THERMODYNAMICS OF PORTLAND CEMENT CLINKERING

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Introduction

The Bogue equations are used to estimate clinker phases in cement manufacture; however, they are limited in general application and cannot be used to study novel cement formulations or the effect of using alternative fuels (e.g. biomass) and/or impure raw materials. They also cannot be used to predict the phases which exist at different stages in the cement kiln.

A new clinker thermodynamic database and simple equilibrium model is presented here which is capable of predicting cement phase stability across the full range of kiln temperatures, including the effect of atmospheric conditions. This is termed an "equilibrium reaction path" and can be used to benchmark the kinetics of reactions which occur in the kiln.

Thermodynamic data

- A number of misprints and errors in published thermodynamic data were found in the literature: such as data for C_3A in the Babushkin compilation (Babushkin et al., 1985), and various coefficients in the NIST data for C-A-S-H systems (Haas Jr et al., 1981).

- A new self-consistent database has been compiled from various sources. In this work, 79 solid phases, 26 melt phases, and 71 gas phases are considered.

Methodology

- To determine the phase compositions at equilibrium, a Gibbs free energy minimization is performed on stoichiometric phases at constant temperature and pressure under the constraints of an elemental balance.

- The kiln atmosphere is assumed to be a single ideal gas mixture at the reference pressure (1 bar) and each solid or liquid phase is assumed to be of negligible volume compared to the atmosphere.

- The liquid and solid phases are assumed to be stoichiometric and immiscible.

Validation

- The described model is validated against existing thermodynamic models (Hökfors et al., 2014) for cement clinkers and the Bogue equations to within 3% by mass.

Results

The model is used to predict the clinker phase composition of a representative OPC plant. The equilibrium predictions are shown in Fig. 1 and can be compared to the textbook diagram shown in Fig. 2.

The model reproduces the qualitative phase chemistry over the entire process temperature range but with higher resolution of the stable phases and their proportions.
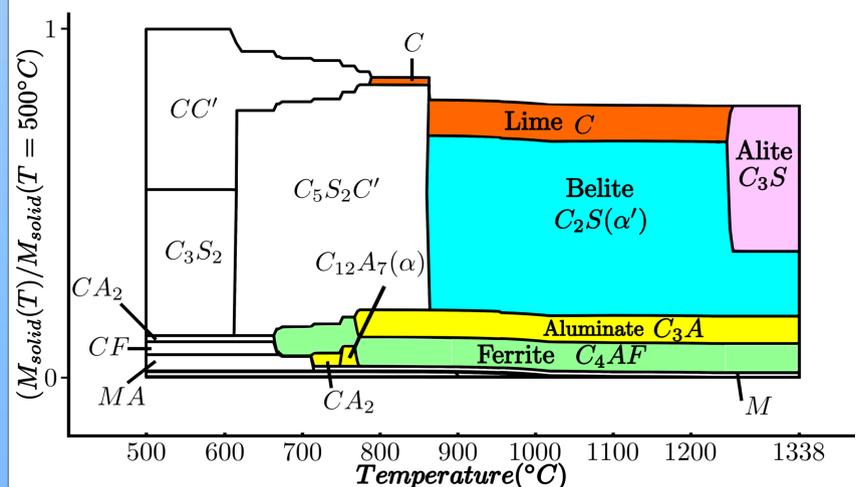

Figure 1: The equilibrium cumulative mass distribution of phases calculated for OPC clinker production.
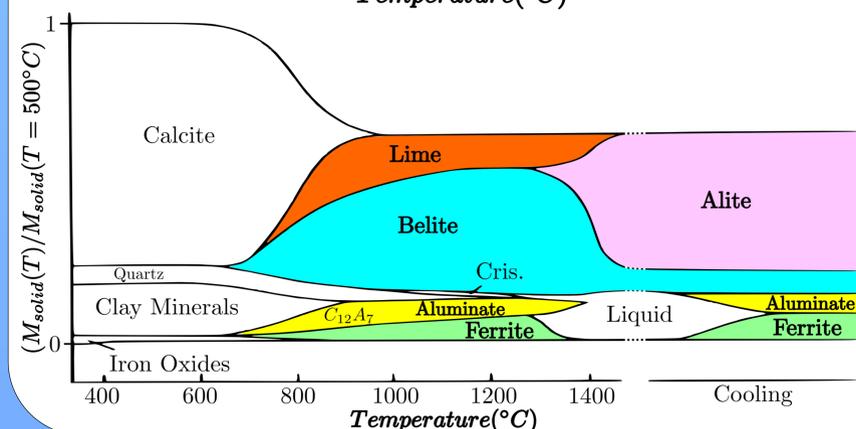

Figure 2: Variations in phases during the formation of OPC clinker. This figure is adapted from Ref . (Taylor, 1997).

Conclusions

The model allows us to calculate the stability of phases across the cement production process and can be used for the optimization of cement formulations as well as to study novel formulations. Preliminary investigations have shown that the kiln atmosphere is a crucial variable controlling the sequence of reactions, the nature of the stable solids, and the reaction path for clinkers heated to progressively higher temperatures.

References

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