Cementitious Materials Compatible with Yucca Mountain Geochemistry

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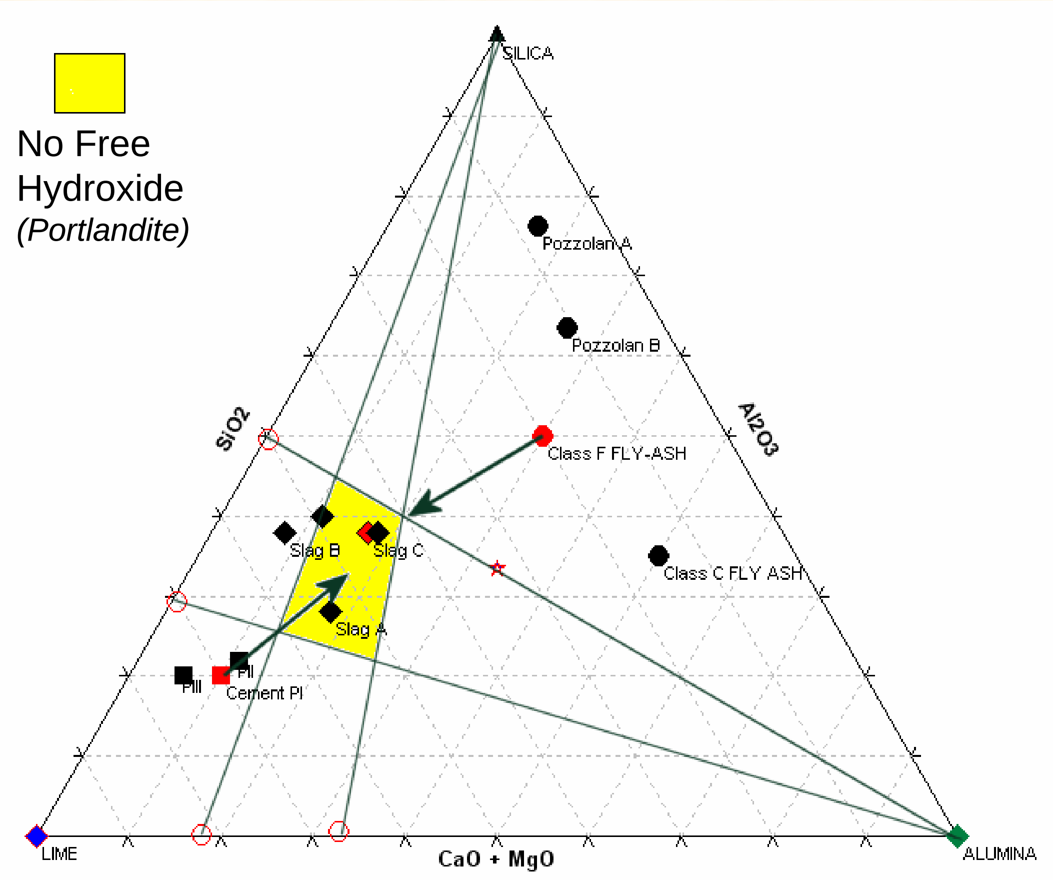
Outline of Current Draft Proposal to Yucca Mountain Project

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



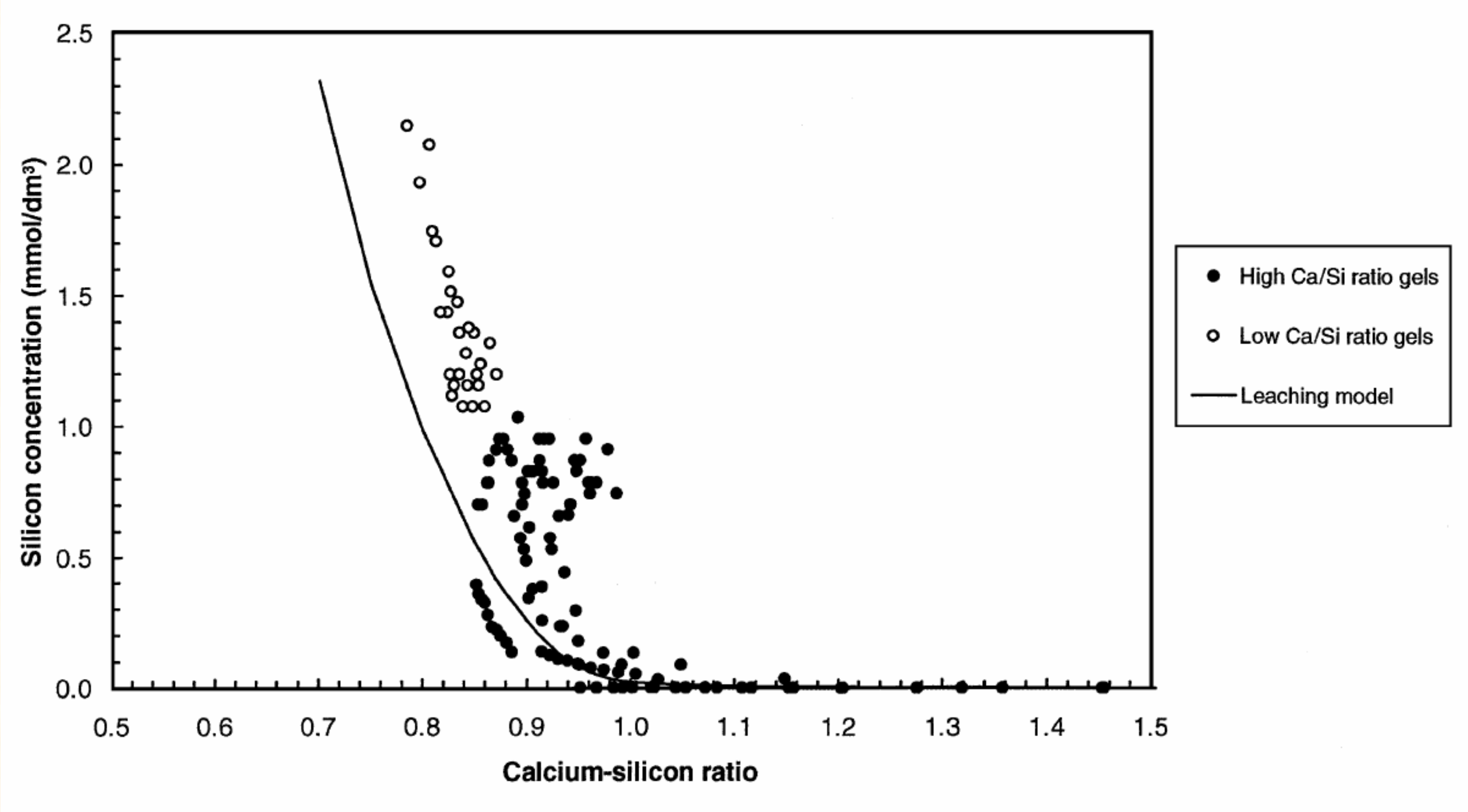
Five YMP Historical Issues with Cementitious Construction Materials

YMP Model Assumptions	Mitigated by High-Silica Cements
Concrete pore solutions with a high pH could increase radionuclide solubility and mobility	High-silica cements reduce the pH of leachates that then react to form insoluble silicates
Water from dehydration of concretes increase the relative humidity in tunnels and drifts	Very fine capillary texture of high-silica cements will minimize moisture loss
The porosity, permeability, and transport properties of the adjacent formation could be changed to effect higher nuclide transport rates	Silica saturated leachates will reduce the porosity and permeability in adjacent vitreous tuff
Superplasticizers in the concrete matrix could form organic acids increasing nuclide transport	High-silica additives are water-reducers and lessen or eliminate the need for organic-surfactants
Organics and sulfate in the concretes could provide nutrients for microbiological growth accelerating corrosion of packages	Can support colonies of biota, but microorganisms cannot extract nutrients from high-silica cements

Unique features of proposed study

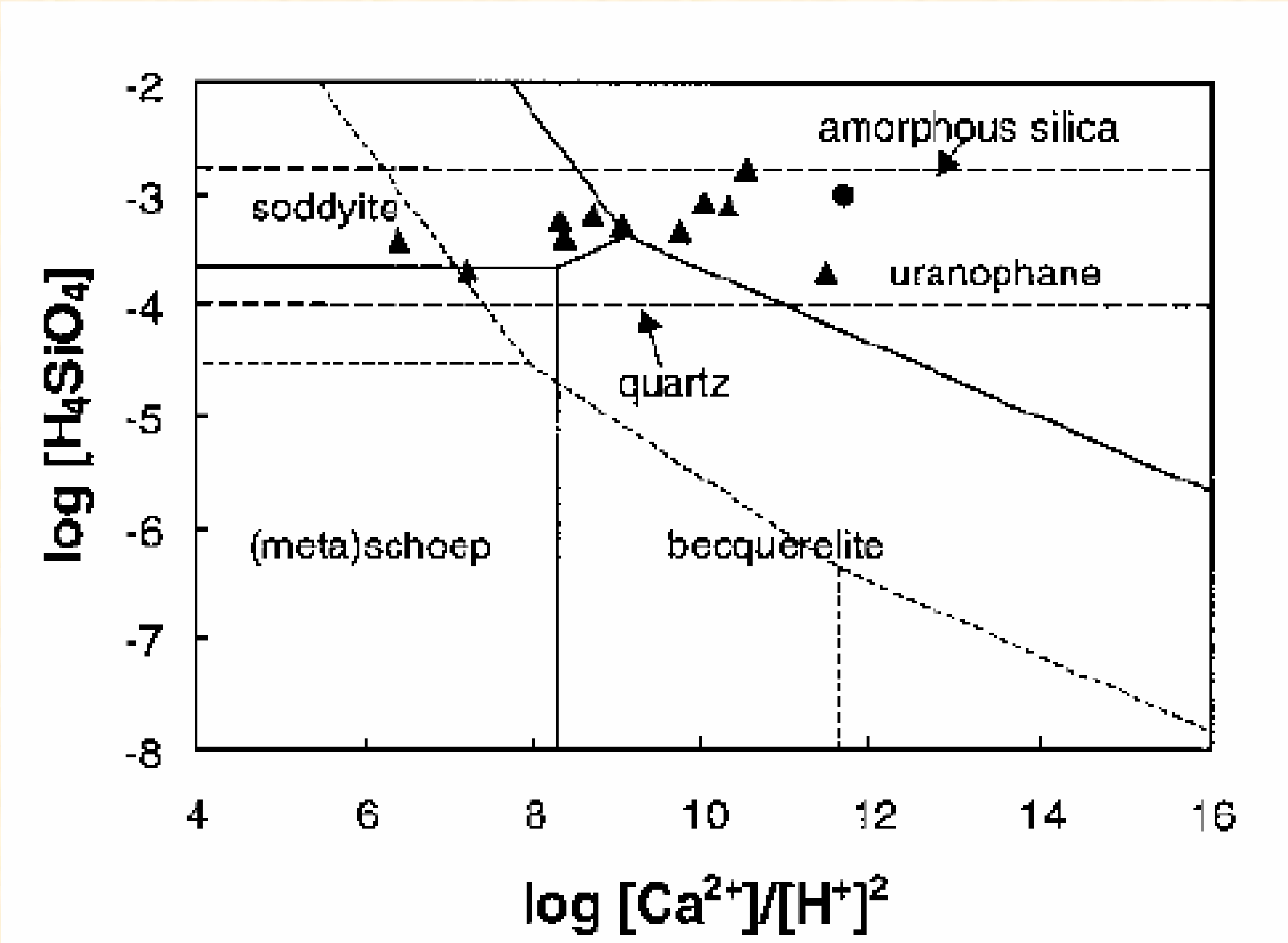
- **Rigorous composition control.**
- **Long-term exposure tests with YM groundwater and conditions.**
- **Comprehensive suite of testing on consistent samples.**
- **Rigorous microprobe examinations of aging phases and alteration products with nanoscale resolution of mechanisms.**
- **Exposed samples compared with anthropogenic and natural analogs, reconciled with application of aging models.**

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



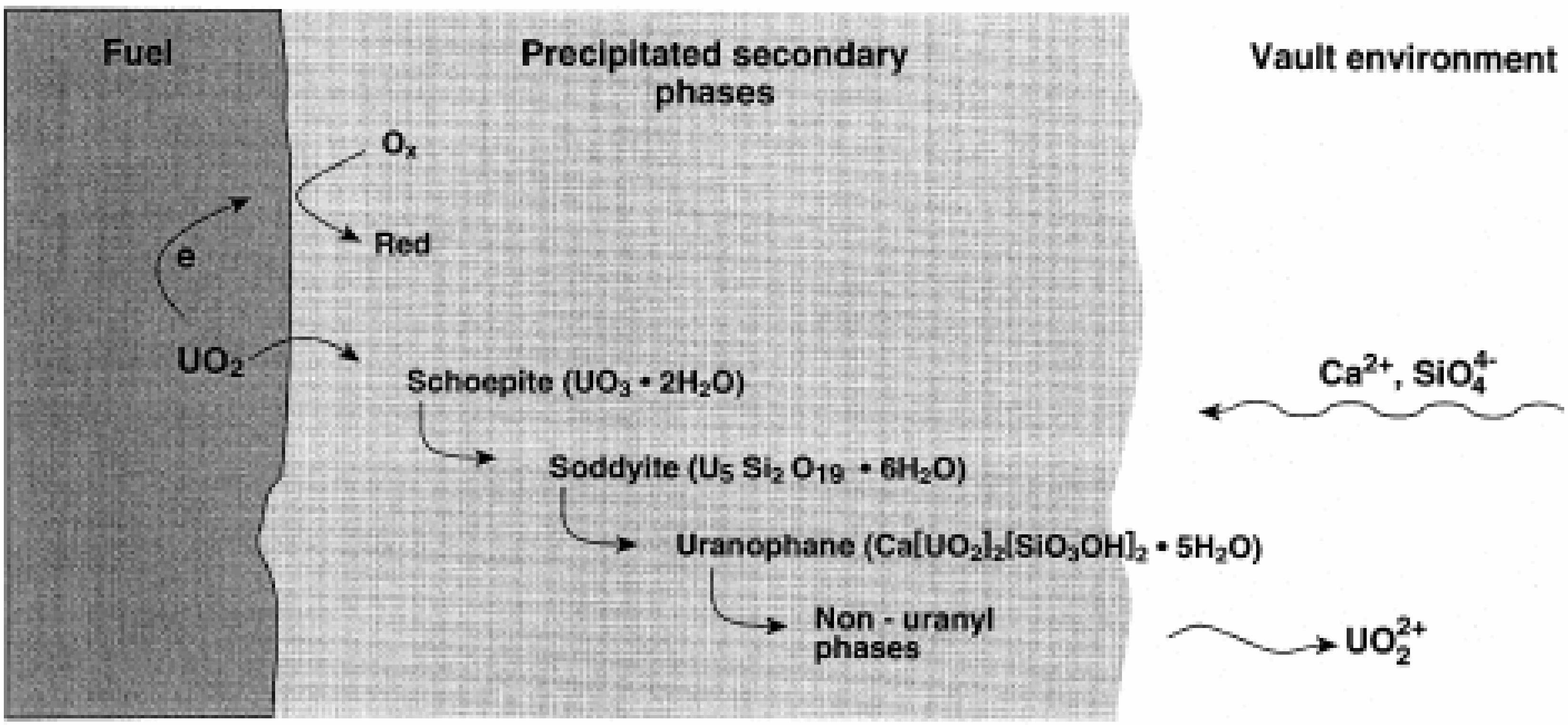
Principal U(VI) Compounds

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

Silicates form a dense diffusion layer on the surface of UO2 even under oxidizing conditions



Saito, Hiroshi and Akira Deguchi, Leaching tests on different mortars using accelerated electrochemical method, Cement and Concrete Research 30, pp 1815-1825, 2000.

Figure (a) These plots show the pore size distributions in normal sand filled cement mortars

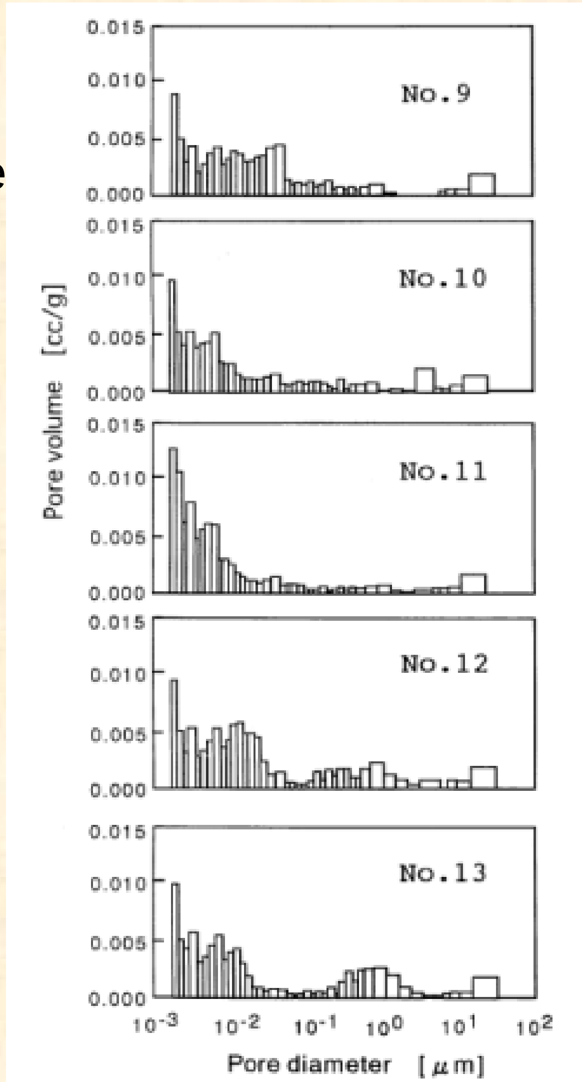
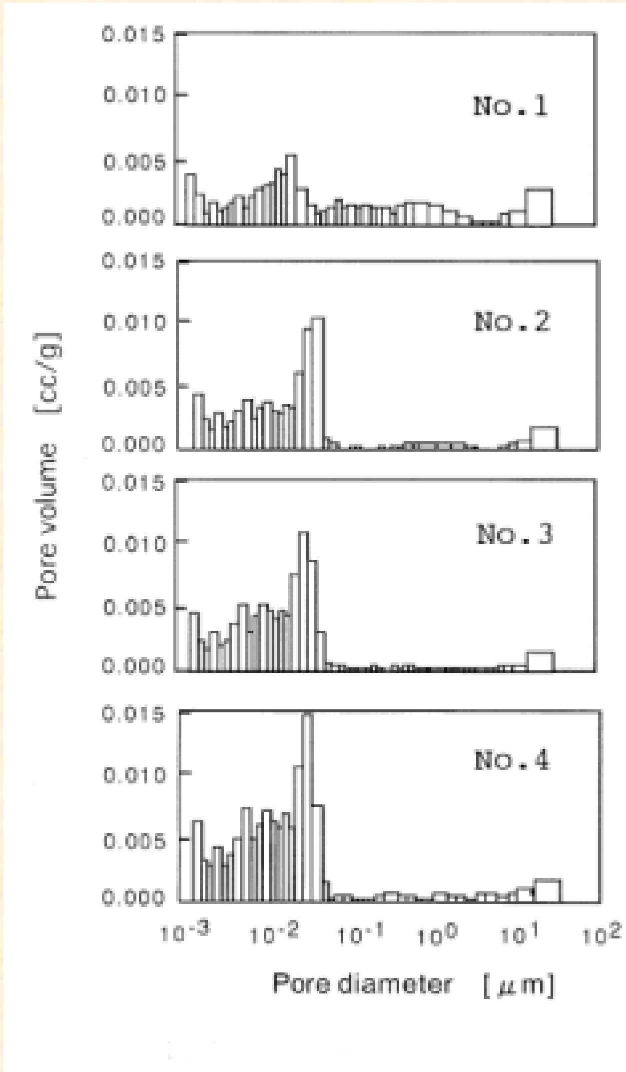


Figure (b) Additions of blast furnace slag and silica fume significantly reduce the pore sizes



Laboratory Research Tasks

1. Static and flow-through (dynamic) tests study interactions of cementitious materials with YM groundwater at 30-160^{o}C.
2. Chemical and physical changes, such as strength, permeability, mineralogy, and corrosion.
3. GFAA, ICP-MS, ICP-AES and IC to monitor the composition and pH of the groundwater.
4. Characterize phases from interaction with groundwater, petrographic and EMPA analyses and SEM and TEM imaging.
5. Isotopically-labeled water and elemental imaging using secondary ion mass spectrometry (SIMS) to track the migration of the fluid.
6. Cost comparison study of current concrete practices with the current YMP construction base line.
7. Laboratory and natural analog data compared with the prediction models of the aging of cements.

Anthropogenic and Natural Analog Tasks

1. **Anthropogenic samples will be collected with the cooperation of museums and archeologists from Europe and Asia**

2. **Natural samples will be collected both by field trips and by cooperation with geologists from the U.S., Europe and Asia**

3. **Archeological and natural samples will be examined with the techniques above and compared to the samples exposed during our laboratory studies**

4. **Laboratory and natural analog data will be compared with the prediction of current, selected models of the aging of cementitious materials**

Purpose of These Discussions:

- **Identify Russian interests and capabilities in resolving particular Yucca Mountain Project Concerns**
- **Prepare description of proposed Russian tasks**
- **Develop tasks and their scope, schedule and costs**

Current Status of Developing High-Silica Concretes for Yucca Mountain

- **Developing high-strength roller-compacted concrete for tunnel floor (invert)**
  - **Bear heavy loads with flexibility**
  - **Surface hardened for abrasion**
- **Developing Shotcrete**
  - **No organic additives**
  - **Metal fiber micro-reinforced**
  - **Used native Tuff as fine aggregate**
- **Forming US project team**
  - **US Army Corps of Engineers on-site engineering experience,**
  - **Lawrence Berkeley National Lab modeling repository impacts and performance, and**
  - **P. Tatnall, consultant on standard practice, mix proportioning, and testing standards.**