

Potential Generation and Consumption of Carbon Dioxide during Treatment of Mine Drainages in South Korea

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Abstract

In this study, direct CO₂ emissions from mine drainages and indirect CO₂ emissions from the potential consumption of hydrated lime were modeled using PHREEQ-N-AMDTreat based on chemical compositions and flow rates at most mine drainage sites (n = 395) across South Korea. When considering CO₂ emissions, passive treatment methods were found to be substantially more advantageous than (semi-)active treatment methods using hydrated lime. Additionally, implementing pre-aeration is a preferable approach for most mine drainages from the perspective of CO₂ emission reduction.

Keywords: Carbon footprint, CO₂ emission, PHREEQ-N-AMDTreat, hydrated lime, pre-aeration

Introduction

Mine drainages often act as CO₂-emission sources because of pyrite oxidation and H⁺ production, which enhances the dissolution of carbonate minerals. Although the treatment of mine drainage with hydrated lime is a common practice to increase pH, the production of lime can generate considerable amount of CO₂, during calcination of limestone.

Lime dosages have been studied and modeled in various mine drainage treatment facilities (Cravotta, 2021; Kim *et al.*, 2023), and life-cycle assessment studies have indicated substantially lower CO₂ emissions associated with passive treatment compared to active treatment using lime (Tuazon and Corder, 2008; Hengen *et al.*, 2014). Unlike active and semi-active methods (e.g., automated lime dosing systems that operates without labor, often accompanied by a large settling pond), which require continuous input of chemicals or energy, passive treatment systems function without such inputs (Younger *et al.*, 2002). Specifically, to increase pH, passive systems

typically utilize limestone or steel slag within SAPS (Successive Alkalinity Producing Systems), slag reactors, or SLBs (Slag Leach Beds), whereas active treatment systems rely heavily on hydrated lime. Despite the growing awareness of CO₂ emissions from industrial lime use, the potential effects of different mine drainage treatment strategies on CO₂ emissions—including the conversion of CO₂ to other species due to pH increase and the indirect CO₂ emissions from lime production—remain largely unassessed. To the best of the authors' knowledge, this gap highlights a critical need for further research.

Thus, the objectives of this study are (1) to calculate CO₂ emissions from most mine drainages in South Korea and evaluate the effect of CO₂ removal through pH elevation, (2) to estimate indirect CO₂ emissions associated with the use of hydrated lime for treating these drainages, and (3) to assess the suitability of pre-aeration as a mine drainage treatment strategy, focusing on its potential to reduce lime dosage and associated CO₂ emissions.



Methods

Survey on mine drainages

In 2016, the Korea Mine Rehabilitation and Mineral Resources Corporation (KOMIR) investigated 395 mine drainages across South Korea. Mine drainages with relatively high contamination and/or flow rates were surveyed four times a year, while those with lower contamination and/or flow rates were surveyed twice a year. The majority of the mine drainages were adit discharges, while some were leachates from dumps of waste rock or tailings.

Data analysis

Seasonal water quality and quantity data of the 395 mine drainages were assessed. Dissolved CO₂ concentrations and the dosages of hydrated lime required to reach specified target pH values were assessed using the Caustic Titration module of PHREEQ-N-AMDTreat version 1.4.5 (Cravotta, 2020, 2021). For this study, the aeration to equilibrium condition with a steady-state partial pressure of CO₂ (p_{CO_2}) of $10^{-3.4}$ atm was applied. When assessing dissolved CO₂ concentrations in mine drainage, samples with a pH lower than 4.5 or without alkalinity were excluded.

To predict maximum CO₂ concentrations that could potentially be degassed from mine drainages by natural aeration ($C_{CO_2(degas)}$), dissolved CO₂ concentration at the equilibrium p_{CO_2} of $10^{-3.4}$ atm ($C_{CO_2(eq)}$) was subtracted from the modeled initial concentration of dissolved CO₂ ($C_{CO_2(dissolved)}$) (Equation 1). The CO₂ flux ($F_{CO_2(degas)}$) was then computed by multiplying this difference in concentration by the cumulative annual flow rate expressed in L yr⁻¹ (Q_{annual}).

The mine drainages were classified into two categories: (1) potential (semi-) active treatment with hydrated lime, which includes 11 (semi-)active treatment facilities

under operation, and (2) others (indicated as “Others” in the relevant plots), which include (a) mine drainages expected to meet discharge criteria in South Korea (excluding arsenic and fluoride) after aeration, (b) mine drainages being successfully treated by passive treatment facilities, and (c) stagnant mine drainages without surface flow.

After the geochemical modeling of each seasonal data subset which is described above, annual averages were used for each mine drainage site (n=395).

Calculation of CO₂ emission from hydrated lime consumption

Emissions of CO₂ from hydrated lime production facilities, categorized as Scope 1 emissions (direct greenhouse gas emissions from sources controlled or owned by the organization), were examined. To focus on the primary and direct sources of CO₂ emissions, calcination and fuel combustion were included, while electricity consumption and limestone quarrying were excluded from the carbon budget.

To convert the amount of quicklime (CaO) to CO₂ generation, an emission factor of 0.75 for lime during thermal decomposition ($EF_{Lime(decom)}$) was applied. This factor was derived from the stoichiometric ratio (SR) of CO₂ to CaO (0.785), and adjusted for the purity (P) of quicklime at 0.95 (IPCC, 2006, 2021; GGIRC, 2022). Subsequently, $EF_{Lime(decom)}$ was multiplied by a conversion factor (CF) for hydrated lime from quicklime (0.757) to obtain the final emission factor for hydrated lime ($EF_{HL(decom)}$) of 0.57 during thermal decomposition (Equation 2; IPCC, 2006, 2021).

Moreover, CO₂ generation from fossil fuel combustion during the calcination of limestone was added to the total CO₂ emission (Shan *et al.*, 2016; Laveglia *et al.*, 2022; Wu *et al.*, 2023). Shan *et al.* (2016) reported mass

$$F_{CO_2(degas)} = C_{CO_2(degas)} \times Q_{annual} = (C_{CO_2(dissolved)} - C_{CO_2(eq)}) \times Q_{annual} \quad (1)$$

$$EF_{HL(decom)} = EF_{Lime(decom)} \times CF = SR \times P \times CF \quad (2)$$

$$EF_{HL(coal)} = EF_{Lime(coal)} \times CF = R_{C-L} \times EF_{Coal} \times CF = \frac{M_{Coal}}{M_{Lime}} \times EF_{Coal} \times CF \quad (3)$$

ratios (R_{C-L}) of coal consumption (M_{Coal}) to lime production (M_{Lime}) ranging from 0.12 to 0.16 in China, with a weighted average of 0.15. The emission factor for coal combustion (EF_{Coal}) was 1.85 t CO₂ per t coal (Shan *et al.*, 2016), resulting in an emission factor for lime during fuel combustion ($EF_{Lime(coal)}$) of 0.27 t CO₂ per t lime (Equation 3). By applying the conversion factor (CF) from quicklime to hydrated lime, we calculated the emission factor for hydrated lime during fuel combustion ($EF_{HL(coal)}$) to be 0.21 t CO₂ per t hydrated lime.

Thus, summing the emission factors for hydrated lime during thermal decomposition ($EF_{HL(decom)}$, 0.57) and coal combustion ($EF_{HL(coal)}$, 0.21) yields 0.78 t of CO₂ directly generated per tonne of hydrated lime produced. When considering the total CO_{2eq} emissions over the entire production process, Laveglia *et al.* (2022) calculated 0.94 t of CO_{2eq}

during hydrated lime production in four EU countries. Additionally, Wu *et al.* (2023) estimated 0.89 t of CO_{2eq} during hydrated lime production in the Yangtze River basin in China. Therefore, the CO₂ directly generated during hydrated lime production ($C_{CO2(HL)}$) was calculated by multiplying the hydrated lime dosage (D_{HL}) by the emission factor for hydrated lime ($EF_{HL} = 0.78$) (Equation 4).

$$C_{CO2(HL)} = D_{HL} \times EF_{HL} = D_{HL} \times 0.78 \quad (4)$$

Results and discussion

The total potential amount of CO₂ generated from the mine drainages was 481 t yr⁻¹, of which 95% was from coal mines. Modeled concentrations of potential CO₂ degassing from mine drainages are plotted against the pH and alkalinity of untreated mine drainages in Fig. 2. The logarithm of the potential CO₂ concentrations degassing from

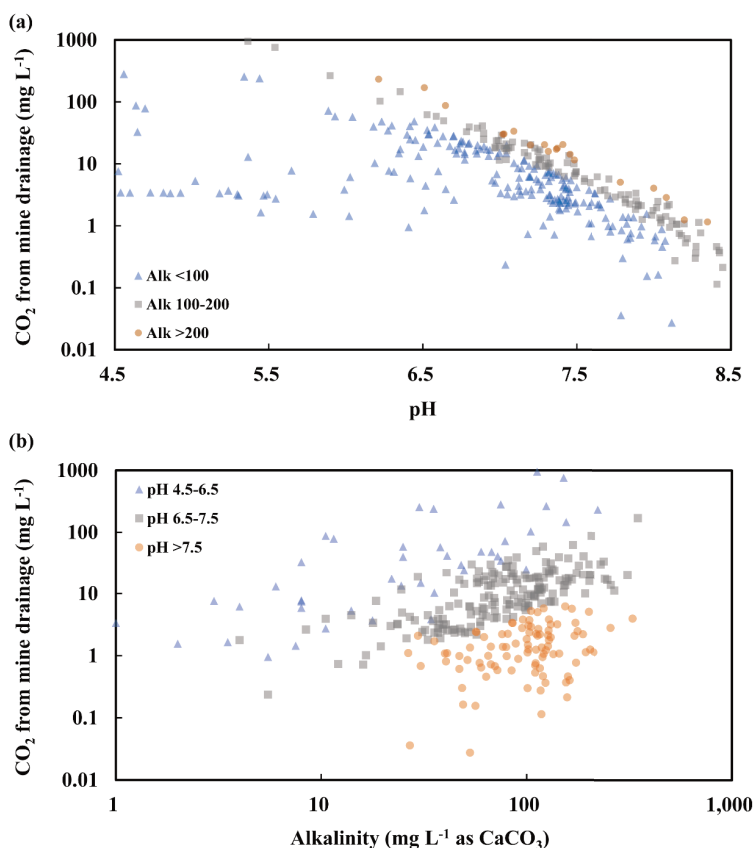


Figure 2 Relationship between modeled concentrations of potentially degassed CO₂ and (a) pH and (b) alkalinity in untreated mine drainages in South Korea. The samples are classified by alkalinity and pH ranges.



mine drainages exhibited a predominantly linear negative relationship with pH within each alkalinity range (Fig. 2a). Similarly, within each pH range, the logarithm of CO_2 concentrations demonstrated a linear positive relationship with the logarithm of alkalinity (Fig. 2b).

Fig. 2a also demonstrate that degassing CO_2 concentrations, which are closely related to dissolved CO_2 concentrations in mine drainage, decrease significantly with increasing pH. This suggests that mine drainage treatment by increasing pH mitigates CO_2 degassing through conversion to HCO_3^- and/or calcite precipitation.

Indirectly generated CO_2 concentrations were calculated based on the modeled consumption of hydrated lime during treatment. The accuracy of predicting

hydrated lime consumption using the same model (Caustic Titration module in PHREEQ-N-AMDTreat) was verified against actual measurements from a full-scale treatment facility in South Korea (Kim *et al.*, 2023). The concentrations of generated CO_2 were compared with pH and alkalinity (Figs. 3 and 4). A notable trend was observed at pH values below 5.5, where decreasing pH corresponded to increased acidity and associated lime dosages, resulting in increasing concentrations of generated CO_2 by lime usage. Similarly, at a given alkalinity, sample groups with lower pH values exhibited higher potential CO_2 generation from lime usage (Fig. 4b). Additionally, a positive relationship was observed between CO_2 generation by lime usage and alkalinity of mine drainages (Figs. 3b and 4b).

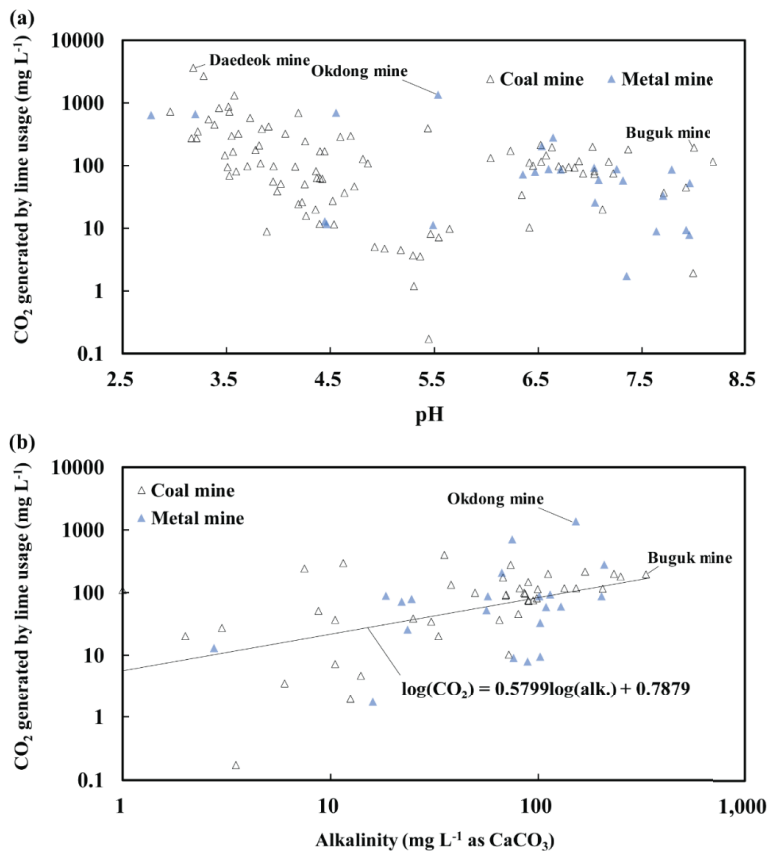


Figure 3 Relationship between calculated indirect emission (in mg L^{-1}) of CO_2 from modeled usage of hydrated lime and (a) pH and (b) alkalinity in mine drainages. The samples are classified based on mine types.

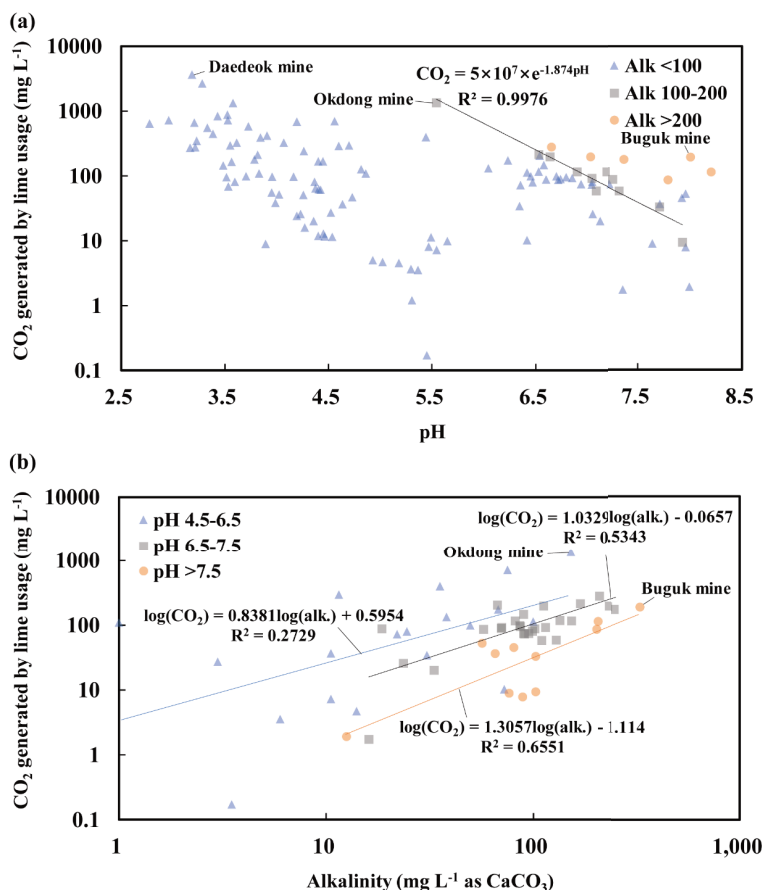


Figure 4 Relationship between calculated indirect emission (in mg L⁻¹) of CO₂ from modeled usage of hydrated lime and (a) pH and (b) alkalinity in mine drainages. The samples are classified based on alkalinity and pH ranges, and samples with pH < 4.5 are excluded in (b). Regression lines correspond to the samples with alkalinities of 100–200 mg L⁻¹ as CaCO₃ in (a) and to samples with three different pH ranges in (b).

Potential consumption of hydrated lime to treat all the sampled mine drainages could generate 2,230 t CO₂ yr⁻¹, which was more than 12 times the CO₂ degassed from drainages, assuming atmospheric equilibrium under surface conditions. Moreover, constructing (semi-)active treatment facilities using hydrated lime consumes substantial amount of cement and electricity.

Pre-aeration to degas CO₂ prior to the treatment of mine drainages has been reported to substantially reduce lime consumption, owing to the decrease of H₂CO₃. We compared direct CO₂ emissions during pre-aeration with indirect CO₂ emissions resulting from hydrated lime usage. The estimated

CO₂ emissions from most drainages were less than 13% of the indirect CO₂ emissions from hydrated lime. As the ratio (13%) was lower than the reported reduction of hydrated lime consumption (22%–50%) by the pre-aeration step of the treatment, the step was preferable for most mine drainages concerning CO₂ emission. Samples with higher alkalinity and pH seem to benefit from pre-aeration in terms of reducing CO₂ emission.

Conclusions

Regarding CO₂ emission, passive treatment is substantially more beneficial than (semi-)active treatment using hydrated lime. Although mine drainages with pH below 4.5



or without alkalinity could not be assessed, pre-aeration was preferred with respect to CO₂ emission for mine drainages with high pH and high alkalinity among the mine drainages with pH above 4.5.

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