

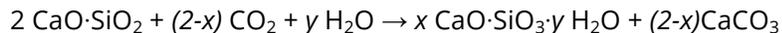
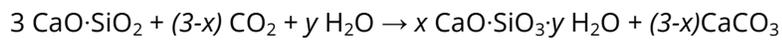
## TECHNICAL NOTE - Chemistry of Fresh Concrete Carbonation

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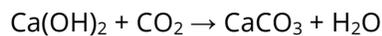
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One potential measure to address carbon dioxide emissions in the cement and concrete industry is to employ the beneficial reaction between carbon dioxide and freshly hydrating cement. An industrial process could successfully use carbon dioxide as a feedstock in the production of concrete building products thereby providing widely distributed carbon utilization that would effectively 'close the loop' for the carbon dioxide emitted during the cement production.

The mechanism of the carbonation-curing of cement was systematically studied in the 1970s at the University of Illinois. The main calcium silicate phases in cement were shown to react in the presence of water to form both calcium carbonate and calcium silicate hydrate gel as (Berger 1972):



Further, any calcium hydroxide present in the cement paste will react with carbon dioxide (Moorehead 1986):



The reaction proceeds in the aqueous state when  $\text{Ca}^{2+}$  ions from the cementitious phases meet  $\text{CO}_3^{2-}$  ions from the applied gas. The carbonation reactions are exothermic with heats of reaction of 347 kJ/mol for tricalcium silicate, 184 kJ/mol for  $\beta$ -dicalcium silicate (Goodbrake et al. 1979) and 74 kJ/mol for calcium hydroxide (Moorehead 1986). The calcium silicate hydrate (C-S-H) gel that forms is understood to be intermixed with  $\text{CaCO}_3$  (Berger 1972). Even in an ideal case of  $\beta$ -C2S and C3S exposed to a 100%  $\text{CO}_2$  at 1 atm there is evidence of some C-S-H gel formation according to the observation that the amount of carbonate formed did not exactly correspond to the amount of calcium silicate involved in the reaction (Goodbrake 1979).

Since carbonation reactions proceed starting with the dissolution of carbon dioxide in water to form carbonic acid, the initial vigorous carbonation stages of carbonation can be described according (Young 1974):



The overall series of steps that occur during the reaction of carbon dioxide with a hydrating cementitious material have been summarized as follows (Maries 1992):

1. Diffusion of  $\text{CO}_2$  in air.
2. Permeation of  $\text{CO}_2$  through the solid.
3. Dissolution of  $\text{CO}_2(\text{g})$  to  $\text{CO}_2(\text{aq})$ .
4. Hydration of  $\text{CO}_2(\text{aq})$  to  $\text{H}_2\text{CO}_3$ . This can be a slow, rate-determining step.
5. Ionisation of  $\text{H}_2\text{CO}_3$  to  $\text{H}^+$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ . This takes place almost instantaneously, lowering the pH locally by 3 or more units, typically from 11 to 8.

6. Cyclic, rapid, exothermic and extensive dissolution of cementitious phases  $3\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$ . The calcium silicate grains are covered by a loose layer of calcium-silicate-hydrate gel, which is quickly dissolved, releasing  $\text{Ca}^{2+}$  and  $\text{SiO}_4^{4-}$  ions. The reaction of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  is minimal, perhaps due to a tight aluminosulphate/carbonate coating.
7. Nucleation of  $\text{CaCO}_3$  and C-S-H. Nucleation is promoted by increasing the temperature and using fine particles that act as heterogeneous nuclei.
8. Solid phases precipitate. The metastable calcium carbonate polymorphs of vaterite and aragonite can form, but eventually they revert to calcite. The final products can be amorphous.
9. Secondary carbonation. C-S-H gel that forms at an early stage can react with  $\text{CO}_2$ . The gel is progressively decalcified leading to the formation of  $\text{CaCO}_3$  intermixed with silicate hydrate gel.

The reaction of carbon dioxide with a mature concrete microstructure can be associated with durability issues such as shrinkage, reduced pore solution pH and carbonation induced corrosion. In contrast, a carbonation reaction integrated into concrete production applies  $\text{CO}_2$  to fresh concrete to react with hydrating cement, rather than the hydration phases present in mature concrete, and does not have the same effects. Beneficial outcomes of exposing precast or masonry concrete to carbon dioxide after product formation have been identified such as: improved strength, reduced absorption, improved resistance to chloride permeability, and improved freeze-thaw performance (Rostami 2012).

Carbon dioxide absorption into the concrete effectively serves as permanent  $\text{CO}_2$  storage in the concrete product allowing producers to create a more sustainable material with improved performance. If carbon dioxide can be beneficially absorbed into wet concrete there will be an attractive new tool for reducing the carbon footprint of the built environment and to help the concrete industry compete with other construction materials in the green building space.

## References

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