Estimation of Drainage Composition Sourced from Lime-Iron Ore Tailings Mixture in Dry Stack Deposit: Laboratory Testing and Numerical Modeling

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Abstract

The closure of traditional tailings dams has driven the adoption of dry stack disposal, presenting both geotechnical and environmental challenges. A critical concern is the chemical composition of effluents generated by these new structures, demanding robust predictive assessments to mitigate environmental risks. Global guidelines advocate for predictive chemical studies prior to constructing tailings containment structures, while the Global Industry Standard on Tailings Management (GISTM) underscores the critical role of such studies alongside multidisciplinary approaches in geochemistry, water quality, hydrology, and geotechnics for the effective design of tailings facilities, including dry stacks. In this context, this study evaluates the environmental and hydrogeochemical implications of mixing iron ore tailings with lime, a strategy to reduce moisture content of filtered tailings and enhance the geotechnical stability of dry stacks. The study was conducted during the project's conceptual phase, adhering to best environmental practices. The methodology integrated laboratory testing with hydrogeochemical numerical modeling to predict the long-term behavior of the tailings-lime mixture. Laboratory tests encompassed static and kinetic drainage predictions, along with chemical and mineralogical analyses of pure iron ore tailings and those mixed with lime in various proportions. Hydrogeochemical modeling, conducted using PHREEQC software, simulated the deposition of the material in a dry stack, accounting for scaling factors, rainwater percolation, site-specific hydrogeology, and partial gas pressure. Results indicate that lime addition induces alkaline pH conditions, promoting silicate dissolution and neo-mineral formation via pozzolanic reactions. Additionally, kinetic tests results showed that alkaline conditions favor the release of metals (e.g. Al, Cr, Cu, Ni), which would otherwise remain relatively inert under neutral pH. Numerical modeling predicts calcium carbonate precipitation under atmospheric exposure, potentially creating low-permeability zones and preferential flow paths within the dry stack. These findings underscore the need for integrated geochemical and geotechnical evaluations in tailings management to ensure compliance with environmental best practices and global standards.

Keywords: Dry stacking, Lime treatment, Hydrogeochemical modeling, Effluent quality, Calcium carbonate precipitation

Introduction

The increasing global demand for sustainable and environmentally responsible mining practices has guided the development of innovative solutions for tailings management. In this context, various organizations and research programs have provided valuable guidance and resources for understanding and addressing these challenges. Examples include the ARD Test Handbook (AMIRA 2002), the GARD Guide (INAP 2009), and the Prediction Manual for Drainage Chemistry from Sulfidic Geologic Materials (MEND/CANMET 2009). These comprehensive resources offer critical methodologies and frameworks to evaluate and manage the environmental risks associated with mining waste, underscoring the importance of integrating standardized approaches into innovative stabilization techniques.

In Brazil, the rupture of iron ore tailings dams in 2015 and 2019 has led to novel approaches in the tailings management methods. In this context, dry stack tailings emerge as a viable substitute for conventional tailings dam projects, aiming to reduce stored water volume and associated hydraulic failure risks. Among these, chemical stabilization using lime presents a promising approach to improve the geotechnical properties of tailings as a mean to control the humidity of the medium. However, the environmental implications of lime addition, including changes in pH and the mobility of potentially toxic metals, remain important concerns that require careful consideration.

This study focuses on the conceptual and practical aspects of chemical reactions involving lime in the context of dry stacking and dam closure, with particular attention to the stabilization of iron ore tailings. To address these challenges, this work integrates laboratory experiments and hydrogeochemical modeling to evaluate the interactions between lime and iron ore tailings. Laboratory tests, including static and kinetic drainage prediction and mineralogical characterization were conducted to assess the chemical and mineralogical transformations induced by lime addition. Numerical modeling using PHREEQC simulated the long-term geochemical behavior of lime-treated tailings under field-relevant conditions, providing insights into the precipitation of calcium carbonate, changes in permeability, and potential environmental impacts. By combining experimental and modeling approaches, this study contributes to the understanding of lime-induced stabilization mechanisms, offering practical guidance for the design and management of dry stacking systems and dam closures in mining operations.

Conceptual Model – Chemical Reactions Involving Lime

Calcium lime is produced from calcitic limestones or marbles via calcination at 900–1,200°C, converting calcite ($CaCO_3$) into lime (CaO) and CO_2. Lime reacts with water at low temperature, forming portlandite [$Ca(OH)_2$], raising solution pH to 12.45 and releasing calcium ions, which can trigger further chemical reactions. Lime is extensively applied to modify the physical properties of fine-grained soils, particularly those containing plastic clays. The addition of lime initiates cation exchange and flocculation/agglomeration, enhancing soil plasticity, workability, and strength.

The reactions between lime, water, soluble silica, and alumina in soil produce various cementitious materials, known as pozzolanic reactions. These include Calcium-Silicate-Hydrates (CSH) and Calcium-Aluminate-Hydrates (CAH), also formed during Portland cement hydration (Terrel *et al.* 1979). The process increases the soil mixture's pH to approximately 12.4, enhancing the solubility of silica and alumina and sustaining pozzolanic reactions as long as sufficient residual calcium and high pH persist (Little 1987). The possible primary sources of silica and alumina in typical fine soils include clay minerals, quartz, feldspars, micas, and other similar natural silicates and aluminosilicates, both crystalline and/or amorphous. The following reactions illustrate the transformation of lime into cementitious products through interaction with soluble silica and alumina: (1) $Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2(OH)^{-}_{(aq)}$; (2) $Ca^{2+}_{(aq)} + OH^{-}_{(l)} + SiO_{2(aq)} \rightarrow$ CSH and (3) $Ca^{2+}_{(aq)} + OH^{-}_{(aq)} + Al_2O_{3(aq)} \rightarrow$ CAH. Another reaction, carbonation, occurs when lime reacts with atmospheric or organic-derived CO_2, forming stable calcium carbonates instead of the cementitious compounds CAH and CSH. This process can interfere with soil stabilization efforts, especially in exposed or operational waste piles.

Methods

Laboratory tests

Laboratory tests were conducted on pure iron ore tailings as well as on tailings mixed with lime in varying proportions. These tests included paste pH measurements, kinetic testing, and mineralogical analyses.

Paste pH analysis is a static test designed to determine whether a sample contains readily available acidity or alkalinity. This analysis involves mixing a specific amount of the solid sample with deionized water, typically in a 1:1 or 2:1 water-to-solid ratio, to create a paste. The pH of this paste is then measured using a pH meter, providing a rapid assessment of the chemical reactivity of the material. Kinetic tests were conducted in humidity cells following ASTM Standard D5744 (2012). The tests lasted 50 weeks and involved 7 tailings samples: one pure tailings sample (Sample 01) and six iron ore tailing mixed with lime in different proportions (Samples 04, 07, 10 13, 16, 19). The tests involved wet-dry cycles and flooding events. Leaching tests began (week 0) with cells flooded with 1000 mL of deionized water, followed by chemical analysis of the solution after 1 hour. Samples were then exposed to three days of dry air (1.5 ± 0.5 L/min), three days of humid air (95% humidity, 18.1°C–30.4°C), and one day of water percolation. This cycle was repeated throughout the 50-week test period. Weekly measurements included pH, redox potential (mV), electrical conductivity (μS/cm), and temperature (°C). Liquid effluent sampling occurred over 20 weeks (at weeks 0, 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 19, 22, 25, 28, 31, 35, 40, and 45) for chemical analysis.

Mineralogical analyses were conducted with the QEMSCAN system using a Scanning Electron Microscope (SEM), FEI Quanta 650F model, operating at 25 kV and 10 nA. Microanalyses were conducted pixel-by-pixel using two Bruker XFlash 6|30 EDS spectrometers. Images were generated by phase recognition combining Backscatter Electron Imaging (BSE) and EDS microanalysis. The modal distribution of minerals, expressed as weight percentage per sample or fraction, was calculated based on area percentages weighted by the density of each phase.

Hydrogeochemical numerical modeling

Hydrogeochemical modeling was performed using PHREEQC software (version 3; Parkhurst and Appelo 2013) to simulate the deposition of the material in a dry stack, considering scaling factors, rainwater percolation, hydrogeology, and partial gas pressure. For the simulation of chemical reactions with lime and the water percolation model, the kinetics of reactions (*KINETICS* data block), chemical equilibrium (*EQUILIBRIUM_PHASES* data block), and 1D (one-dimensional) transport (*TRANSPORT* data block) were simulated.

Results and Discussion

Mineralogical analysis indicates that the iron ore tailings are predominantly composed of quartz and Fe oxides, followed by phyllosilicates and Mn and Al oxides. Additionally, CaAl silicates (anorthite) and CaFe silicates (tremolite) were identified. In the iron ore tailings mixed with lime, the formation of calciosilicate phases was observed, which were absent in the iron ore tailings. These phases are likely formed through pozzolanic reactions between portlandite and soluble silica, resulting in the generation of CSH-type minerals. Fig. 1 illustrates details of the lime agglomerate, as well as neoformed calcium silicate, identified as the mineral tobermorite.

The pH paste results for the iron ore tailings samples show an average value of 7.35. For the tailings samples mixed with lime, the pH values range from 12.18 to 12.32. This high pH is related to the presence of lime in the tailings and does not vary with the proportion of lime added to the mixture. This aspect indicates that the pH range measured in the samples mixed with lime is due to the thermodynamic equilibrium of the reactions.

The results of the kinetic tests indicate that pH conditions are neutral to slightly basic for the iron ore tailings samples and basic for the iron ore tailings mixed with lime samples. The iron ore tailings sample (Sample 01) exhibited a pH of 6.95 during the first effluent discharge (Week 0) and maintained a pH range of 6.95 to 8.00 in the leachates from Week 1 to Week 50 (Fig. 2). The effluents from the iron ore tailings mixed with lime (Samples 04, 07, 10, 13, 16 and 19) display pH values close to 12 in Week 0, then decreased to a range of 7 to 10 between Weeks 1 and 4 and stabilized between 7 and 9 from Week 5 through Week 50 (Fig. 2). These results indicate the precipitation of mineral phases that reduce the pH to near-neutral values.

Kinetic tests showed that the alkaline conditions favor the release of metals into solution, which would otherwise remain relatively inert under neutral pH. Higher concentrations of aluminium (Al) were identified in Week 0 in the iron ore tailings mixed with lime samples compared to the pure tailing sample, followed by a more evident decline starting from Week 1 (Fig. 2). The iron ore tailings mixed with lime showed an average Al concentration of 0.27 mg/L, while the pure tailing sample exhibited <0.02 mg/L of Al.

Copper displayed higher values, particularly in Weeks 0 and 1, with fluctuations until Week 6. Chromium (Cr) concentrations exceeded 0.05 mg/L in the effluents during the initial weeks for most iron ore tailings mixed with lime samples, while the pure tailings sample showed no variation in Cr levels (Fig. 3). Tailings samples exhibited higher concentrations of Cr up to approximately Week 10, with peaks observed during Weeks 1, 6, and 8. These characteristics suggest that the initial shift to basic pH, followed by a transition to neutral pH, promotes the progressive leaching of mineral phases, enabling the chemical mobility of metals during the early weeks. It is worth noting that some of these values exceed the maximum limits permitted by Brazilian legislation for surface waters, thus raising an environmental concern.

The hydrogeochemical numerical modeling were performed using the software PHREEQC to investigate reactions between lime and iron ore tailings and their impacts on effluents and precipitates. In Simulation 1, a closed system without CO_2 were simulated. The results display that lime is completely

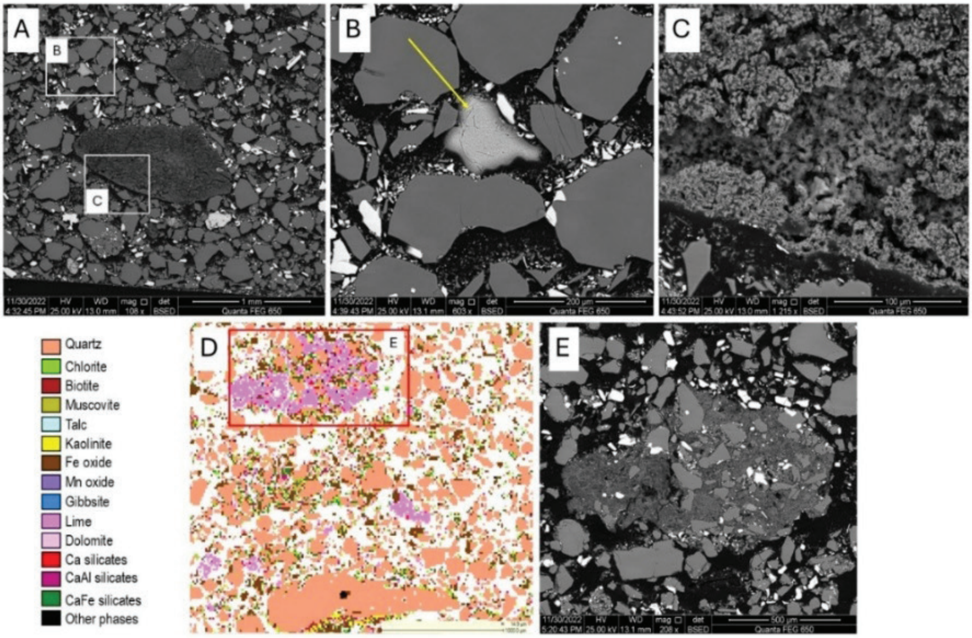

Figure 1 *A) Backscatter Electron Imaging (BSE) of iron ore tailings mixed with lime. B) Neoformed calcium silicate C) Detail of lime agglomerate. D and E) QEMSCAN and BSE images of iron ore tailings mixed with lime.*

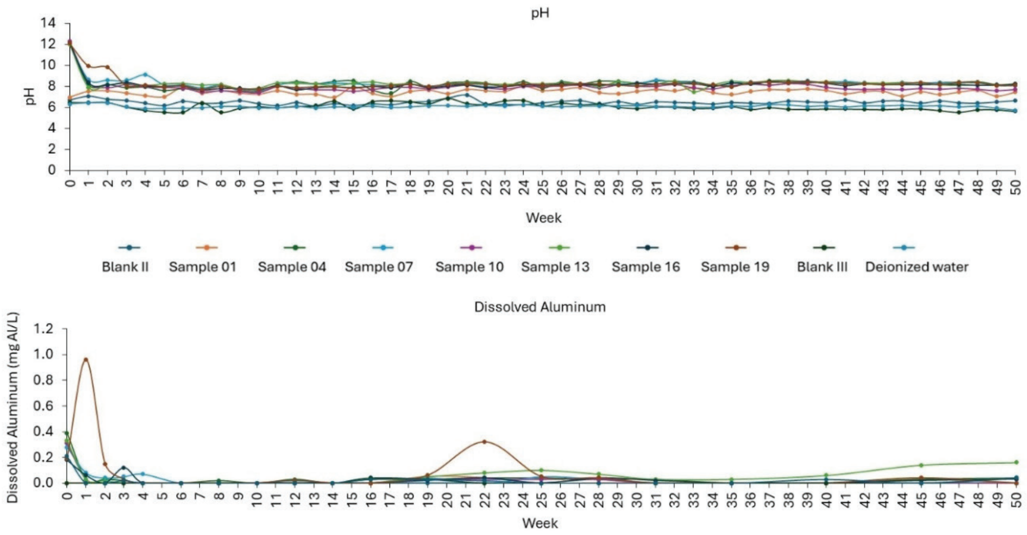

***Figure 2** Kinetic Test Results for pH and Aluminum Concentration Over Time.*

consumed, forming portlandite and raising the pH to an average of 12.26, similar to what was observed in pH paste tests. The pH remains high, and the amount of lime does not limit the reactions or pH increase. In Simulation 2, considering an open system with CO_2, the reaction with lime consumes CO_2, resulting in calcite supersaturation and a slightly lower pH of 11.56 compared to the closed system. The calcite saturation index is 6.15. Tests with varying PCO_2 values (-3.5, -2.5, and -1.5) showed no significant changes in pH or calcite saturation, regardless of the CO_2 concentration.

Simulation 3 aimed to simulate reactions with lime in the presence of silicates and iron oxide in an open CO_2 system. Hematite and kaolinite were considered at equilibrium,

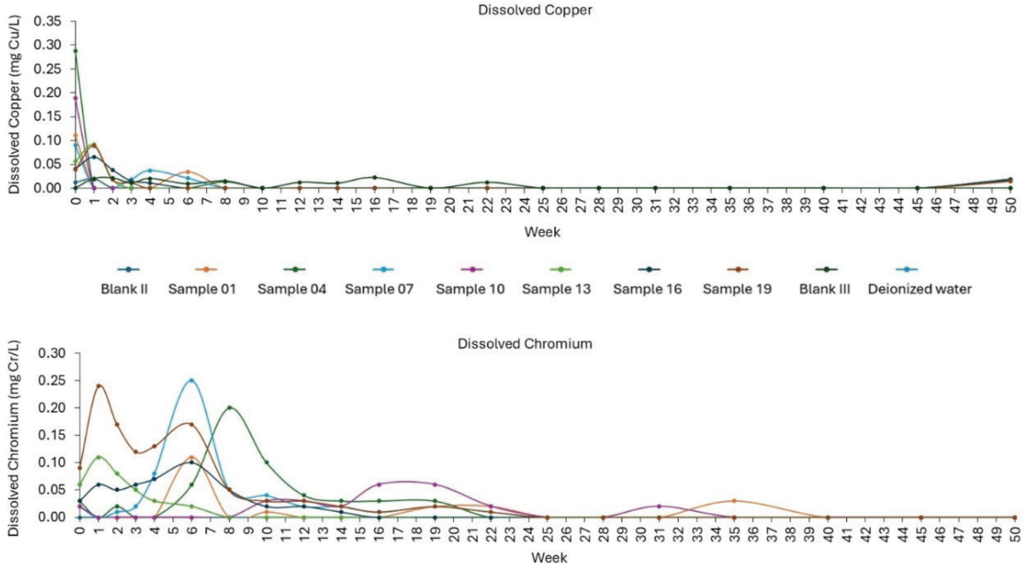

***Figure 3** Kinetic Test Results for Dissolved Copper and Dissolved Chromium Concentrations Over Time.*

while the reaction kinetics of anorthite were included. The high pH promotes silicate dissolution, releasing silica and alumina, which react with lime in pozzolanic reactions to form CSH and CAH minerals. Mineralogical analyses revealed increased amounts of calcium silicates, calcium-aluminum silicates, and calcium-iron silicates, interpreted as neoformed silicates. The simulation showed supersaturation of both calcite and neoformed silicates. Simulation 4 evaluated calcite and neoformed silicates at chemical equilibrium in an open CO_2 system. The presence of both calcite and neoformed silicates caused a further pH reduction due to mineral precipitation.

In addition, a simulation was conducted on a hypothetical dry stack accounting for scaling factors, rainwater percolation, site-specific hydrogeology, and partial gas pressure. The results showed that lime is instantly consumed in the first equilibrium (step 0 in the transport model), transforming into calcite. As calcite precipitates, it captures alkalinity and Ca^{2-} ions, reducing the pH to near-neutral values. However, this occurs only after all lime is depleted. With a constant addition of lime-treated tailings, reactions may continue, maintaining the pH near 12. A significant effect of these reactions is mineral precipitation, which can alter the material's physical properties, such as porosity and permeability.

The numerical modeling indicates that calcium carbonate precipitation may occur under atmospheric exposure, potentially creating low permeability zones and preferential flow paths within the dry stack structure. These factors should be carefully considered in geotechnical designs. This study highlights key factors related to effluent quality and environmental impacts that must be addressed in projects involving the mixing of iron ore tailings with lime.

Conclusions

The study demonstrates that mixing iron ore tailings with lime has both environmental and geotechnical implications. The elevated pH can dissolve mineral phases that are stable under neutral conditions, releasing chemical species previously confined to the solid phase. These released species may pose environmental risks and complicate wastewater treatment processes. Conversely, in the presence of CO_2, lime reacts to form carbonate, which lowers the solution's pH to near-neutral levels. This precipitation process tends to fill the material's interstitial spaces, reducing porosity and potentially causing chemical clogging within the structure. Such intense precipitation can lead to the formation of cemented zones with low permeability in the tailings, a critical factor to consider in geotechnical design. The study was conducted during the project's conceptual phase, in adherence to best environmental practices.

References

AMIRA (2002) ARD test handbook. AMIRA P387A project: prediction and kinetic control of acid mine drainage. Melbourne, VIC: AMIRA International.

ASTM – American Society for Testing Materials (2012) ASTM D5744-07e1 Standard Test Method for Laboratory Weathering of Solid Materials Using a Humidity Cell, 19p. DOI: 10.1520/D5744-07E01

GISTM (2020) Global Industry Standard on Tailings Management. Global Tailings Review, 40p.

INAP (2009) The International Network for Acid Prevention. Global Acid Rock Drainage Guide (GARD Guide). http://www.gardguide.com

Little DL (1987) Fundamentals of the Stabilization of Soil with Lime (Bulletin 332), NLA, Arlington, VA. http://www.lime.org/publications.html

MEND/CANMET (2009) Mining and Mineral Science Laboratory. Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials. MEND Report 1.20.1.

Parkhurst DL, Appelo CAJ (2013) Description of input and examples for PHREEQC version 3–A computer program for speciation, batch-reaction, one dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497p. http://pubs.usgs.gov/tm/06/a43/

Terrel RL, Epps JA, Barenberg EJ, Mitchell JK, Thompson MR (1979) Soil Stabilization in Pavement Structures: A User's Manual, Volumes I and II, FHWA.