Improved Acidity Estimation by Integrating Comprehensive Dissolved Metal(oid)s Data: A Geochemical Modeling Case Study of Highly Mineralized Mine Waters

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Abstract

This study introduces a geochemical modeling approach using PHREEQC to improve the accuracy of acidity estimates in waters influenced by acid mine drainage (AMD). AMD, common in regions like the Iberian Pyrite Belt, is characterized by low pH and high concentrations of metals, sulfate and acidity. Conventional methods, such as net acidity, often underestimate actual acidity by excluding additional metal(oid)s and bisulfate, particularly in highly mineralized waters. By incorporating factors like Fe, Al, Mn, other metal(oid)s, and bisulfate, these methods improve acidity estimation accuracy. Results demonstrate that these methods provide more precise acidity measurements, enhancing AMD monitoring and treatment strategies.

Keywords: Mine waters, acidity, PHREEQC, metal(oid)s concentration, modeling

Introduction

Acid mine drainage (AMD), which may be characterized by low pH and elevated concentrations of acidity, sulfate, and metaloids, can be a long-term environmental problem in coal or metal-mining regions (Nordstrom, 2011). The consequences of AMD include degradation of water quality, soil, and aquatic life. Portugal and Spain exemplify the environmental impact of AMD, particularly due to their long tradition of mining in the Iberian Pyrite Belt (IPB), which dates to pre-Roman times. The IPB is one of the world's largest metallogenic provinces, with approximately 90 identified massive sulfide deposits (Inverno *et al*., 2015). A detailed geological overview of this region can be found in the works of Leistel *et al*. (1997), Barriga (1990), and Tornos (2006). Most of the mines are currently abandoned, with only a few undergoing rehabilitations. This region has been the focus of numerous studies of AMD and its possible remediation, particularly the mining-influenced waters exhibiting extremely low pH and high mineralization levels.

Acidity is one of the key parameters in the characterization, monitoring, and neutralization of mining-influenced water; it indicates the intensity and extent of mineralization and the corresponding alkalinity needed for AMD neutralization. The acidity concentration and loading are useful to determine a watercourse's capacity to neutralize AMD inflows or to estimate the necessary amount of caustic agent to achieve neutralization through treatment. Laboratory analysis involves the hot peroxide acidity method, which consists of titration of an oxidized sample with a strong base (NaOH) to a pH endpoint of 8.3 (APHA, 2012). Alternatively, estimation of this parameter can be achieved through the utilization of the computed net acidity or net alkalinity (Hedin, 2004, 2006; Kirby and Cravotta, 2005a, 2005b), which considers only pH and the concentrations of Fe, Al, Mn, and alkalinity. However, in cases of extreme mineralization, net acidity can underestimate the measured acidity due to the contributions of additional constituents that can interact with the base added. Thus, the objective of this study is to develop and demonstrate an improved method to estimate the acidity that has broad applicability to AMD with low pH and high concentrations of various solutes.

In this context, the present study proposes a geochemical modeling approach using the PHREEQC geochemical speciation program (Parkhurst and Appelo, 2013), which considers the pH, Fe, Al, Mn, additional metal(oid)s, and bisulfate (HSO_4^-). PHREEQC was used to estimate acidity according to four methods: net acidity, total acidity, acidity by speciation, and caustic titration. The net acidity uses the pH and the analytical concentrations of Fe, Al, Mn, and alkalinity, as explained by Hedin (2004, 2006). The total acidity also uses these analytical concentrations, but for an expanded list of elements, with contribution factors from -1 to +3. A factor from 0 to 1 is multiplied by the analytical sulfate concentration, depending on how much is present as HSO_4^- (factor of 1) versus SO_4^{-2} (factor of 0). Similar to total acidity, the speciated acidity assigns a contribution factor to each of the species, following the method of Kirby and Cravotta (2005a, 2005b), but considering an expanded list of constituents. Last, the caustic acidity is computed by PHREEQC as the amount of base added to reach pH 8.3, after a sample has been equilibrated with the atmosphere.

Methods

About 200 water samples were collected from two abandoned and highly contaminated mining areas of the IPB: the Trimpancho mining complex and the São Domingos mine (Barroso *et al.*, 2024; Gomes and Valente, 2022). The water samples were collected from rivers affected by AMD, pit lakes, acid lagoons, and tributary mixing sites (Fig. 1). During sampling, pH, electrical conductivity, and temperature were measured using a multiparameter instrument (Thermo Scientific Model Orion Star A Series), while oxidation-reduction potential was measured with an ORPTestr 10. Dissolved oxygen was also measured using the HACH HQ30D portable multiparameter. All instruments were calibrated with the respective standard solutions prior to each analysis. Other parameters, such as the hot peroxide acidity, alkalinity, sulfate, and metal(loid) concentrations, were analyzed

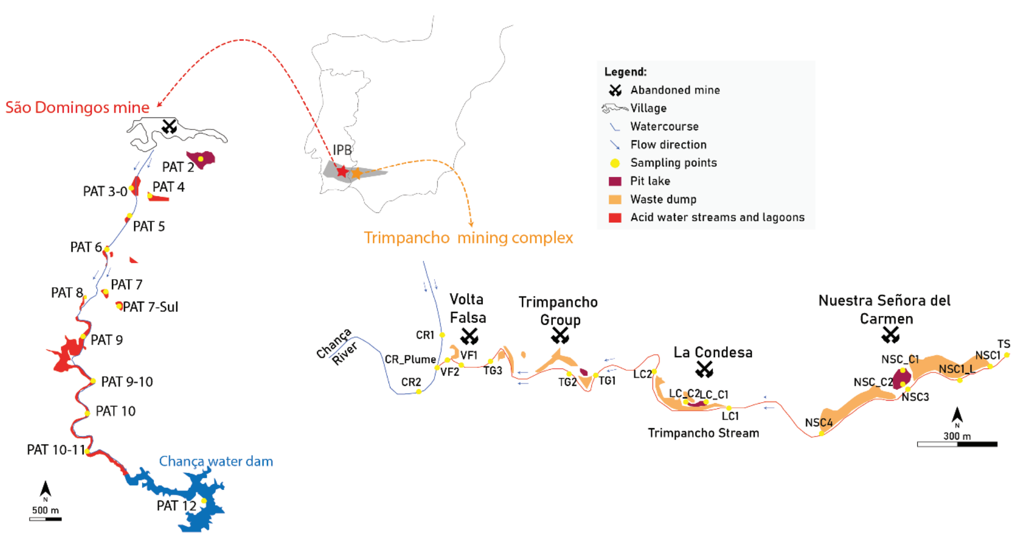

***Figure 1** Location of water sampling points at the São Domingos mine (Portugal sector of IPB) and the Trimpancho Mining Complex (Spain sector of IPB).*

in the laboratory. Acidity and alkalinity were determined by volumetric titration (standard method 2310 B) and sulfate concentration was obtained using turbidimetry (standard method 4500-SO_4^{2-} E) (APHA, 2012). Metal(oid)s concentrations were analyzed by inductively coupled plasma optical emission spectrometry in filtered and acidified aliquots.

Results and discussion

In general, the water samples collected showed a wide range of acidity (22 to 429 250

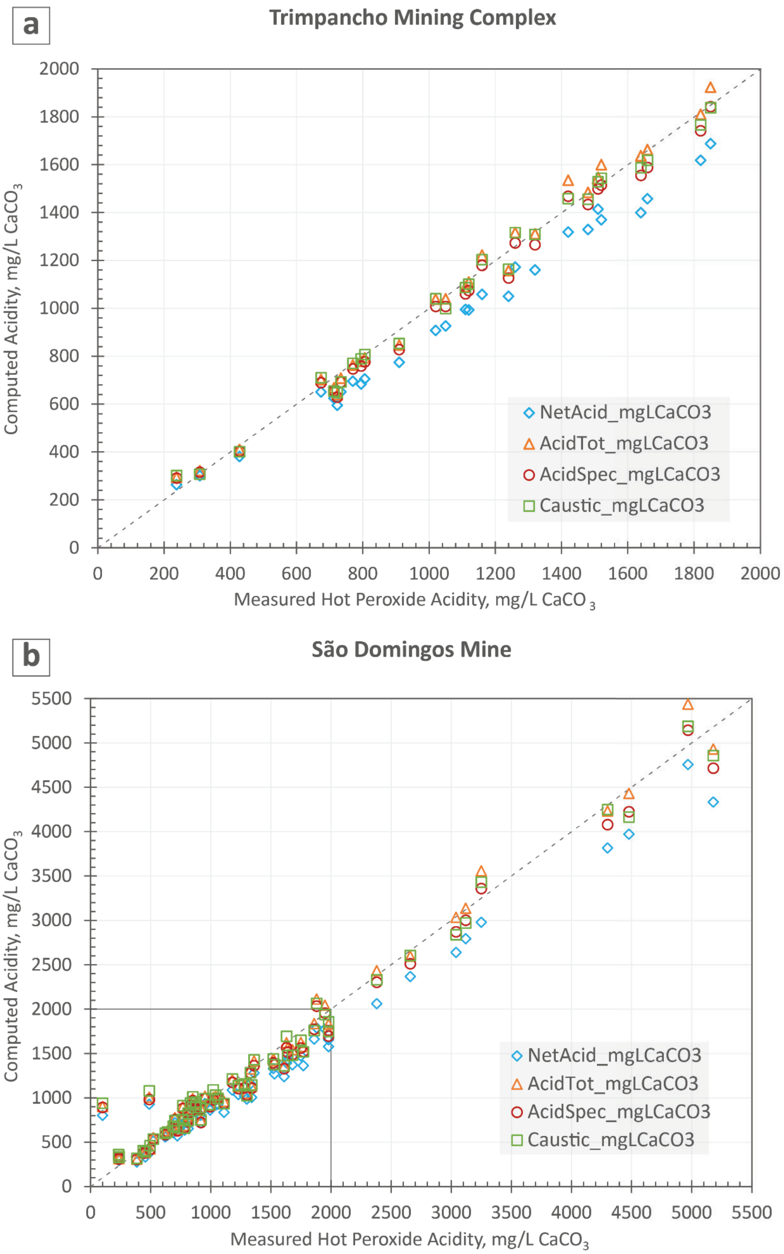

Figure 2 *Comparison between measured hot peroxide acidity and computed acidity (Net Acidity, Total Acidity, Acidity by speciation, and Caustic) using PHREEQC: (a) Trimpancho mining complex and (b) São Domingos mine.*

mg/L as $CaCO_3$), pH from 0.44 to 8.57, and sulfate concentrations up to 410 600 mg/L. The dominant dissolved cations were Fe and Al; however, many of the samples with lower pH showed high concentrations of Zn, Cu, As, Mn, Cd, Pb, and Sb. For geochemical modeling, computations with PHREEQC used the wateq4fREYsKinetics.dat database (Cravotta, 2022), which was expanded from the wateq4f.dat (Ball and Nordstrom, 1991) to include speciation data on rare earth elements and other trace elements. To ensure the accuracy of the results, the charge balance calculated by PHREEQC was verified, and only samples with a charge balance of less than ±15% were accepted for interpretations of speciation results (McCleskey *et al.*, 2023).

Fig. 2 shows the comparison of the measured hot peroxide acidity and the computed acidity results for each of the mining areas. In general, for both mining areas, the total acidity, acidity by speciation, and caustic methods show a strong agreement with the acidity measured in the laboratory. On the other hand, net acidity tends to underestimate acidity values compared to laboratory measurements. These results demonstrate the importance of potential contributions from HSO_4^- and various metal(oid)s when calculating acidity, especially highly mineralized mine waters with low pH.

The three new methods of calculation provide improved estimates of acidity and are similar in value to one another. The main difference is that speciation computations are needed for the speciated acidity and the caustic titration acidity. On the other hand, the total acidity uses only analytical concentrations, without speciation, so it may be computed using a spreadsheet or other calculator.

Conclusions

In conclusion, the developed approach provides a reliable means of estimating acidity for environments of extreme contamination. The findings show close alignment with laboratory-measured acidity values, reinforcing the validity for practical applications. Thus, by refining acidity estimation, this study contributes to effective environmental monitoring and offers insights for determination of remediation measures.

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