

Interferometric study of pyrite surface reactivity in acidic conditions

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ABSTRACT

Production of acid mine drainage (AMD) is in large part due to pyrite oxidation. The tie-in between environmental remediation and pyrite oxidation requires understanding pyrite oxidation in aqueous systems. In this study, ex-situ measurements using vertical scanning interferometry (VSI) were utilized to investigate pyrite surface reactivity under AMD conditions, such as pH 1 (HCl), an O₂-saturated atmosphere, and room temperature, including (1) ex-situ measurements using vertical scanning interferometry (VSI) and (2) solution chemistry measurements using a flow reactor. In the former, two fragments were immersed in the acidic solution for 27 days at undersaturation with respect to pyrite. Weathered surfaces of pyrite that showed surface history (e.g., existence of terraces, steps, etch pits, and non-uniform surface roughness) were selected to examine surface topography changes with time.

Based on the VSI measurements, the reaction mechanism includes the formation and coalescence of etch pits leading to overall surface retreat. This result is consistent with the stepwave model that predicts that, under sufficiently high undersaturation (i.e., $\Delta G < \Delta G_{\text{crit}}$), pit opening and generation of stepwaves are mechanisms that control mineral dissolution. Surface reactivity was not uniform over the entire surface, yielding surface regions with a considerable variety of dissolution rates that ranged from 1.7×10^{-7} mol/(m²·s) to lower than 2×10^{-11} mol/(m²·s). The overall pyrite dissolution rate calculated over the explored surface was 2.8×10^{-9} mol/(m²·s), which agrees very well with the absolute rate measured [3.1×10^{-9} mol/(m²·s)].

Based on the release of Fe in the flow experiment and normalizing with the geometric surface area, the steady-state pyrite dissolution rate obtained was $7.2 \pm 1.5 \times 10^{-9}$ mol/(m²·s), i.e., a factor of about 2 higher than that determined by VSI. Collectively, these rates also agree with pyrite dissolution rates obtained by bulk dissolution measurements. These results highlight (1) “local” dissolution rates vary widely over mineral surfaces at the short range scale from nano- to millimeter lengths; (2) inferred dissolution rates that are usually based on topographic changes on rather small (micrometer-scale size) surface regions are not necessarily representative of rates under field conditions; and (3) BET surface area and geometric surface area associated with reactive surface area and used to normalize the pyrite dissolution rates yield a variation in rate that ranges from 6.3×10^{-11} to $7.2 \pm 1.5 \times 10^{-9}$ mol/(m²·s).

Keywords: Pyrite oxidation, surface reactivity, vertical scanning interferometry, AMD, stepwave model