



Experimental determination of CO₂ mineralization depth of slag minerals at CO₂ concentrations available in iron and steelmaking flue gases

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Abstract

It is now widely acknowledged that to meet the 2 °C Scenario endorsed by the Paris Climate Accord, global CO₂ neutrality in the mid to second half of the 21st century is necessary, followed by implementation of negative emission technologies at the gigatonne scale. Implicit in this timeline is the assumption that all sectors of society must be functionally CO₂ neutral, with impetus for complete neutrality proportional to a sectors' total emissions. The large CO₂ footprint of the ironmaking and steelmaking sector, along with its projected growth coinciding with population increase, modernization of developing countries, and climate change-related adaptation, suggests that it will need to become a CO₂ neutral process. Direct CO₂ emissions in ISM come primarily from the use of coal as a reductant and for process heat. However, roughly 5-10% of CO₂ emissions are attributed to the decomposition of (Ca,Mg)CO₃ (limestone/dolomite). The (Ca,Mg)O generated from limestone/dolomite calcination reacts with impurities from the iron ore and scrap metal, generating the by-product called slag. The mineral composition of slag is dependent on the furnace type and variations in the input material, but is broadly comprised of (Ca, Mg, Fe)-silicates, (Ca, Mg)-aluminates, (Ca,Mg)-ferrites, and simple oxides. It has long been recognized that the calcium and magnesium content of slags are a potential feedstock for CO₂ mineralization. Ideally, slag-based CO₂ mineralization would form a closed loop of CO₂ associated with impurity removal, which can be simplified as CaCO₃ (limestone) → CaO (lime) → Ca_xSiO_y (slag) → CaCO₃ (limestone). Moreover, CO₂ could be sourced from one or more of the many flue gas streams in iron and steelmaking, thus simplifying the application of carbon capture and sequestration to the remaining gas streams. In practice though, the mineralization of CO₂ using slag has been plagued by slow reaction rates, low conversion extents, and high energy/material requirements. To enhance mineralization reactions, researchers have explored a variety of mechanical, thermal, and chemical protocols. However, the use of chemicals and intense processing conditions incurs CO₂ penalties from chemical and energy production. When the entire process and material chain are considered, slag-based CO₂ mineralization utilizing chemicals or intense processing conditions results in meager CO₂ emissions reduction and, at times, net CO₂ emissions increase.

In contrast to the large interest in processing routes and equipment, there is surprisingly little research into the impact of slag mineral composition on CO₂ mineralization efficacy. Slag-based CO₂ mineralization follows the tenets of the shrinking core model, with the product layer of carbonates and silica inhibiting ingress of CO₂ into the core of slag particles, effectively passivating the slag to further CO₂ mineralization. The reaction depth at which this passivation effect becomes prominent is mineral-dependent. Ostensibly similar minerals have been shown to display up to 4

orders of magnitude difference in CO₂ mineralization depth under identical processing conditions. Minerals with a strong passivation effect can prevent CO₂ from contacting more reactive minerals, so-called ‘mineral locking’. The impact of mineral locking on net CO₂ mineralization is dependent on the ratio of the slag particle size distribution to the mineral grain size distribution and on the mineral-specific CO₂ reaction depth. Distressingly little data is available on the CO₂ reaction depth of most of the minerals common to iron and steel slag. As such, it is currently impossible to determine the extent of mineral locking occurring in slag-based CO₂ mineralization processes; accordingly, attribution of performance to specific equipment/operational design is tenuous at best.

We report the depth of CO₂ mineralization for minerals commonly encountered in iron and steel slag. Due to a lack of commercial availability, the targeted minerals were synthesized using solid state sintering and verified using X-ray diffraction. Following synthesis, the minerals were ground in a ball mill, sieved to remove fines, and the particle size distribution was obtained via laser diffraction. CO₂ mineralization was then induced under CO₂ concentrations covering the range of gases present in the iron and steelmaking process chain (400 ppm to 30% molar). The temperature was held at 30 °C for optimal chemical kinetics and 95% humidity was maintained to prevent sample dry out and flooding. Samples were taken every 24 hours over the course of 14 days. The CO₂ mineralization extent was determined by thermogravimetric analysis and X-ray diffraction. Reaction depth was determined by applying the shrinking core model to the measured CO₂ uptake and particle size distribution. The accuracy of this method was further verified by examination of the depth-dependent mineral composition of the reacted slag. The results indicate that CO₂ reaction depth is strongly mineral dependent, and researchers should account for mineral locking effects when evaluating slag-based CO₂ mineralization system performance.