



Is It Time To Consider Deliberately Carbonated Precast Concrete Elements?

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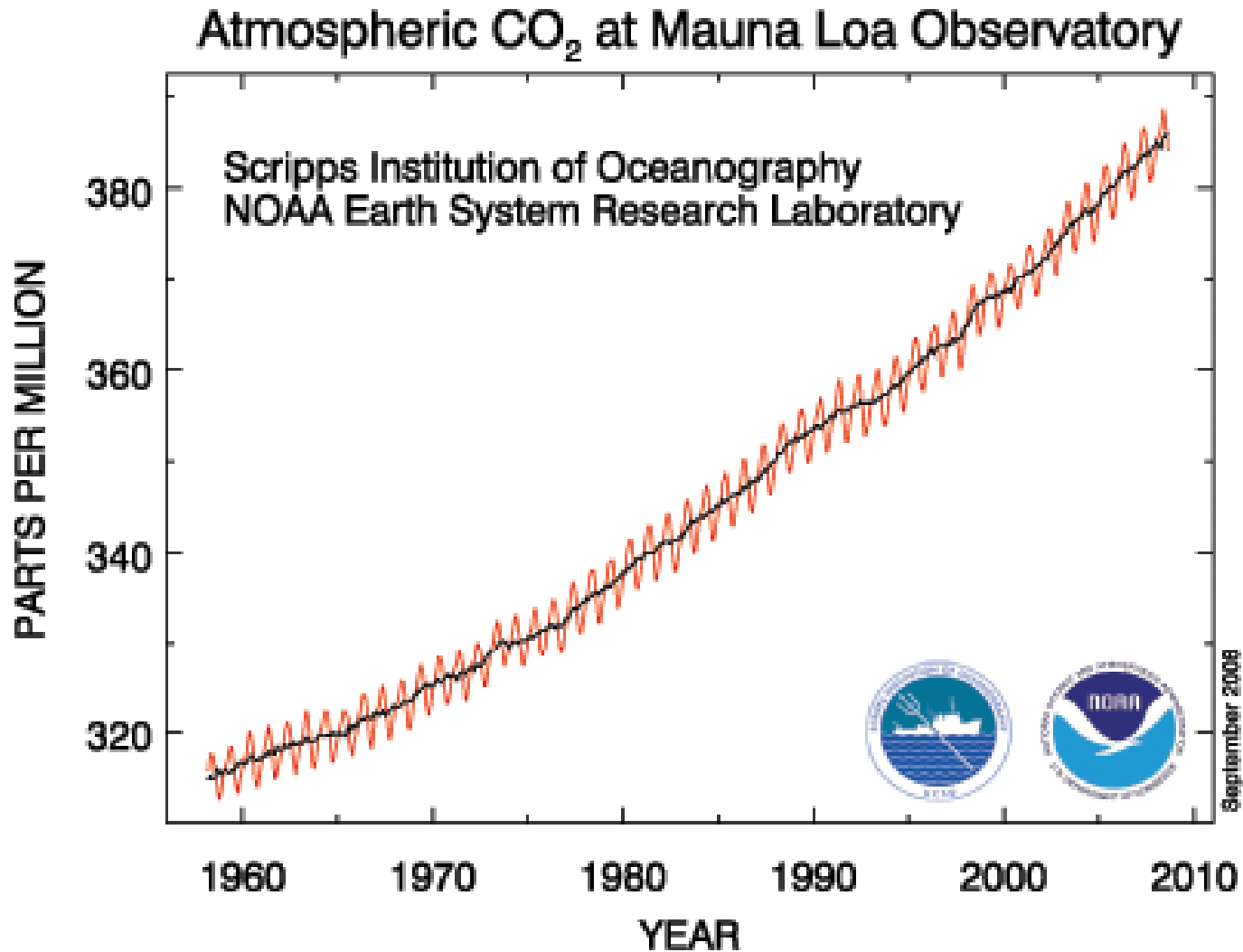


Global warming and anthropogenetic carbon dioxide emissions

- There now seems to be clear evidence that “global warming” is occurring extremely rapidly.
- There is still some scientific uncertainty as to whether it is due to man-induced CO₂ emissions, but there is clear evidence that the CO₂ content of the atmosphere has increased steadily year by year. Scripps Institute-NOAA data, taken continuously at Mauna Loa since 1959, is very clear.



Annual increase In atmospheric CO₂ content since 1959





The carbon footprint problem

- The cement industry is clearly under the gun with respect to carbon dioxide emission, regardless of what 'cap and trade' (or other) system is mandated in the future.
- While some 'credit' can ensue from the practice of crushing recycled concrete and letting it carbonate for some years, the rate of carbonation of crushed concrete is slow, and the benefits are somewhat ambiguous.



Re-jiggering concrete binder compositions

- Reduction in cement content by substituting fly ash, slag, etc, obviously needs to be pursued, but the availability of these substituants is limited. Use of fluidized bed combustion fly ash in concrete binders is problematical.
- Changing the typical clinker composition to favor belite over alite is helpful, and belite cements are obviously worth pursuing.



The possibility of “carbonation hydration” of precast concrete products

- About 35 years ago, investigations were carried out mostly at the University of Illinois on “carbonation hydration”, that is to say reacting fresh (unhydrated) cement mixes in CO₂ gas. Strengths of the order of 20 MPa were obtained in **five minutes**, at the same time binding substantial amounts of CO₂.
- Is it time to re-examine the prospects for such technology in terms of reducing the carbon footprint of the cement and concrete industry while at the same time producing economic precast products?



The science behind the idea (1)

- Klemm and Berger (1972) found that that a kind of combined hydration and carbonation reaction with cement occurs very rapidly in the presence of carbon dioxide to produce a dense almost fully reacted carbonated structure from cement components in a matter of minutes.

W. A. Klemm and R. L. Berger, Accelerated Curing of Cementitious Systems by Carbon Dioxide, Part 1, CCR 2 (5) 567-576 (1972)



Some specifics from the original Klemm-Berger report

- 1. Small mortar samples compacted at low water contents (ca. w/c 0.1) worked best.
- 2. Exposure was for **only 5 minutes**, to gaseous CO₂ under 4 atm. Pressure - applied immediately immediately after mixing.
- 3. Extensive reaction heat was produced.
- 4. 20 MPa strength was immediately secured.
- 5. Subsequently autoclaving the carbonated product quickly generated additional strength.



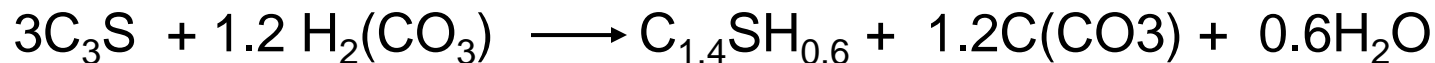
Strengths from more prolonged carbonation

- Young et al. (1974) produced carbonated mortars with strength varying from 50 MPa to 70 MPa in less an 1-1/2 hrs. of exposure to CO₂, depending on conditions. Flowing CO₂ was better than static CO₂.
- The problem is that these were small mortar specimens – and most of the strength was in the periphery – the cores were “sealed off” from exposure.



The science (2)

- Both C_3S and $\beta-C_2S$ worked as well as cement, indeed, it was later found that even non-hydraulic phases like $\gamma-C_2S$ carbonated and gained some strength.
- Young et al later (1974) provided an equation for the rapid combined hydration and carbonation as follows:



R. L. Berger and W. A. Klemm, Accelerated Curing of Cementitious Systems by Carbon Dioxide, Part 2 CCR 2 (6) 647-652 (1972)

J. F. Young et al. Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO₂, J. Amer Ceram Soc. 57, 168-171 (1974)



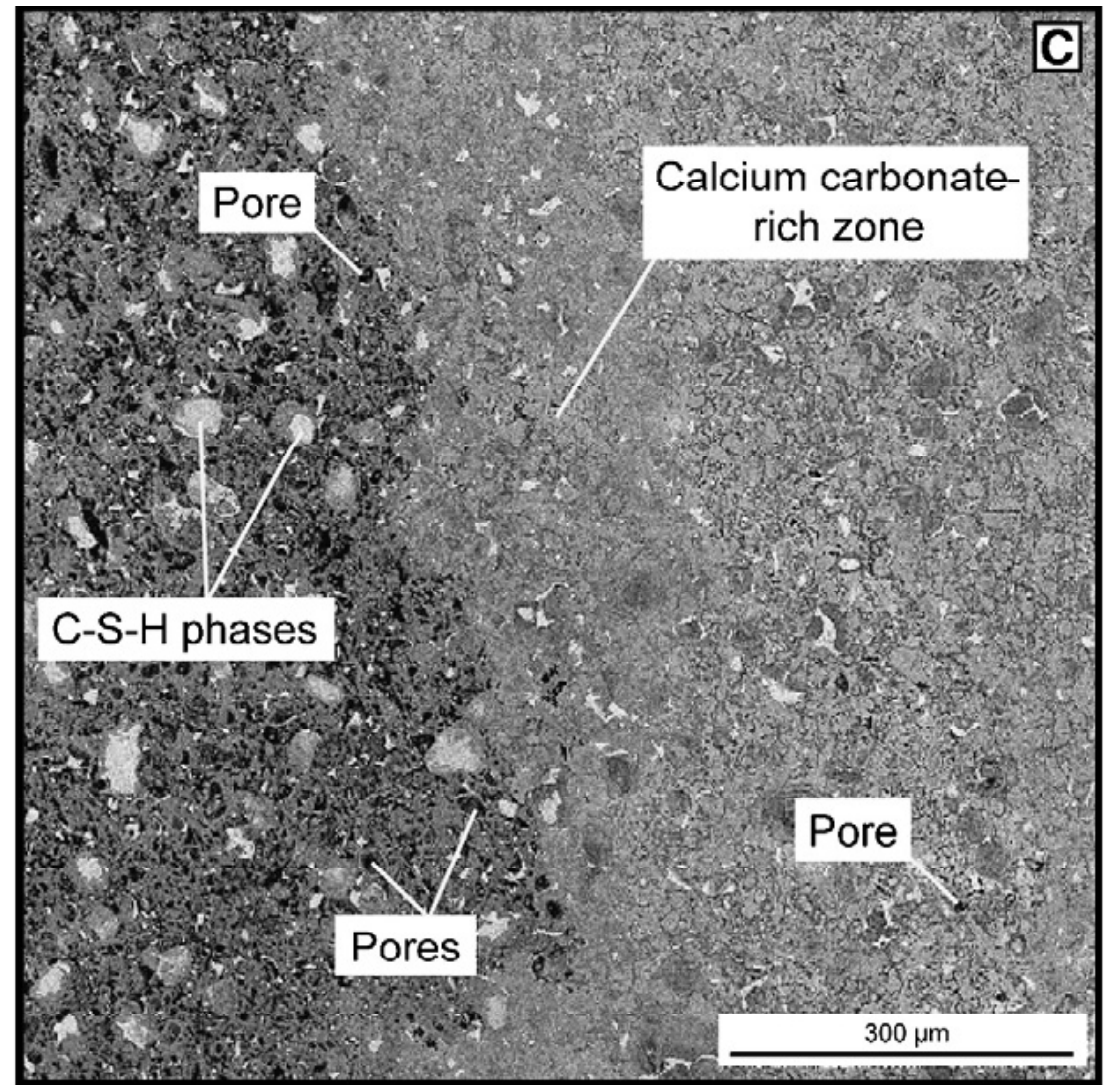
The science (3)

- Apparently the CO₂ dissolves quickly to generate carbonic acid in the mix water, and then “forced” hydration of C₃S (or C₂S, or whatever!) almost immediately occurs, to produce intermingled CaCO₃ and some version of C-S-H – which then also carbonates on continued exposure.
- Unfortunately, this was before the days of backscatter SEM, and they couldn’t directly investigate details of the microstructure produced.



A hint from a current paper

- A new paper by Gaetan, et al. (*CCR 38 (2008) 1038-1048*) investigated the effect of forced carbonation of hydrated cement down a previously cemented oil well bore hole.
- A very clear distinction between the dense carbonated zone and the normally porous paste not yet carbonated is evident



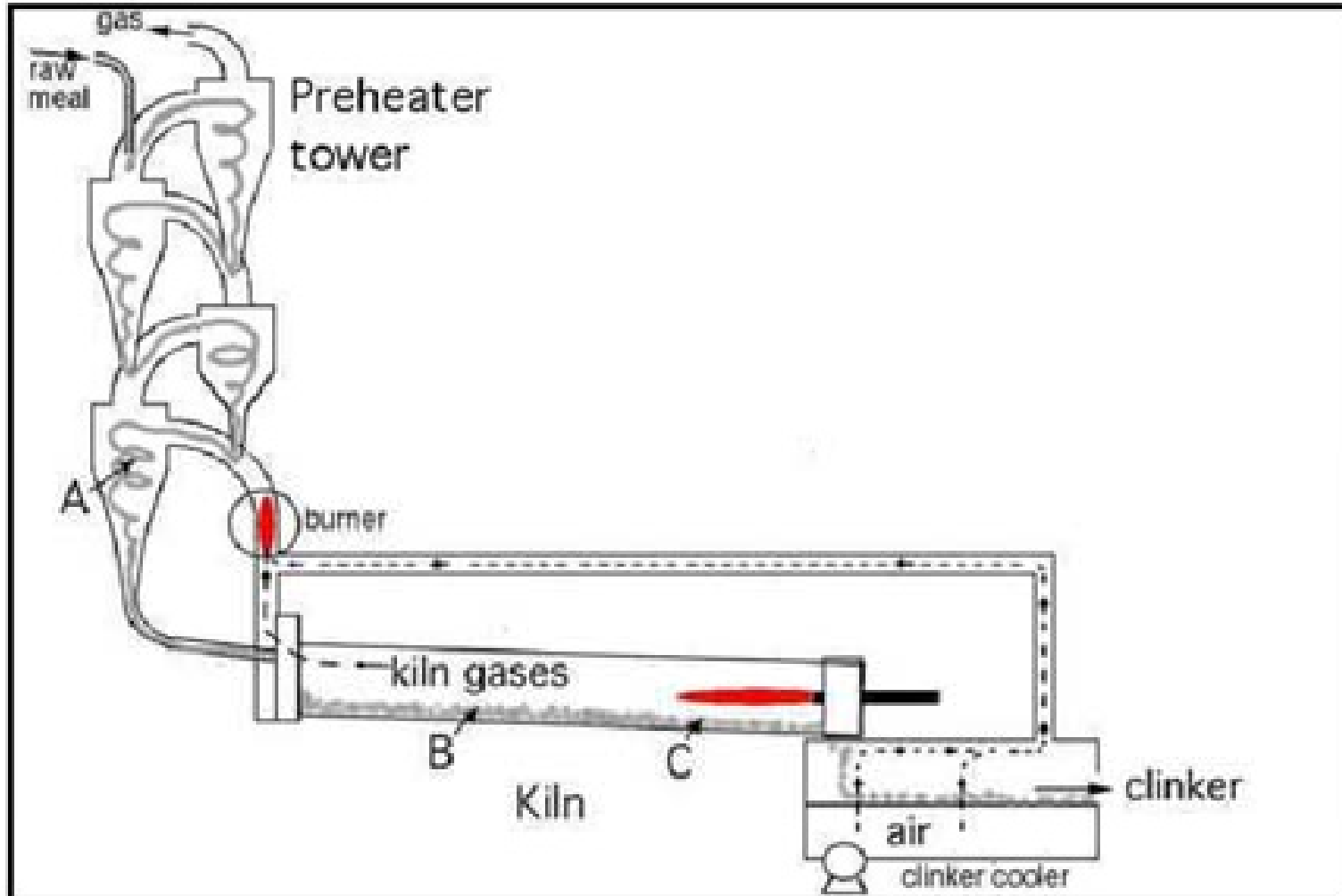


Combined CO₂ sequestration and production of carbonated products – the general idea

- The notion: collect CO₂ liberated in cement plant operation, convey it to an adjacent precast product plant, and “consume” the CO₂ usefully in producing strong, cheap, fully carbonated products.
- Is it “practical” – probably not, but maybe worth looking at, if the CO₂ sequestration generates enough financial return.



Cement plant CO₂ source





How “concentrated” does the CO₂ have to be?

- This is obviously an important consideration.
- The U. of Illinois work used “pure” CO₂, under varying pressures – the higher the pressure the better.
- Do you need to isolate the CO₂ from the air? A recent paper* implies that you do, viz.

“The primary control upon accelerated carbonation, after the chemistry of the sample, is the use of a 100% CO₂ atmosphere. If the sample chamber is not completely purged of air prior to the experiment the rate and extent of reaction are greatly reduced”.

Unfortunately, no data were supplied, so I don’t know what “greatly reduced” means. Flue gas captured from cement plants are said to be about 20% CO₂, which is obviously not 100% CO₂.

D.C. Johnson, “Accelerated Carbonation of Waste Calcium Silicate Materials”, Society of Chemical Industry lecture paper series, 108 (2000). Accessed at www.soci.org., Sept. 2008.



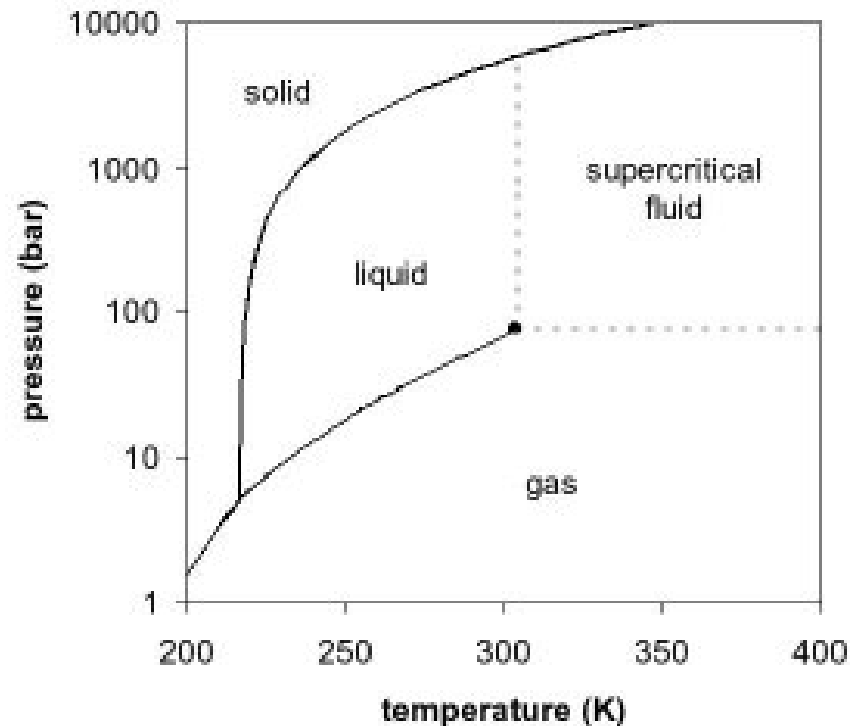
Mixing and forming products under CO₂ gas

- It seems possible to get around the “perimeter sealing” problem by mixing and casting the product under CO₂ gas rather than trying to carbonate an already formed product. Various patents to this effect have been granted.
- The problem of practical forming or casting at the low water contents that seem to be required would need to be addressed. Some patents exist here as well.



Supercritical CO₂

- **Supercritical CO₂ is commercially available and is considered a “green” material.**
- **The needed pressure is only 7.4 MPa and temperature above 31° C.**
- **Supercritical CO₂ is seriously proposed to be injected down bore holes as a way of indefinitely sequestering the material from the atmosphere.**





Supercritical CO₂ to carbonate concrete products?

- Several recent patents contemplate the use of supercritical CO₂ to rapidly carbonate “**large cement structures**” by forming and hardening cement in a mold “**under high carbon dioxide density, such as supercritical or near supercritical conditions**”.
- The supercritical material is “sort of” a liquid that penetrates interstices very rapidly, and would seem to be very effective; however obviously pressure containment vessels would need to be used for the carbonation process.
- Whether cement plant flue gas could be economically purified and rendered supercritical is an open question.



Is anybody making CO₂- sequestering concrete products?

- Apparently not yet.
- However, a potential pilot plant is mentioned at the web site of a start-up firm in Nova Scotia called Carbon Sense Solutions, Inc. and a popular article referring to it appeared in the MIT Technology Review earlier this year. Trial runs were apparently scheduled for some time in 2008.
- The plant was said to employ a procedure where freshly mixed concrete is exposed to a stream of carbon dioxide-rich flue gas to speed up the cement reaction “virtually eliminating the need for heat or steam”. Technical details were not provided.



Conclusion

- I think the possibility exists – and it may even be practical, given the right financial circumstances.
- But an awful lot of process engineering might need to be done if directly captured CO₂ from cement plants were to be used.
- If “exchange credits” were forthcoming for use of CO₂ captured elsewhere and used in concrete manufacture especially in supercritical form), this would make it much more interesting, and perhaps render use of supercritical CO₂ a practical possibility.



Thank you very much!