Underestimation of alkaline dosage and precipitate amount during water treatment: Role of inorganic carbon and use of PHREEQ-N-AMDTreat

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Extended Abstract

Predicting the dosage of alkaline agents and the amount of sludge for wastewater treatment is crucial for designing and operating treatment facilities. Accurate predictions can contribute to reducing chemical usage and CO_2 emissions. However, commonly used calculations based solely on pH and metal concentrations may lead to inaccuracies (e.g.≈2000%). Thus, theory-based geochemical modeling and its validation with experiments is necessary.

In this study, the key factors influencing the dosage and PHREEQ-N-AMDTreat models (Cravotta, 2020, 2021) were assessed using actual (n = 11) and synthetic (n = 7) mine drainage as well as operational data from pilot- and full-scale facilities, targeting pH of >8.3 to treat Mn (Fig. 1, Kim et al., 2023). The Caustic Titration module in the PHREEQ-N-AMDTreat modeling program predicts the dosage of alkaline agents, the amount of generated precipitates, and effluent chemistry across a range of pH values while considering DIC (dissolved inorganic carbon) species with a user-friendly interface (Cravotta et al., 2015).

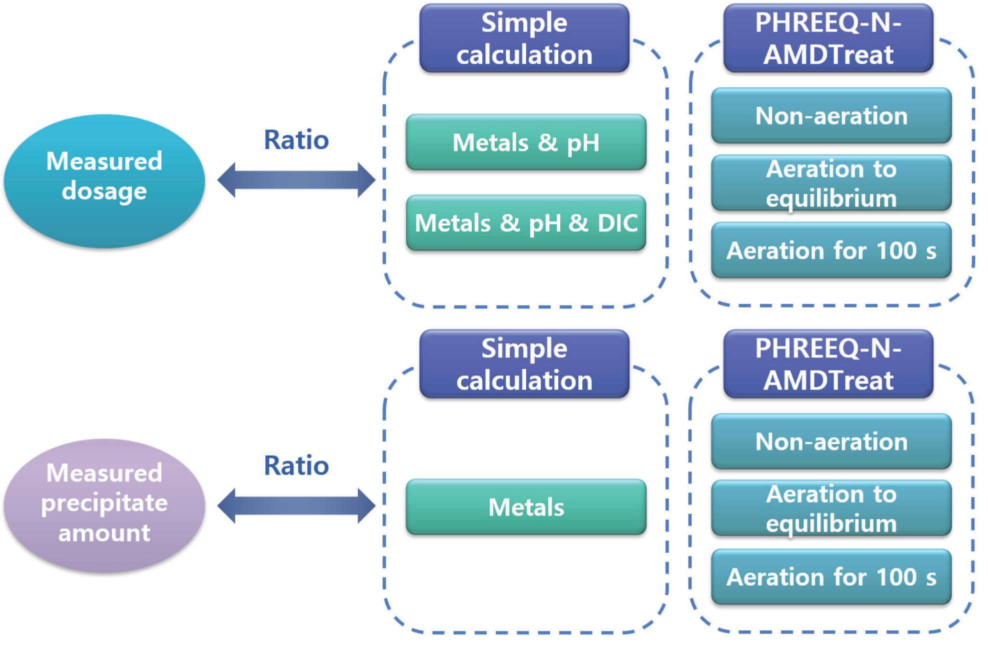

Figure 1 Schematic diagram of calculation and modeling methods for alkaline dosage and precipitate amount in this study (Kim et al., *2023)*

The ratios of the actual and calculated dosages had a positive linear relationship with the alkalinity of the raw water. Moreover, PHREEQC modeling revealed that the effect of the DIC on the dosage increase was more dominant compared to that of calcite precipitation. These findings suggest that the discrepancy of dosage arises because $H_2CO_3^0$ and HCO_3^- are important components of acidity, particularly when the pH is increased to >8.3. Among the three aeration conditions of PHREEQ-N-AMDTreat, aeration to equilibrium exhibited predictions closest to the measured values, owing to the most accurate prediction of Mn concentrations in the treated water. Furthermore, because alkalinity decreases the predicted dosage of hydrated lime in PHREEQ-N-AMDTreat, high alkalinity in the model may underestimate the hydrated lime dosage, resulting in excess ratios between the actual and predicted dosages. Aeration to equilibrium, which decreases excess DIC via equilibrium with air, can also reduce excess alkalinity, leading to a more accurate prediction of the hydrated lime dosage (Kim et al., 2023).

Thus, PHREEQ-N-AMDTreat under the condition of aeration to equilibrium could predict the alkaline dosages and sludge amounts for wastewater treatment at pH >8.3, with average actual/predicted values of 119% and 124%, respectively. These ratios can be used as reference factors for predicting alkaline dosages and sludge amounts when using PHREEQ-N-AMDTreat during the design and operation of treatment facilities. In practical terms, the modeled dosages and precipitate amounts obtained using PHREEQ-N-AMDTreat may be multiplied by 119% and 124%, respectively, to increase accuracy, especially when targeting a pH above 8.3 (Kim et al., 2023).

In the future, further studies, especially those involving diverse full-scale treatment facilities, could help in refining the discrepancies (119% and 124%) and understanding the underlying causes of them. These studies may focus on the discrepancies that may arise from alkalinity changes between raw water and treated water and their incorporation into the modeling of alkaline dosage. Moreover, it is suggested that PHREEQ-N-AMDTreat incorporate direct input parameters for Cu and Zn to provide more precise results for metal mines.

Keywords: Alkaline dosage, hydrated lime, active treatment, sludge amount, PHREEQ-N-AMDTreat

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References

Cravotta CA, Means BP, Arthur W, McKenzie RM, Parkhurst DL (2015) AMDTreat 5.0+ with PHREEQC titration module to compute caustic chemical quantity, effluent quality, and sludge volume. Mine Water Environ. 34: 136–152. https://doi.org/10.1007/s10230-014-0292-6

Cravotta CA (2020) Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage (software download): U.S. Geological Survey Software Release. https://doi.org/10.5066/P9QEE3D5

Cravotta CA (2021) Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage. Appl. Geochem. 126: 104845. https://doi.org/10.1016/j.apgeochem.2020.104845

Kim DM, Kwon HL, Park MS (2023) Underestimation of alkaline dosage and precipitate amount during water treatment: Role of inorganic carbon and use of PHREEQ-N-AMDTreat. J. Cleaner Prod. 433: 139683. https://doi.org/10.1016/j.jclepro.2023.139683