Sustainable Cements: Challenges, Opportunities and Applications

Improving Cement Performance to Enhance Sustainability

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Present situation

- Industry is under pressure to reduce emissions and conserve resources, yet deliver an improved product- cheaply!
- The industry is not doing anything *wrong* but is <u>not perceived as being positive about change</u>
- The way forward certainly involves effort by companies and individuals but also, collective action to make new developments possible (standards, customer education and training, etc.)

Existing Technologies (1)

- Use of slags, fly ash and other bulk industrial wastes has reached practical limits in many markets
- As coal is phased out and iron makers pre-purify ores, volumes of ash and slag can only decline; certainly they are also likely to change in composition
- Natural and semi- synthetic pozzolanic resources are still largely unexploited (metakaolin excepted)

Existing Technologies (2)

- My contention is that we can still exploit existing products and processes to make them “smarter”- and thereby conserve energy/ reduce pollution
- I will explore a case study and present ideas

Case study: Limestone in cement

- Limestone has been used as a “filler” for Portland cement since its advent in the 1820’s.
- Perhaps 1000 papers/ technical studies exist showing that a trade- off exists : more limestone, -up to 50%, means lower strength and higher permeability

Optimising calcite additions (1)

- Limestone (mainly $CaCO_3$) is often viewed as being not reactive with cement, but scope for reaction exists.
- Reaction is mainly with the AFm phase: normally it contains $(SO)_4$ and OH anions but in the presence of calcite, monocarboaluminate is stabilised.
- Sulfate displaced from AFm cannot form gypsum because Portland cement is undersaturated with respect to gypsum after the first few hours.

Optimising calcite..(2)

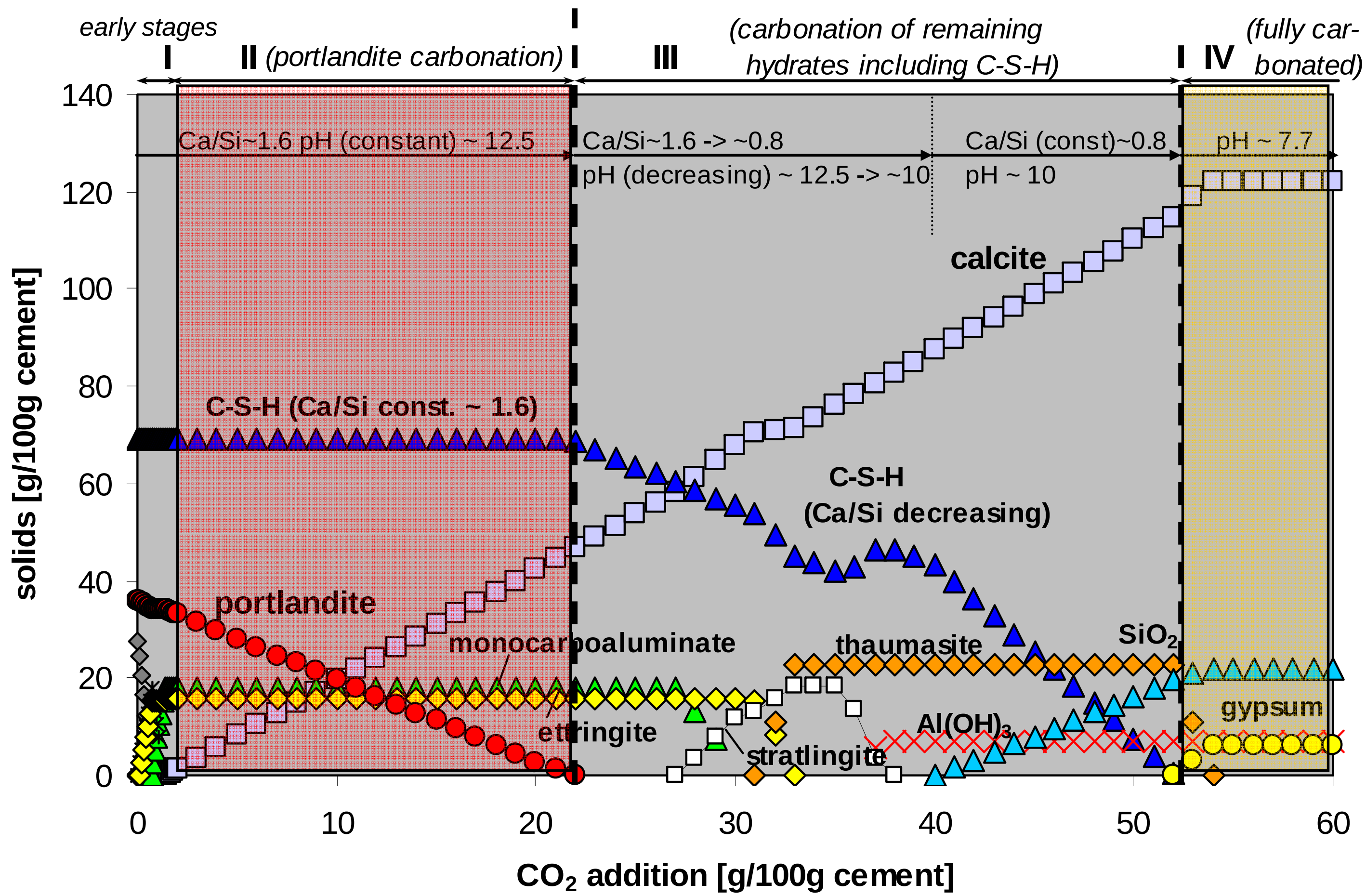
- Instead, sulfate enhances ettringite formation
- This results in an increase in specific volume of solids (low density of ettringite relative to its precursors)
- Reaction with interground calcite is rapid
- The volume change typically occurs while the cement is still plastic and does not significantly affect the external dimensions.

Optimising calcite…(3)

- Better space filling, in turn, enhances strength- not by much, but the effect can be optimised by controlling the alumina and sulfate contents
- Matschei, *et al* developed the underlying principles for proportioning to optmise space filling (ZKG, 2007)
- Of course it is not necessary to enhance strength: instead economies can come from using more than the optimum calcite and thereby , use less cement

Results

Calculation of zonation in the course of carbonation

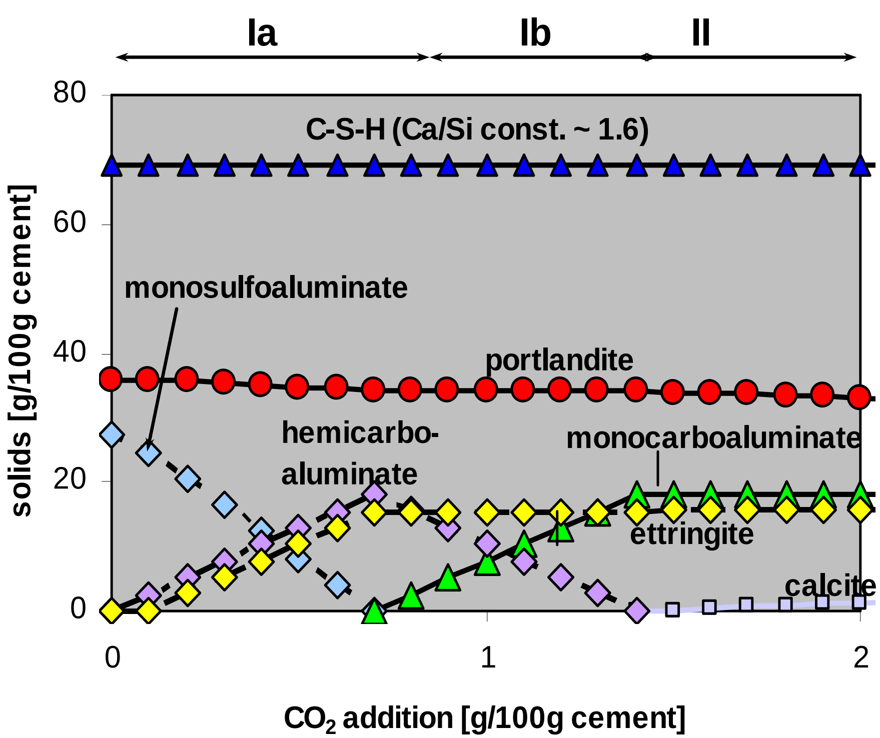


Carbonation is a very complex process (calculated formation of 13 different zones)

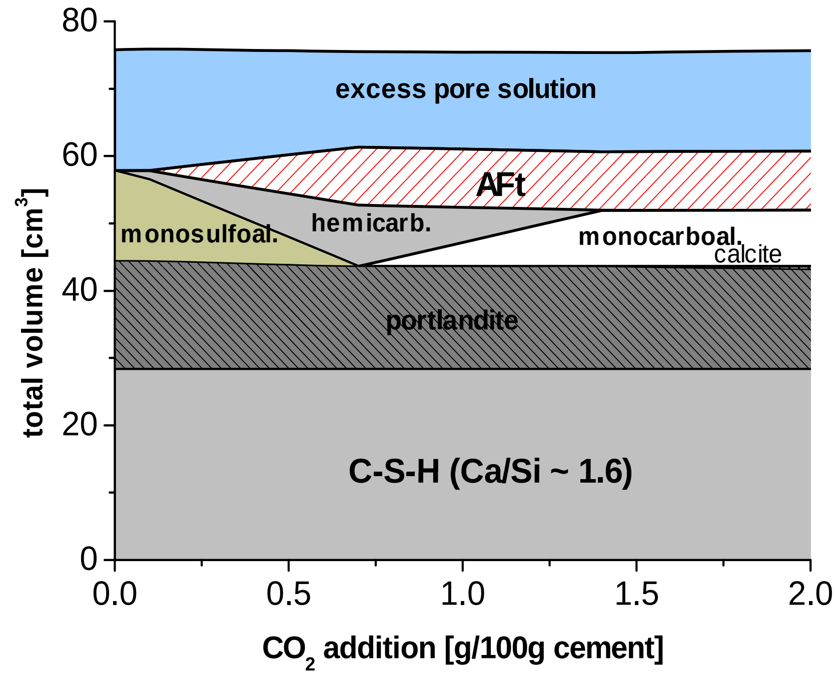
Results

Early stages of carbonation

Mass balance changes



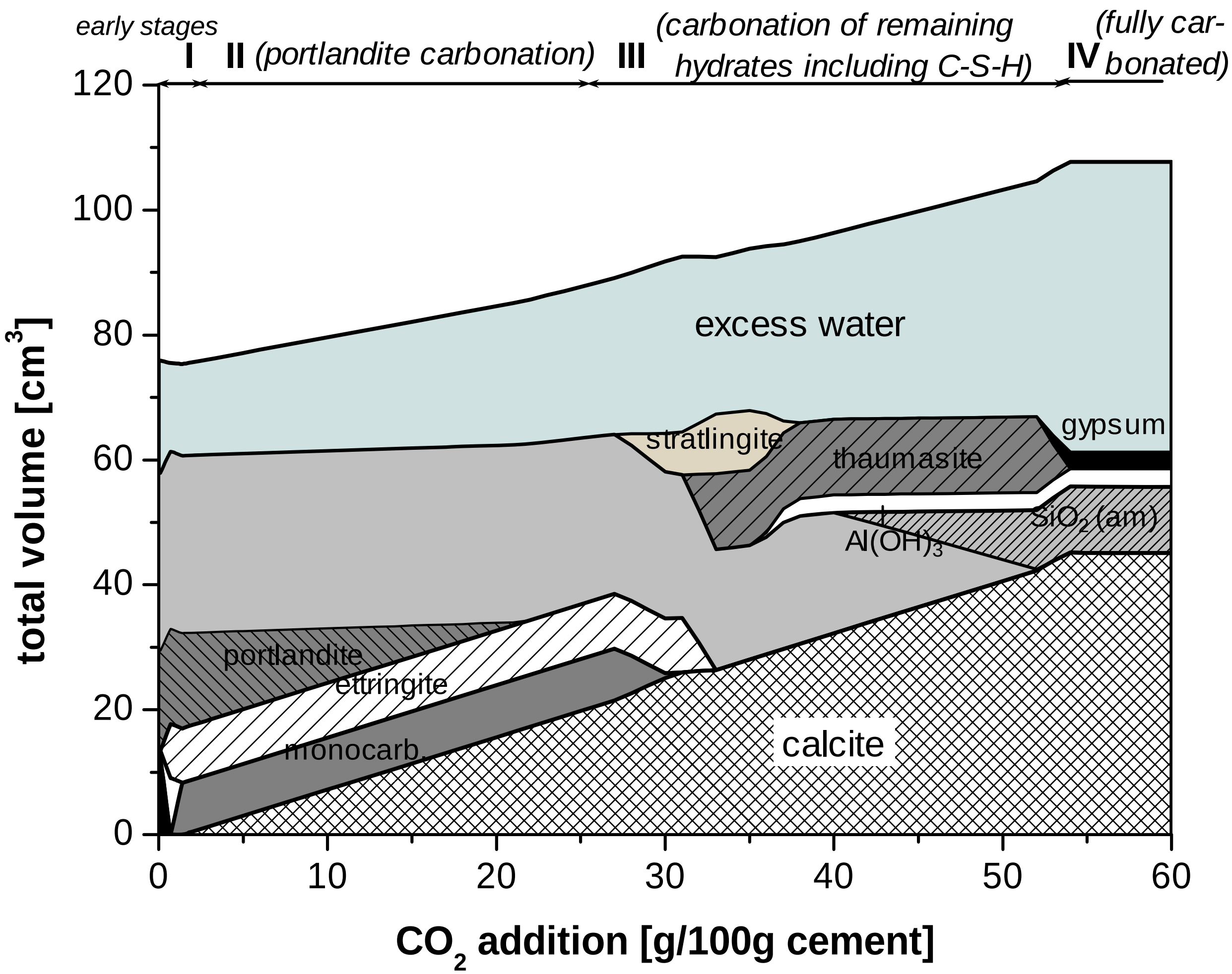
Volume changes



The early stages may be achieved by „normal“ Portland cement which contains small amounts of carbonate, sufficient partly to prevent formation of monosulfoaluminate

Results

Volume changes due to carbonation



Space filling effect due to carbonation and densification of cement paste

Generic nature of the calculation

- Although the calculation presented here is for one composition a cement with 4.5% alumina, sensitivity calculations show that the calculation has generic applicability: the maximum exists for all compositions

Questions?

- Why should properties be so sensitive to space filling? (better space filling reduces porosity). Does it matter which phase or phases are filling space? How far can these relations be extended?
- Answers to these questions illustrate that our knowledge of the property/ composition/ microstructure relationships needs to be enhanced!

Supplementary issues

- What is the role of the ferrite phase in cements?. It contains much of the Al (and most of the iron) ; how reactive is itand how does it control alumina available for hydration? The fact that we do not know the answers reflects on the adequacy of our data base: many important data have never been obtained.
- Not only does this reflect on hydrate phase balance and space filling, it also radically affects how we formulate cements for sulfate resistance

The payoff (1)

- I think of materials in construction of having a sustainability factor, SF, defined as:

  SF = performance lifetime/ energy input

- If we can improve performance, or reduce energy input (or both) we have a benefit
- Design, workmanship and formulation all contribute to performance. I concentrate on only one of these but accept that all are important

The way forward

- We are entering a new era of cement, not in terms of how we make cement (although that too could change) but in how we use cement.
- The old order, of empirical studies on a grid basis will not be sufficient to cope: too many potentially relevant factors have to be omitted to keep the grid manageable

The way forward (2)

- Only computational methods will handle the many potentially relevant variables
- Probably you are sceptical about these “wonder” models
- And you may be right- models often rely on inadequate databases and different models do not link

Progress

- But we know have a comprehensive data base for cement substances useful over a broad range of temperatures, 0-90*C
- We also know that hydration produces metastable phases (C-S-H) but that these are amenable to treatment and that otherwise, hydration approaches equilibrium

New tools

- Thermodynamics is like a tool kit- it has to be applied intellegently
- It copes well and rapidly with “what if” scenario using a transparent methodology
- Links naturally to mineralogical mass relations which convert to volumes (critically compiled densities available soon)

Use of the tool kit

- As one of the first fruits, we have calculated (with selected experimental verification) the impact of low temperature on cement mineralogy. (to be submitted)
- But what I want to do is to encourage you to use these new tools to improve cement performance.
- We have several projects at the inception stage but are convinced we are only scratching the surface.

The way forward (3)

- Cement science is changing. We need to develop more sophisticated and smart approaches to developing models with priority accorded to those seeking to relate primarily *physical* properties to *chemistry/ mineralogy/ microstructure* –especially now that we can quantify the mineralogy.

The way forward(4)

- I am often asked “what about the kinetics”?
- At present we cannot adequately define kinetics because the underlying mechanisms are not sufficiently well understood.
- But once we understand <u>mechanisms</u>, we can define appropriate kinetics- the kinetics will sort themselves!

Acknowledgement

- I thank the many people who have been sounding boards for my ideas. Their scepticism has proven a useful antidote to my enthusiasms. Nanocem is particularly to be commended: its sponsors were not convinced at the outset about the value of our approach but nevertheless took the chance!