The CaO-MgO-CO2-H2O-organo system revisited: New insights from thermodynamic modelling of mineral phase transformations

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The refractory industry is increasingly using carboxylic acids, such as acetic and citric acid, to control the hydration behaviour of cast products containing periclase [MgO]. The reaction pathways of MgO dissolution and subsequent Mg-aquo/organo complexation, as well as the precipitation/re-dissolution of Mg-organo salts versus the hydration of MgO to form brucite [Mg(OH)₂] are still poorly constrained. The common mineral impurities in the active or dead-burnt MgO products, such as lime [CaO], calcite [CaCO₃] or dolomite [CaMg(CO₃)₂] complicate the process understanding. Using the computer code PHREEQ-C and the carbfix.dat database, which was adapted by reported and experimentally obtained solubility data of various Mg/Ca-organo salts, we have modelled a series of reaction pathways in the CaO-MgO-CO2-H2O-organo system. The developed thermodynamic models allow an enhanced understanding of i) the respective stabilities of the relevant binder phases and ii) the organo-complexation behaviour of Mg and Ca as a function of the prevailing pH, acid concentration and Mg/Ca ratio.