

ABSTRACT

Ashraf, Warda. Ph.D., Purdue University, May 2017. Reaction Kinetics, Microstructural Features and Mechanical Properties of CO₂ Activated Low-Lime Calcium Silicate Binders. Major Professor: Jan Olek

Relatively high CO₂ footprint (5 to 8% of global CO₂ emission) of ordinary portland cement (OPC) is mainly due to the following two factors: a) calcination of large quantities of limestone in order to produce high-lime calcium silicates (i.e., alite - Ca₃SiO₅ and belite -Ca₂SiO₄) which constitute the main components of the ordinary portland cement (OPC) and, (b) high production temperature (~1450 °C) required to form these calcium silicates (thus requiring high amounts of energy derived from burning of fossil fuels). The ability to utilize calcium silicates with lower calcium-silica ratio (such as rankinite- Ca₃Si₂O₇) and wollastonite – CaSiO₃) as the primary compounds of the cement would lead to substantial reduction of its CO₂ footprint as these compounds will require less limestone and could be produced at lower temperatures. The reason such low-lime calcium silicates are preferentially excluded from the composition of the typical OPC is that they are non-hydraulic (i.e. are practically non-reactive in the presence of water).

However, some of the recent studies showed that the reactivity of these low-lime calcium silicates can be substantially enhanced in the presence of CO₂. This opens up the possibility of utilizing these low-lime calcium silicates as CO₂ activated binders, thus offering viable (and more sustainable) alternative to OPC.

In order to successfully develop this new binder type as a practical replacement for the OPC, a fundamental, in-depth understanding of the variables controlling the reactivity of these materials along with the understanding of the properties and characteristics of the reaction products is required. This dissertation presents a comprehensive investigation of the novel, CO₂ activated binders with a broader aim to contribute in the further development and long term successful application of similar alternative cementitious materials. The specific focus of this study was in the following areas: (a) effects of CO₂ on the reactivity of pure calcium silicates, (b) carbonation reaction kinetics of pure calcium silicates and industrial grade low-lime calcium silicate cement (CSC) (c) chemical composition, molecular arrangements, and elastic/ viscoelastic properties of the carbonation products of pure calcium silicate phases and CSC, and (d) The macroscale

mechanical properties of carbonated matrixes.

For systematic presentation of the above-mentioned research areas, this dissertation was broadly divided into two parts. The first part of the thesis focused on the CO₂ activation of pure calcium silicates, which include tricalcium silicate (alite - 3CaO.SiO₂, (C₃S)), β and γ- dicalcium silicates (2CaO.SiO₂, belite, C₂S), tricalcium disilicate (3CaO.2SiO₂, rankinite, C₃S₂), and monocalcium silicate (CaO.SiO₂, wollastonite, CS). It was observed that, under specific carbonation scenario, non-hydraulic low-lime calcium silicates such as γ-C₂S, C₃S₂, and CS can achieve a reaction rate close to that of hydraulic C₃S. The final carbonation products of calcium silicate phases are Ca-modified silica gel and calcium carbonate. The Ca-modified silica gel is composed of highly polymerized silica clusters. Both, crystalline (i.e., calcite, vaterite, and aragonite) and amorphous (ACC) forms of CaCO₃ was found to form in the carbonated calcium silicate systems. It was also determined that the intrinsic elastic modulus of the Ca-modified silica gel and calcium carbonate are higher than those of the product phases (C-S-H and Ca(OH)₂) present in conventional OPC paste. Thus, the effective elastic moduli of the carbonated calcium silicate matrixes are higher than that of the hydrated OPC matrixes. The strength of the carbonated matrixes found to be influenced by the morphology of CaCO₃ present in those systems. Specifically, the presence of amorphous and/or poorly crystalline forms of CaCO₃ tend to increase the strength of the matrix. On the other hand, the viscoelastic performance of the matrix was dependent on the chemically bound water content of the Ca-modified silica gel. Chemically bound water contents, in turn, depend on the starting calcium silicate phases.

The next part of the study focused on the industrial grade low-lime calcium silicate cement (CSC). This cement (also known as SolidiaTM cement) primarily consist of wollastonite/ pseudo-wollastonite, rankinite, belite, and amorphous phases. The emphasis of this study was to monitor the microscopic phase (both, amorphous and crystalline) evolution, reaction kinetics, and strength of carbonated mortar samples. It was observed that in addition to calcium silicates, CSC also contains melilite and quartz phases, which do not participate in the carbonation reaction. The carbonation reaction rate constants for CSC found to be affected by w/c ratio, temperature, and CO₂ concentration. The final microstructure of the CSC paste was composed of five distinct phases, these are porosity, Ca-modified silica gel, composite phase, calcium carbonate, and unreacted grains. The composite phase was formed due to the intermixing of calcium carbonate

and Ca-modified silica gel. The strengths of carbonated CSC mortar samples were found to vary from 20 MPa to 40 MPa, depending on the w/c ratios.

In summary, this dissertation presents a study on the multi-scale chemo-mechanical behavior of the novel CO₂ activated calcium silicate binders. It is expected that the knowledge gained from this study will be useful in selection of the types of the calcium silicate phases and/ or curing regimes that will yield optimized reaction rates for industrial-grade CO₂ activated binders.