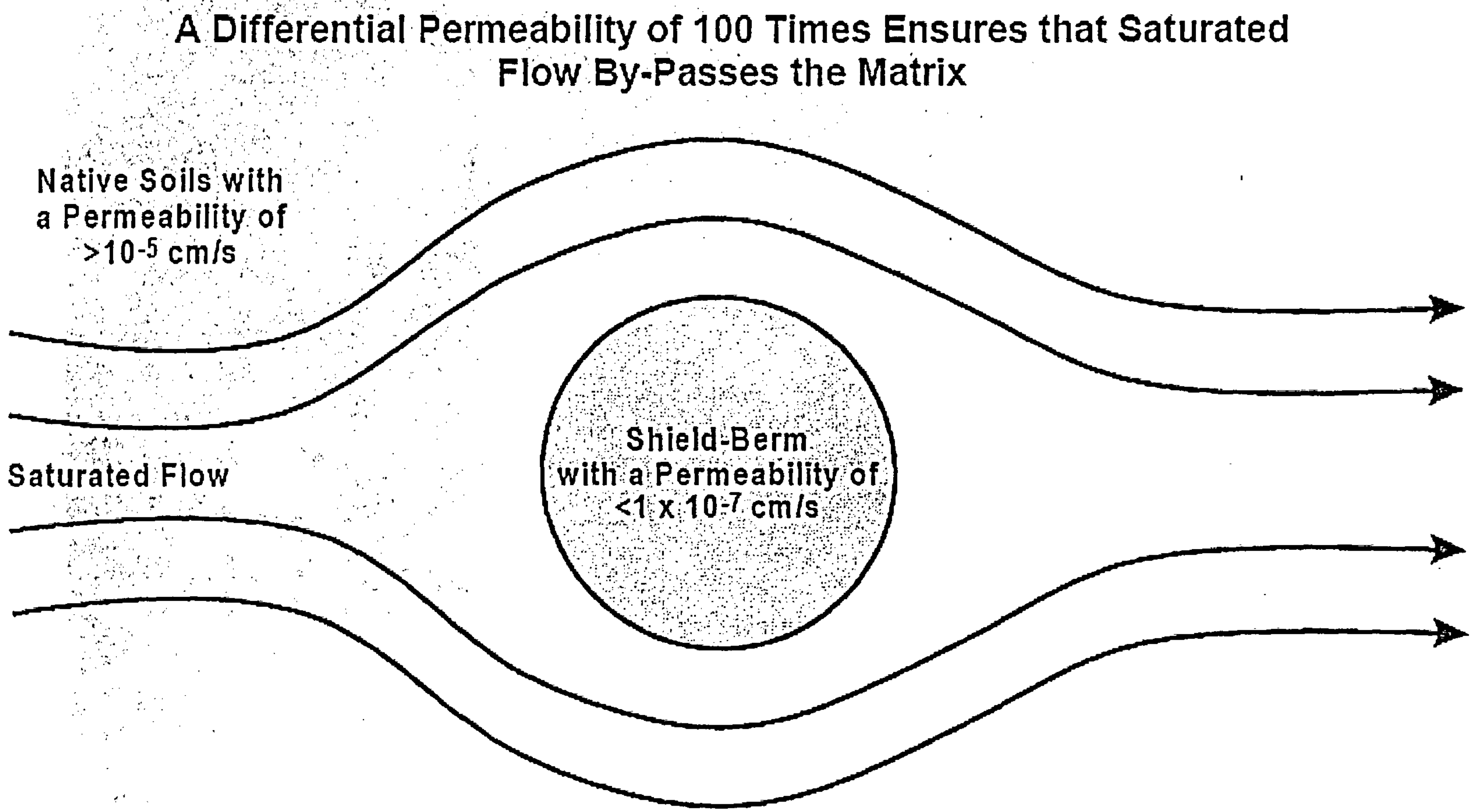


C C C

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:

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

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

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

Fraction Released

$F_{30} = 0.091$

$F_{300} = 0.303$

$F_{500} = 0.379$

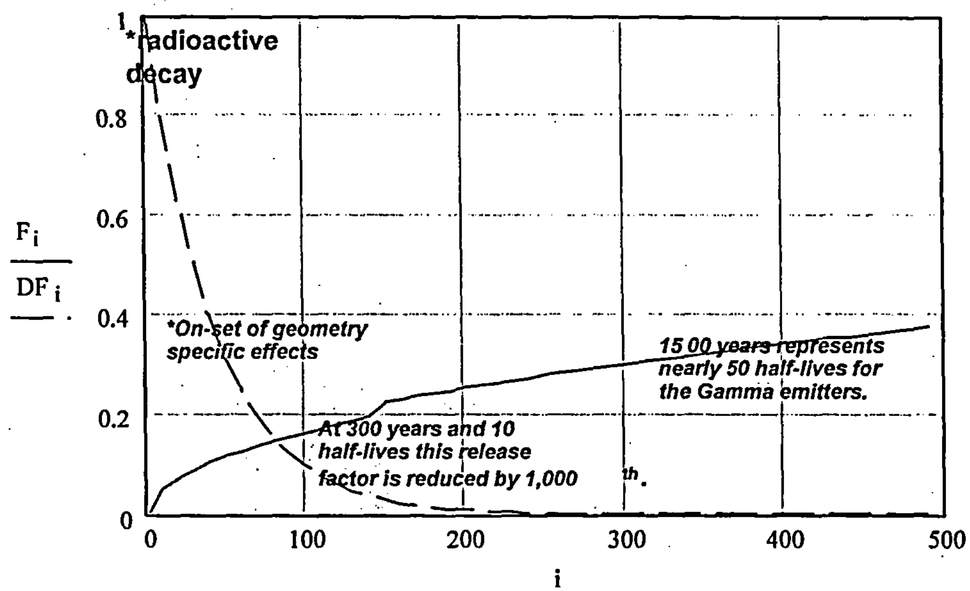
Radioactive Decay Factor

$DF_{30} = 0.5$

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

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

CURIE RELEASE FROM W9 MONOLITH as Sr-90



Decay Fraction X Release Fraction

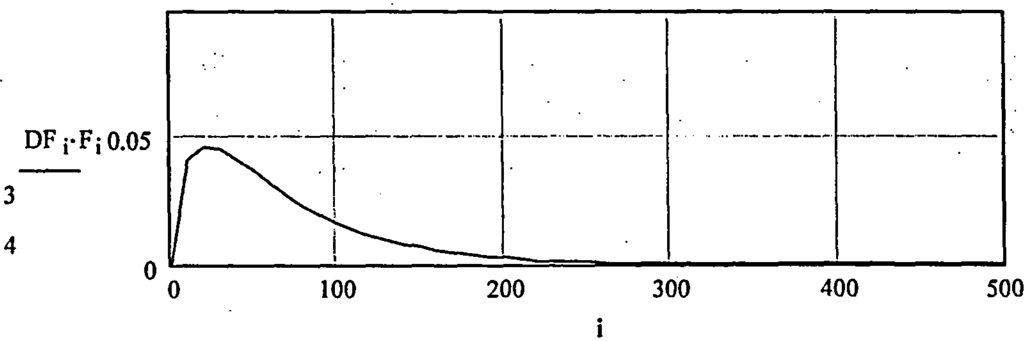
$DF_{30} \cdot F_{30} = 0.045$

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

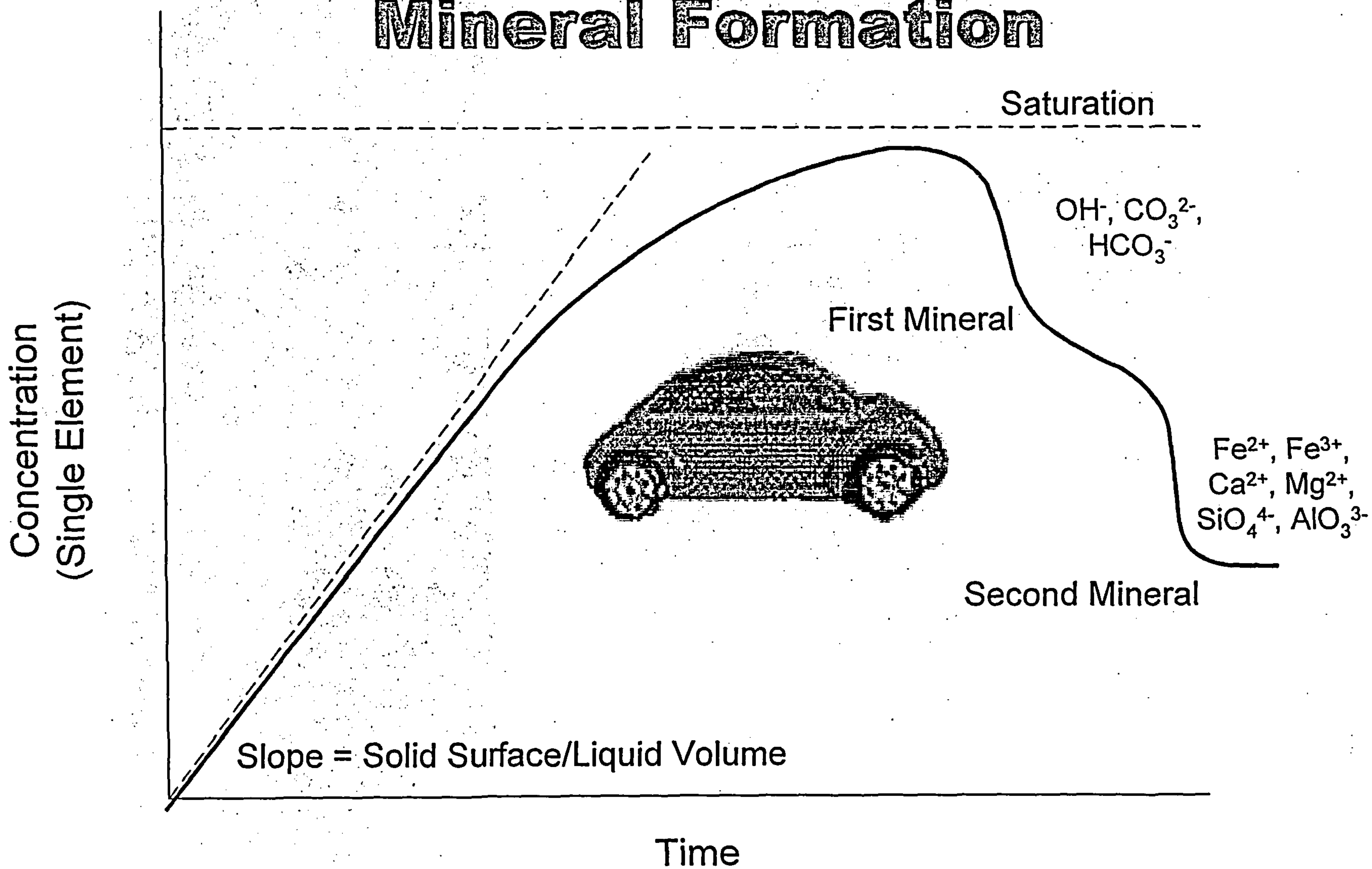
$DF_{150} \cdot F_{150} = 7.047 \times 10^{-3}$

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

Combination of Decay and Diffusion Controlled Release



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

Carl Steefel and John A. Apps

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

Carl Steefel and John A. Apps

Modeling Long-Term Durability of Cementitious Materials (LBNL)

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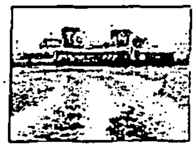
Carl Steefel and John A. Apps

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

Current capabilities to predict the conditions and processes important to cement failure: Computation





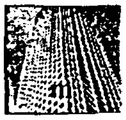
Edward J. Garboczi
Materials and Construction Research Division
Building and Fire Research Laboratory
National Institute of Standards and Technology
ACNW 7/18/06

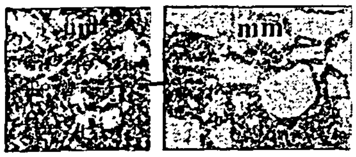
Discussion of current capability to predict the conditions and processes important to cement failure, and the effect of failures on cement performance, based on computation

NIST Inorganic Materials Group

- Provide scientific and technical foundations for performance-based selection and use of concrete
  - improved materials science basis for accelerated tests and performance-based standards
- Complexity of concrete problems demands computational materials science
  - validated computational tools for industry and government

The Length Scales of Concrete





Main NIST materials research

Note: Durability prediction requires information at all length scales

Early stage research

Definition of problems

- Time scales
- Structural complexity

Shorter time scale

- Low transport property barrier structure
  - Higher structural complexity (e.g. new nuclear power plants)
  - Lower structural complexity (e.g. low-level radioactive waste isolation)
- Should remain crack-free, immune to usual degradation processes over 100-300 year time span
- Must also remain resistant to any other chemicals that might be in the waste (e.g. WIR, spent fuel pools)
- Prediction is not an easy problem

Longer time scale

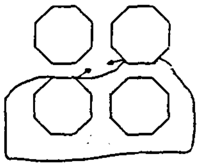
- Longer time spans – concrete must continue to function as physical and chemical containment
  - Must avoid usual shorter-term degradation processes
  - There are ways to make progress on this (later)
  - Prediction is even harder than in the shorter time scale case

General problem of cement-based materials

- Why is prediction difficult?
- Formation, properties, and degradation are hard to compute for any time scale, using basic science, since they all involve the complex interplay of:
  - Chemistry
  - Microstructure
  - Micro-mechanics
  - Cracks

Example: Formation

- Hydration induces chemical shrinkage (products take up less space than reactants)
- Chemical shrinkage results in air-water menisci (self-desiccation)
- Menisci induce tensile stresses
- Tensile stresses induce cracking



Example: Degradation

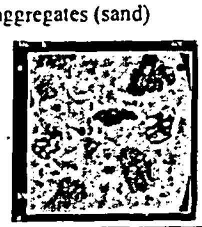
- Alkali-silica attack – alkaline pore solution reacts with amorphous silica in aggregates, produces gel that can swell and cause cracking in aggregates and cement paste
- Introduction of fibers near aggregate-paste interfaces can reduce cracking and change kinetics and products of ASR reaction (Ostertag, Berkeley)

Example: Cracking

- Predicting change in transport properties due to cracks is possible, provided that the cracks can be characterized spatially and topologically
- Predicting the occurrence of cracking is harder, much better to prevent in the first place
  - structural design
  - concrete mix design
  - proper curing

Alleviate cracking

- Internal curing
- Supply water reservoirs inside the concrete, which can be drawn on when local supply of water runs out
- One example – water tied up inside porous fine aggregates (sand)



2-D image with water evacuated regions (pores) overlaid on original mortar microstructure (4.6 mm by 4.6 mm)

Mineral Admixtures

- A monkey wrench?
  - fly ash, blast furnace slag, metakaolin, silica fume are very common these days
  - their reactions and interactions are not well-understood
- Used to deliver (usually successfully, if no additional cracking) many things, including low permeability, low heat of hydration
  - tend to ameliorate usual degradation mechanisms
  - also tend to lower pH of pore solution, so trade-off with cements containing no admixtures
- Internal curing probably more important with mineral admixtures, as chemical shrinkage is greater than with plain portland cement (Bentz, NIST)

Predicting durability/failure from first principles

- Need to correctly predict:
  - *transport and reaction mechanisms*
  - interdependence of material microstructure and properties (transport and mechanical) and how both change with time
  - expected service environment
  - relevant thermodynamics
- Predictions must be accompanied by the results of valid accelerated tests

NIST current capabilities in prediction

- Highlight is the VCCTL = Virtual Cement and Concrete Testing Laboratory
  - use known physics, chemistry, and materials science to develop predictive models of properties and performance
  - role of experimental materials science
  - role of computational materials science
  - focused mainly, for now, for predicting current properties
  - intent is to be able to use for durability in the 50 year to 100 year time frame

VCCTL partners

GRACE Construction Products
Sika
BASF Master Builders
Chemical admixtures

ICAR International
Aggregate manufacturers

NRMCA
Ready-mixed concrete

Verein Deutscher Zementwerke e.V. Forschungsinstitut der Zementindustrie
ATILH
PCA Portland Cement Association
Cement manufacturers

VCCTL 5.0

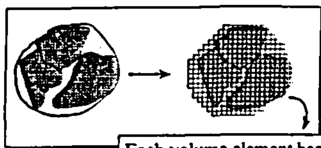
Databases
Build Microstructure
Hydration
Analysis
$\frac{\partial C_i}{\partial t} = \nabla \cdot (L_{ij} \cdot \nabla \mu_j)$
Transport Properties
Rheology
Mechanical Properties
Degradation

Some current prediction capabilities

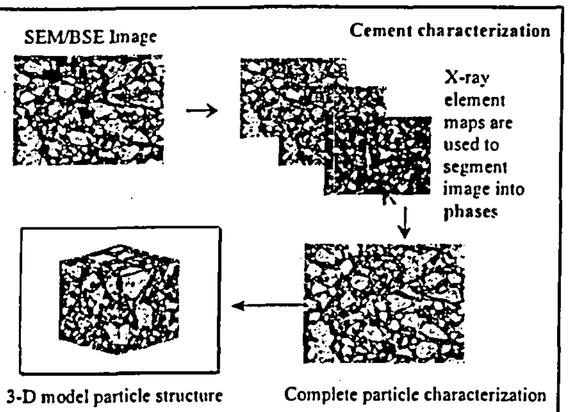
- Hydration – microstructure formation – chemical interaction
- Rheology
- Micro-mechanics
- Transport
- Thermodynamics
- Accelerated durability tests

Cement hydration modeling approach

- Microstructure-based
  - Spatial resolution at the sub-particle level using small volume elements



Each volume element has properties of the phase at that location in space



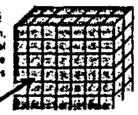
Change in models

- Current cement hydration model is rule-based physical model but with rules based on chemistry
- Now working on a true chemo-physical model - HydratiCA
- Note: working with admixture companies
  - lots of experience with inorganic and organic chemicals interfacing with cement chemistry
  - applications to "dirty" cement?

HydratiCA

- Object-oriented approach (C++)
  - Algorithms designed to model reaction-transport equations
  - Third-generation hydration model
  - Real kinetics

Mesh Class
Dimensions, resolution, clock, phase stats, thermal condition, moisture conditions, databases



Node Class
neighbors, volume, materials, methods for transport and reaction

Derived Material Classes
(Liquid, Solid, Gel, Crystal, Solute)
Methods for material-specific behavior encoded here

Base Material Class
ID, composition, ρ, Ω, C_p, ΔH, log K_{sp}, porosity, mobility, virtual methods for material-specific behavior

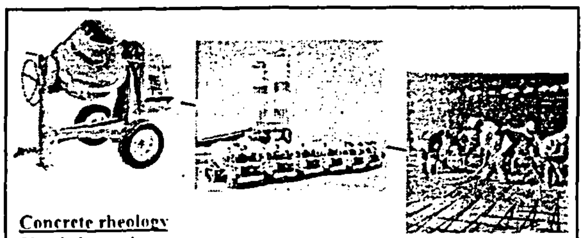
Material Database Class

Reaction Database Class
ID, reactants, products, molar stoichiometric coefficients, activation enthalpy, baseline rate constant

Ion Database Class
ID, mol wt, radius, intrinsic diffusivity, charge (immutable)

"A-void-ing" voids in new concrete

- Rheology – viscosity and yield stress
- Measure experimentally
- Predict computationally
- Modern drive in rheological research in concrete has been self-consolidating concrete
  - ideal for heavily reinforced structures

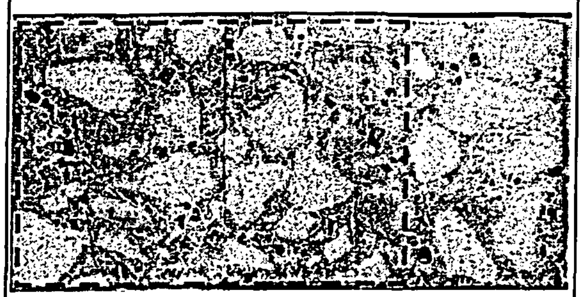


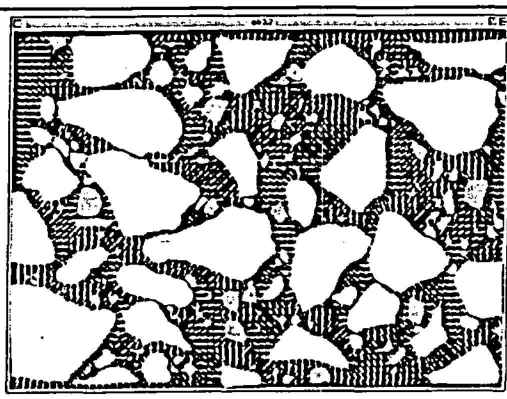
Concrete rheology
Simulation and measurement of the mixing, flow, and consolidation process

Micro-displacement in concrete

- Many different mechanisms:
  - Alkali-silica reaction (aggregate expands)
  - Freeze-thaw (paste expands, sometimes aggregate expands)
  - Sulfate attack (paste expansion)
- Common to all mechanisms:
  - Tensile and compressive stresses are set up due to differential expansion/shrinkage between phases
  - Distribution of tensile stresses drive cracking

Finite element modeling at the microstructural level





Probable crack directions (all aggregates expand)

Transport + reaction + degradation

- Transport via concrete pore solution – a nasty problem
  - High ionic strength
  - High pH (10-14)
  - Many chemical species
- Full problem is coupled problem:
  - Transport + reaction + degradation → change in transport properties via changes in microstructure
- Requires a physico-chemical approach: **4SIGHT**

Concrete performance assessment

- 4SIGHT – trying hard to avoid empiricism
  - *model of transport and reaction in concrete pore solution*
  - fundamental physico-chemical treatment of concentrated ionic solution
  - can accommodate many ionic species
  - can predict onset of severe degradation
  - not a model of mechanical failure
  - can be systematically extended to:
    - radionuclide chemistry
    - other species like boric acid
    - surface complexation

Refs: K.A. Snyder et al., Cem. Conc. Res. 33, 793 (2003); K.A. Snyder, Conc. Sci. Eng. 3, 216 (2001); K.A. Snyder and J. Marchand, Cem. Conc. Res. 31, 1837 (2001).

Thermodynamics

- A possible experimental approach for simulating longer-term problems:
  - determine, thermodynamically, what crystalline C-S-H phases there will be at advanced ages (> 10^4 years)
  - synthesize in laboratory and measure properties (e.g., binding of radionuclides)
  - we are presently synthesizing some of these minerals
- Note: oil well cementing people work at high T and P, where crystalline phases form instead of metastable amorphous C-S-H – can we make use of their experience?

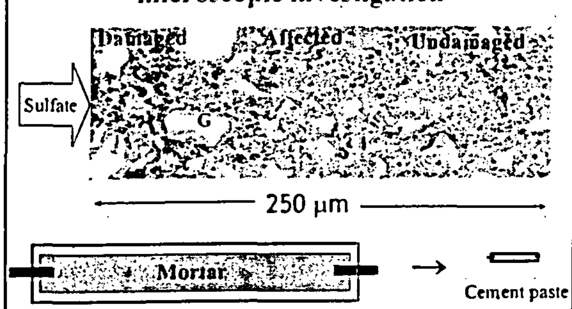
Current "accelerated" durability tests

- Lots of standard durability tests
  - most purport to be "accelerated" tests
  - acceleration is totally empirical
- Typical test
  - make bar and drop into bucket of concentrated "bad stuff"
  - measure length change every so often
  - after six months, do for another six months because answer is not clear
  - repeat (endlessly)

Start of a more correct procedure

- Development of an accelerated sulfate attack test (in collaboration with PCA)
  - small samples and controlled environment
  - factor of 3-5x time faster than old method
  - still empirical acceleration but with SEM investigation of mechanism of chemical/microstructural attack

Sample size reduction and microscopic investigation



The way forward for durability

- Radionuclides and compounds like boric acid should be handled in a similar way
  - *enumerate possible reactions*
  - use SEM to quantify microstructural effects of degradation products
  - add binding chemistry measurements
  - correctly accelerate degradation mechanisms
  - use small samples, high throughput

Research needs

- Further development of HydratiCA, add information on ionic species of interest to radioactive waste containment problems
- Further development of 4SIGHT, eventual unification of 4SIGHT and HydratiCA
- Fundamental research needed on properly accelerating correct degradation mechanisms
  - mechanistic research needed
  - *research into complex chemistry of WIR applications*
- Experimental measurements on properties of cement pastes composed of thermodynamic endpoints of C-S-H, eventual computational modeling

Summary

- Combine
  - prediction tools based on carefully characterized materials and fundamental physics and chemistry and thermodynamics
  - materials-science based standards experiments using small samples, controlled environment, acceleration of correct mechanisms, crystalline "C-S-H" forms

- Produce
  - accurate predictions of the durability of cementitious materials
  - long term durability prediction for NRC
  - predictable durability for concrete industry