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Passive mineral carbonation of Mg-rich mine wastes by atmospheric CO_2

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Abstract

Mg-rich process tailings and waste rocks from mining operations can react spontaneously with atmospheric CO_2 to form stable carbonate minerals by exothermic reactions. Over the last decade, we have conducted a number of laboratory and field experiments and surveys on both mine waste rocks and different types of mine tailings from Ni-Cu, chrysotile, and diamond mines. The experiments and surveys cover a wide range of time (10^3 to 10^8 s) and mass (1-10^8 g) scales. Mine waste rich in brucite or chrysotile enhances the mineral carbonation reactions. Water saturation, but more importantly, watering frequency, are highly important to optimize carbonation. Adjusting the chemical composition of the interstitial water to favour Mg dissolution and to prevent passivation of the reaction surfaces is crucial to ensure the progress of the carbonation reactions. Preservation of the permeability structure is also critical to facilitate water and CO_2 migration in the rock wastes and tailings. In field experiments, CO_2 supply controled by diffusion in the mining waste is slower than the reaction rate which limits the capture of atmospheric CO_2. Industrial implementation of passive mineral carbonation of mine waste by atmospheric CO_2 can be optimized using the above parameters.

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1. Introduction

Passive mineral carbonation of Mg-rich mine wastes is an attractive process to capture atmospheric CO_2 from natural and anthropogenic sources, past or current. In particular, it is one of the few methods for scrubbing CO_2 from diffuse sources, such as transportation or housing, that are not amenable to capture at the emission point [1]. Passive mineral carbonation removes CO_2 from the atmosphere thereby directly addressing the goal to reduce warming caused by greenhouse gases. To this end, we have conducted experiments at various time (10^3 to 10^8 s) and mass (1-10^8 g) scales, using benchtop laboratory experiments, field experimental cells , as well as within instrumented boreholes in a Mg-rich mine waste pile. The objective of these experiments has been aimed at identifying critical parameters that control reaction rates in order to optimize carbon sequestration and recovery of the geothermal energy associated with the exothermic mineral carbonation reactions.

2. Experimental results

2.1. Laboratory

Laboratory experiments have shown that brucite, followed by chrysotile, are the most reactive minerals for carbonation of Mg-rich mine waste and their proportions in mine waste are critical to assess the carbon capture potential [2, 3]. A supply of air with CO_2 and the degree of water saturation at the reaction sites are the limiting steps for the progress of the carbonation reactions [4]. Optimal water saturation of the mine waste or tailing residue (ca. 30-50 %) is a function of the physical properties of the mining waste. In addition, increased watering frequency near optimal water saturation increases the efficiency of the mineral carbonation reactions [3]. A water composition (pH, chelates) favouring dissolution of Mg from mining waste is also critical for the progress of mineral carbonation. The process involves dissolution of gaseous CO_2 from within the mining waste pore space into the interstitial water which precipitates hydrated magnesium carbonates. However, the mineral carbonation reactions are impeded by precipitation of amorphous silica, carbonates and Fe-hydroxides on the mineral and rock fragments of the mining waste [5]. Laboratory conditions of temperature and CO_2 partial pressures favor formation of metastable nesquehonite ($MgCO_3 \cdot 3H_2O$). The morphology of the precipitated carbonate minerals evolves from a flaky and porous phase to less porous, elongated crystals of nesquehonite [6], that may be evidence of passivation control of the reactive surfaces. The neoformed carbonates cement together the rock and mineral fragments of the mine waste or tailing residue [6, 7]. However, the integrity of the carbonate layer may be manipulated over time rendering the unreacted cores accessible [8]. The development of a CO_2 consumption test enabled to quantify the CO_2 flux sequestered by mining wastes [9, 10].

2.2. Field experimental cells

Long-term monitoring (up to four years) of field experiments using four pilot-scale mine waste cells, located at Thetford Mines and Amos (Québec, Canada), allowed studying the carbonation reaction under atmospheric weathering conditions. The cells were constructed from mining or milling wastes (tailings) and instrumented with gas sampling ports to measure the interstitial gaseous composition as well as with probes to measure temperature and water saturation. At the bottom of the cells a drain allows collecting leachate water [11, 12, 13]. One of the cells at Thetford Mines has been dismantled to investigate the carbonation products. A fully instrumented weather station was also installed at each site in order to measure the ambient conditions and precipitation.

Within the cells, the CO_2 concentration was observed to decrease from local atmospheric levels (~400 ppmv), to values as low as 5 ppm inside the cell. The dominant CO_2 transport mechanism in the cell's porous medium is diffusion [11]. The carbon content in the mining residues increased over time, captured in neoformed carbonates (pyroaurite, nesquehonite, dypingite, hydromagnesite) [11, 12]. Over the same time period, the carbon isotopic composition of CO_2 in the interstitial air became heavier, from $\delta^{13}C$ values of -8‰ at the surface, to values as high as 15‰ in the

center of the cells. This indicates kinetic carbon fractionation during CO_2 dissolution into the interstitial water, in cells where advection of CO_2 is limited [11]. The diffusion-controlled CO_2 supply in the cells is the rate-limiting step of the carbonation reaction [12].

2.3. Mining waste pile

We drilled a 90 meter-deep sonic borehole into a 300 Mt mine waste pile, at the Black Lake mine, Thetford Mines, Canada, in order to scale-up the laboratory and experimental cell results to the conditions of field implementation at the mine scale. The six-inch diameter well was instrumented with 22 thermistors and nine gas sampling ports for monitoring temperature, differential pressure and interstitial air composition, including the concentration and carbon isotope composition of CO_2, within the waste pile. A weather station, installed at the top of the mining waste pile, provides local environmental conditions in order to investigate correlations between the meteorological conditions and in-situ measurements. Measurements of gas composition show that air within the mine waste is depleted in CO_2 (<10-200 ppm) compared to the atmosphere (400 ppm). In situ temperatures measured in the borehole, show thermal anomalies as a result of the exothermic mineral reactions inside the mining waste pile. The lower 50 meters of the borehole show an average geothermal gradient of about 45 ºC/km, twice the regional thermal gradient, whereas the upper 40 meters have a geothermal gradient of about 18 ºC/km. The temperature profile is complex as a result of the internal structure of the waste pile that creates distinct hydrodynamic regimes of air and water advection. Snow cover and frozen ground at the surface of the mine waste pile during winter, as well as wind speed and direction, and the density of the air seems to be correlated with air and CO_2 migration into the mining waste pile.

3. Conclusions

Selecting mine waste rich in brucite or chrysotile enhances mineral carbonation reactions. Water saturation, but more importantly, watering frequency, are highly important to optimize the carbonation process. Adjusting the chemical composition of the interstitial water to favour Mg dissolution and prevent mineral precipitation which passivates the reaction surfaces is crucial to ensure the progress of the carbonation reactions. Preservation of the optimal permeability structure is also critical to facilitate water and CO_2 migration to the reaction sites. The CO_2 supply by diffusion into the mining waste appears slower than the reaction rate which limits the capture of atmospheric CO_2. Under the current natural conditions, the 300 Mt of chrysotile-rich mine wastes from the Black Lake mine at Thetford Mines are estimated to be passively capturing circa 0.002 tonnes CO_2/tonne mine waste per year, or 0.6 Mt CO_2/year. Injection of CO_2 and water to the reaction sites could significantly enhance mineral carbonation in, or on top of a mine waste pile, such as in heap leach mining operations.

Acknowledgements

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