DoE Workshop
Savannah River, December 2006

"Cement Conditioning of Nuclear Wastes- Where Do We Go ?"

F.P.Glasser, University of Aberdeen,

Old Aberdeen AB24 3UE Scotland.

1495 UNIVERSITY OF ABERDEEN

Basic properties of Portland cement relevant to immobilization - (1)

- High pH conditioning ability **buffered** by reserves of solids.
- Slightly oxidizing but largely **unbuffered** Eh.
- High chemical potentials for Ca, etc with high surface area of solids also available for sorption and precipitation.

Basic properties of Portland cement relevant to immobilization - (2)

- The additional *chemical* potential for reaction with potential immobilization makes cement unique as a reactive barrier.
- The chemical potential is active inside the matrix but may also operate at a distance, the so- called “alkali plume”.

Basic properties of Portland cement relevant to immobilization – (3)

- In general binding is weak for monovalent ions, e.g., Cs but stronger for cations with high formal charge, >1. The binding for anionic species is highly variable. And for some radwaste entities, the speciation is not well known
- Nor do we have adequate data on Eh. Potential redox couples in cement *might* involve the iron (ferric) component and/or sulfate (S(VI) and its lower oxidation states). Only the sulfur couples are active.
- However added materials, especially those having low Eh, may superimpose their electroactivity on the cement matrix. We do not know the consequences of this influence.

Basic properties of Portland cement relevant to immobilization – (4)

- For example, corroding iron lowers the redox potential. Field measurements often disclose Eh of minus several hundred miilivolts (relative to a hydrogen electrode) compared with plus several hundred millivolts in normal cement.
- But the effectiveness of this lowered Eh to reduce redox sensitive species varies with the chemical nature of the species and we lack specific data on interactions.

Basic properties of Portland cement relevant to immobilization – (5)

- For example, hexavalent chromium ,Cr(VI), is rapidly and quantitatively reduced to Cr(III) by ferrous sulfate, by tin (II) salts, by sulfite and thiosulfate, etc.
- But hydrogen, released from water by corroding metal , is often ***not*** an effective reductant for Cr (VI). More kinetic studies needed!

Basic properties of Portland cement relevant to immobilization - (6)

- Furthermore we suffer from lack of basic knowledge about the redox behavior at high pH of some species: for example, Tc and actinides. Data in the literature enabling predictions appear not to have been critically tested in alkaline conditions.

Basic properties of Portland cement relevant to immobilization – (7)

- We must also recall that fresh cement must have certain short term property sets: flow characteristics, volume stability, heat evolution and permeability are important factors in emplacement and performance assessments.
- Many of the formulations used (or suggested for use) are unconventional and we have little experience of them in civil engineering.

Criteria for Grout Formulation

- Goals for selection of formulation have not always been clear; what properties have been selected for optimisation and why?
- Holistic solutions to achieve balanced property set (short and long term) have not been addressed with clear priorities.

Fundamentals - (1)

- The specific volume of cement solids is *always* less that the volume of solids plus water of hydration. Therefore chemical shrinkage will *always* occur. The solution is:

  (i) not to exacerbate shrinkage by using formulations known to shrink, e.g., with silica fume, unless necessary and;

  (ii) manage shrinkage so as to avoid few, but large cracks.

Role of the Aggregate - (1)

- Acts as a useful diluent for heat- generating substances and as a thermal sink.
- Reduces shrinkage by diluting cement
- But, to avoid excess voidage and poor permeation, the aggregate needs careful size grading.
- Reduces concentration of pH conditioning mass.
- Formulation must compromise between short and long term requirements!

Role of the Aggregate - (2)

- Aggregate *mineralogy* could give rise to long term dimensional instability. For that reason it may be desirable to avoid siliceous aggregates using instead limestone.
- While limestone reacts with cement, the nature and extent of reaction are understood and are generally complete within a decade without harmful consequences.
- Potential problems should be eliminated or mitigated at the design stage.

Formulation

- We have seen that formulation is a compromise. The logic underlying selection needs to be presented with a convincing case for priorities presented.
- The changing nature of “cement” needs to be addressed: presently available formulations may change.

“Scaling up”

- The NRC report comments that more use should be made of “test beds”, (scaled up trials). I agree but add the recommendation that the designers of the grout formulations and modellers should where possible participate in the design and interpretation of these trials alongside those actually doing the trials.

Crack Healing

- Cement matrices are dynamic and crack. But cracks can reheal. The original mechanical properties may not be restored but permeation properties can recover.
- Time does not permit more detail but in general this is a much neglected area of study- under what conditions do cracks heal ? And with what impact on properties?

Accelerated Testing - (1)

- The NRC report recommends that more use be made of *accelerated testing* to evaluate post-closure performance. In theory, I agree. But in practice, this is <u>not likely to succeed.</u>
- History shows that accelerated test do not achieve their intended purposes - see, for example the history of ASTM recommendations.

Accelerated Testing - (2a)

- For example, take a simple case: the durability of portlandite to dissolution in the presence of water and dissolved $C0_2$.
- We know that portlandite, $Ca(OH)_2$, is not very persistent in initially pure water: it is too soluble, *ca* 1.1g/l at 20*C.
- *Contd*……

Accelerated Testing - (2b)

- We also know that dissolved CO_2, as "carbonic acid" attacks and dissolves portlandite. Such aggressive waters occur in nature (but fortunately such waters are uncommon).
- So it might appear that attack could be simulated by using carbonic acid solutions of varying strength.
- *Contd…*

Accelerated Testing - (2c)

- However there are intermediate concentrations of CO_2, in which calcium carbonate precipitation is favoured.
- In this regime, the solubility of calcite is two to three orders of magnitude less that that of portlandite.
- A self- healing and protective “skin” of calcite forms on portlandite with the result that cement becomes partly self- protecting.

Accelerated Testing - (2d)

- Many environmental reactions do not necessarily degrade the performance of cements (it depends on what criteria are chosen for “degradation”).
- Particularly where several processes are coupled, we cannot adequately anticipate these in the design of accelerated tests.

Modelling - (1)

- In the present state of knowledge, we are going to have to depend on models and modelling, perhaps supplemented by focussed experimental work.
- The NRC report accepts this and commends models such as those developed at NIST. I agree.
- There are however a wide range of models, chemical as well as physical.

Role of Modelling - (2)

- Ultimately, modelling will be required to predict the long term (>100-200 year) evolution of properties.
- Models of the chemical evolution are arguably at a more advanced state than models of physical performance.

Modelling - (3)

- However the nature and sophistication of the models are likely to be constrained by lack of data.
- Parallel efforts to improve the data base used for modelling is important.

Modelling - (4)

- Of course we would like an “everything” model but we are some way from achieving that goal and for the present will have to use a range of partial models, some modelling chemical features/properties and others, physical features/properties.
- Models -unlike testing - exhibit great flexibility.

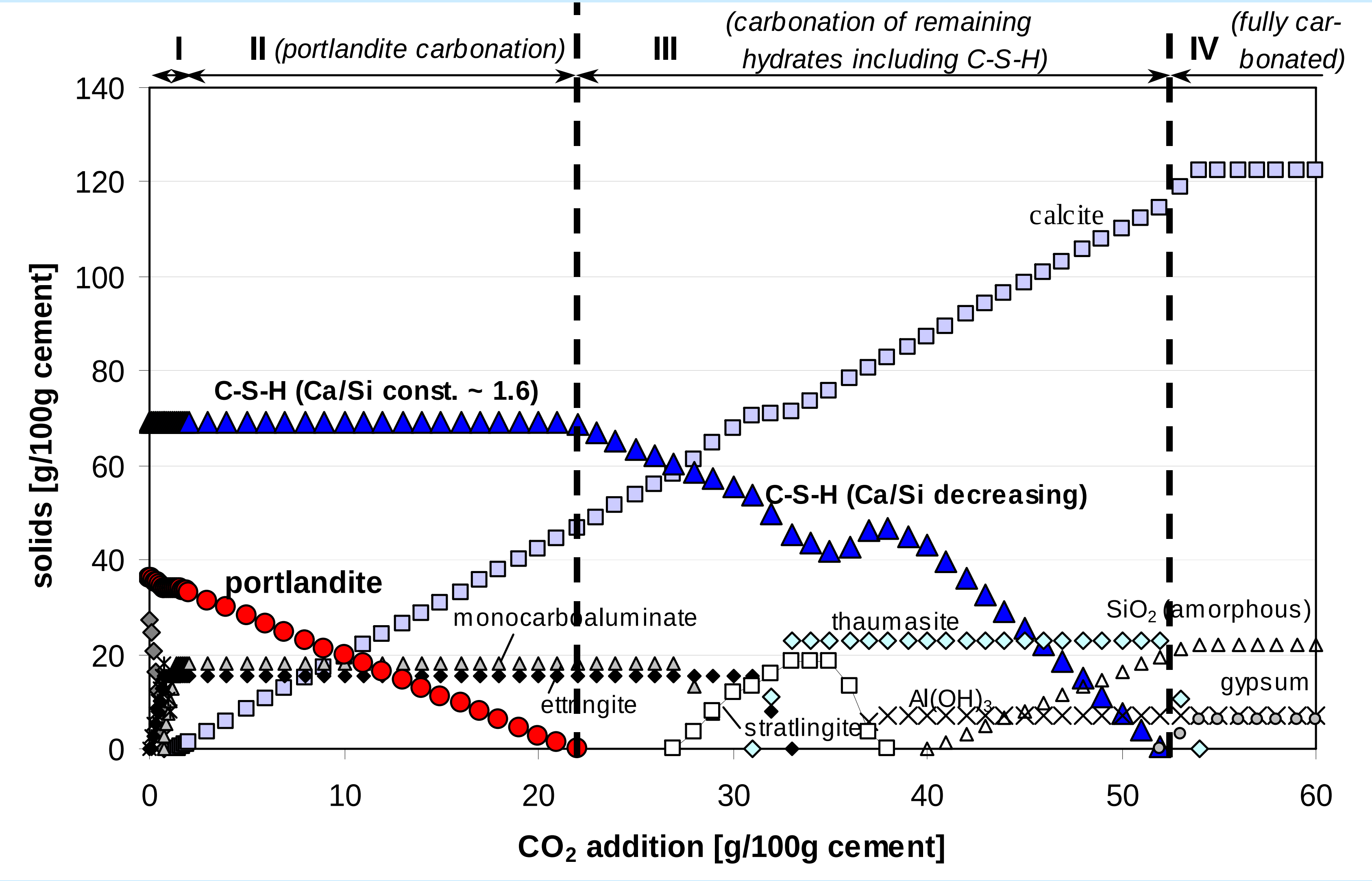
Equilibrium and Kinetics

- A contention of experimenters is that modelling does not adequately address the kinetics.
- This is only partly true- many equilibrium calculations reveal to a skilled observer what factors are likely to control kinetics.
- In any event I would not recommend total reliance on modelling- it is best used to focus experiments and thereby reduce the time and effort required.

Carbonation of Cement

- Our chemical model is used to follow the mineralogical changes and potential for volume changes attending carbonation.
- The model cement composition is an average of commercial cement, minus the iron oxide.
- The cement is” titrated” with CO_2 to simulate progressive carbonation.

Carbonation Simulation



Carbonation

- The model predicts that, in a gradient of CO_2 activity, the carbonation of $Ca(OH)_2$ will occur <u>before</u> that of C-S-H.
- This has been observed in practise and assumed to be a matter of kinetics but is in fact also an equilibrium feature!.
- Thus equilibrium and kinetics can (sometimes) be reconciled!

Summing Up - (1)

- Timescales for experiment and modelling are longer than other steps.
- Steady effort over a longer time is better than crash programs.
- We are in a position to assess data needs and procedures - reliance, it is suggested, should be on modelling for the long term.

Summing Up - (2)

- Define objectives realistically.
- Agree implementation.
- Develop and coordinate work packages.
- Conduct actual trials and learn from scale-up.
- Integrate repository planning with support activities.
- Develop, present and gain approval for plans.

Summing Up - (3)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.

Summing Up - (3a)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.

- Bonding mechanisms of radwaste species in fresh and altered matrices.

Summing Up - (3b)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.
- Bonding mechanisms of radwaste species in fresh and altered matrices.

- Formulation priorities: establish protocols including changing nature of “cement” and aggregates.

Summing Up - (3c)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.
- Bonding mechanisms of radwaste species in fresh and altered matrices.
- Formulation priorities: establish protocols including changing nature of “cement” and aggregates.

- Scale up effects.

Summing Up - (3d)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.
- Bonding mechanisms of radwaste species in fresh and altered matrices.
- Formulation priorities: establish protocols including changing nature of “cement” and aggregates.
- Scale up effects.

- Cracking and crack healing: impacts on permeation.

Summing Up - (3e)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.
- Bonding mechanisms of radwaste species in fresh and altered matrices.
- Formulation priorities: establish protocols including changing nature of “cement” and aggregates.
- Scale up effects.
- Cracking and crack healing: impacts on permeation.

- Role of accelerated testing.

Summing Up - (3f)

Action check list:

- Matrix properties: evolution of pH and of electroactivity of redox couples.
- Bonding mechanisms of radwaste species in fresh and altered matrices.
- Formulation priorities: establish protocols including changing nature of “cement” and aggregates.
- Scale up effects.
- Cracking and crack healing: impacts on permeation.
- Role of accelerated testing.

- Development of modelling protocols: verification/validation of model predictions and integration of models for “physical” and “chemical” attributes of performance.