Abstract

The gap between political promises of CO$_2$ mitigation and realized emissions reductions continues to grow. One of the barriers to short-term action is the scale and interconnectedness of traditional CO$_2$ capture, transport, geological injection, and long-term monitoring (CCS). Though there are no debilitating technical issues to implementing CCS, the size and complexity of the CCS system means that financial, regulatory, and public acceptance concerns often hinder rapid deployment. The magnitude of cost and risk involved also tends to push more conservative designs to the forefront, limiting the learning rate of the industry. A process that could be implemented on a small scale by a single entity without the need for regulatory oversight or public approval would allow for faster kaizen and learning by doing. A prime candidate to realize such a process is above ground CO$_2$ mineralization, where gaseous CO$_2$ is converted into solid, thermodynamically stable calcium or magnesium carbonates.

Previously, we have developed the foundations above ground CO$_2$ mineralization by determining the rate-limiting phenomenon of gas-solid CO$_2$ mineralization (Myers et al., IJGGC 2019), the mineral-dependent mineralization rates (Myers and Nakagaki, ERL 2020), and elucidated the relative efficacy of rate-enhancing activities such as grinding, increasing the CO$_2$ partial pressure, and controlling relative humidity (Myers et al., PCCC-6 2021). In general, selection of the mineral compounds used to stabilize CO$_2$ provides the longest lever to accelerate CO$_2$ mineralization. However, the abundance of minerals suitable for above ground CO$_2$ mineralization is roughly inversely correlated with their reactivity towards CO$_2$ in the ambient environment. Once the parent mineral has been selected, we have found the relative humidity and grain size to be the critical factors to providing CO$_2$ mineralization rate enhancement. Higher relative humidity provides a faster diffusion rate through the product layer of carbonates that form on the exterior of reactive grains. Smaller grain sizes increase the gas-solid surface area and decrease the ultimate product layer thickness required to reach full conversion to carbonates. While this latter fact suggests that finer and finer grinding should provide more and more rapid CO$_2$ mineralization, we have found both theoretically and experimentally that excessive grinding decreases the mineralization rate due to amorphization of the parent mineral. This would seemingly imply that grinding-induced amorphism sets the upper limit of gas-solid CO$_2$ mineralization rates. We have overcome this limit by pairing continuous, low-energy grinding with the gas-solid CO$_2$ mineralization reactions. By limiting the energy imparted to minerals through grinding, amorphization can be avoided. Due to the relative weakness of bonds between the parent mineral and generated carbonates, low energy grinding acts to remove the product layer and, by extension, its passivating influence.

We demonstrate continuous CO$_2$ mineralization with several parent minerals in a continuously feed bead mill reactor at the ~t-CO$_2$/y scale. Carbon dioxide concentrations from atmospheric to 100% and relative humidity from dry to 100% are evaluated. Pure minerals (MgO: Periclase, Mg(OH)$_2$: Brucite, CaSiO$_3$: Wollastonite), natural rocks (Serpentine, Dunite, Peridotite), and industrial wastes (basic oxygen furnace slag, electric arc furnace slag, coal

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gasification slag) are tested. We show that the passivating effect of the product layer can be eliminated, leading to an order of magnitude enhancement of the CO$_2$ mineralization rate (Fig. 1a). The energy consumption of the current system is measured real time, allowing for determination of the operating cost and the net CO$_2$ mineralization as a function of the CO$_2$ intensity of electricity (Fig. 1b). We find, for example, that MgO derived from desalination brine (Myers and Nakagaki, GHGT-15 2021) can be fully converted to Mg-carbonate at ambient temperature and pressure in <1 day with an energy penalty of ~0.9 kWh/kg-CO$_2$. If tied to low-carbon electricity grid (e.g., <50 g-CO$_2$/kWh), the CO$_2$ emissions associated with energy consumption reduce the net CO$_2$ mineralization by only <5%. The operating cost of such a process, accounting for the increased cost of a low carbon grid, is ~65–75 USD/t-CO$_2$. If a purpose-built renewable energy supply was used (e.g., solar PV with battery 4-hour battery backup), the levelized operating cost is estimated to be ~35–40 USD/t-CO$_2$ in 2030.

Importantly, scale-up of the current system from the ~t-CO$_2$/y scale to the ~kt-CO$_2$/y scale is not hindered by financial, regulatory, or public acceptance issues. This may allow for niche applications that are either too small or too remote to be considered for traditional CCS. Moreover, the conversion of CO$_2$ into a stable solid makes quantitative verification of CO$_2$ removal simple and robust, opening up carbon offset markets if appropriate parent minerals are used. The current system also allows for industries producing reactive wastes (e.g., iron and steel, mining, cement making) to quickly reduce their CO$_2$ emissions via their legacy and newly generated waste streams.

Figure 1. General performance of continuous gas-solid CO$_2$ mineralization with concurrent current in terms of a) the increased mineralization rate provided by concurrent grinding and b) the cost and impact on net CO$_2$ mineralization of supplying electricity for grinding.

**Keywords:** CDR; negative emissions; distributed systems; small-scale CO$_2$ capture and storage