Kinetic study on fly ash mineral carbonation

Seyed Zuhair Bolourchian Tabrizi[1,2], Wilson Ricardo Leal da Silva[1], Elena Barbera[2], Fabrizio Bezzo[2]

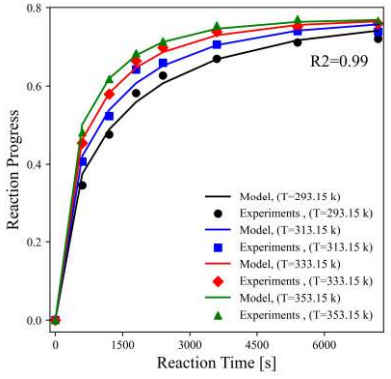
[1]*FLSmidth Cement, Green Innovation, Denmark;* seyedzuhair.bolourchiantabrizi@phd.unipd.it

[2]*Department of Industrial Engineering, University of Padova, via Marzolo 9, 35131 Padova PD, Italy;*

Keywords: CO_2 Utilization; Kinetic Model; Sensitivity Analysis

CO_2 emissions from the cement industry present a significant environmental challenge, prompting the development of Carbon Capture, Utilization, and Storage solutions. Among these, mineral carbonation stands out, driving the development of carbonation reactors that could enable the carbonation of Supplementary Cementitious Materials. The availability of reliable mathematical models describing the key phenomena occurring in a carbonation reactor would represent a valuable tool to simulate and optimise the behaviour of the unit operation and to provide quantitative insight on its performance. However, this is not trivial, due to the complexity of the phenomena taking place and to a general scarcity of experimental data which adds difficulty in model identification. In this study, we compare the fitting performance of different possible formulations for shrinking-core kinetic models with an approach to simplify these models, making identification easier while ensuring they remain accurate enough.

Shrinking-core models are based on particle-fluid processes and formulated by considering a network of resistance in solution-diffusion-reaction pathway. They provide a mechanistic insight into the carbonation process and are evolving based on particle geometry, rate limiting steps (surface reaction and film / product layer diffusion), and diffusion term (reaction time correlated, and non-Fickian diffusion). We used published kinetic data for wood combustion fly ash to identify these models. Our results show that R^2 can increase from 0.33 to 0.99 depending on the model being used – Fig.1 shows the best model performance.



A Modified Shrinking Core Model

Shape: spherical particles
Rate limiting step: product layer diffusion
Diffusion term: Fickian and correlated with reaction time

Model Structure: $A \cdot e^{\frac{-Ea}{RT}} = \frac{\frac{-\rho_s \cdot f_{CaO} \cdot r_0^2}{t \cdot k_2} \cdot \ln\left[1-k_2 \cdot \left(1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}\right)\right]}{2M_{CaO} \cdot \frac{P_{CO2}}{2.82 \cdot 10^6 \cdot e^{\frac{-2044}{T}}}}$

A: pre-exponential factor [-], E_a: activation Energy [kJ.mol^{-1}], k_2: secondary reaction coefficient [-], ρ_s: true density of mineral [kg.m^{-3}], f_{CaO}: CaO Content of fresh mineral (wt%), r_0: mineral particle mean radius [m], M_{CaO}: CaO molecular weight [g.mol^{-1}], P_{CO2}: CO_2 partial pressure [pa], T; reaction temperature [K], X: reaction progress [-], R: universal gas constant (8.314 kJ.mol^{-1}.K^{-1})

Fig.1. Reaction progress data and model behaviour for a shrinking core model.

A global sensitivity analysis (Sobol's method) on model parameters reveals the dominance of activation energy across the entire reaction field, with other kinetic parameters exhibiting minor importance, regardless the models. In particular, this analysis shows a negligible sensitivity of models to pre-exponential factor, which is consequently difficult to estimate with limited experimental data. To ease model identification, we fix this parameter to nominal values for different evolutionary models and estimate the remaining parameters. Results show that the simplified model is still able to fit data with good accuracy.

In conclusion, mineral carbonation-related kinetic studies demand reliability and cost-effectiveness due to the expense associated with kinetic data. Our study demonstrates the potential to reduce the number of parameters without compromising the model reliability, and thus to exploit the information in experimental data more effectively.