

PROBLEMS WITH MANGANESE AND MAGNESIUM IN HOT ACIDITY TITRATIONS¹

² C.S. Kirby and B. Means

Abstract: Standard Method “Hot Acidity” titrations to an endpoint of pH 8.2 or 8.3 are commonly employed to evaluate the contributions of hydrogen ions and hydrolyzable metals to the acidity of mine drainage. These titrations employ steps (addition of hydrogen peroxide, sulfuric acid, boiling followed by cooling) to improve the reproducibility of the methods. Coal mine drainage from the bituminous coal fields of Western Pennsylvania commonly contains concentrations of Fe, Al, and Mn in excess of 20 mg/L and Ca and Mg in excess of 100 mg/L. High concentrations of Mn and Mg in solutions can create difficulties in the interpretation of the values estimated for acidity.

We performed Hot Acidity titrations on mine drainage solutions with a wide range of chemical compositions. The pH and measured Hot Acidity were recorded, and filtered aliquots were analyzed for metals and sulfate at several stages of each titration (raw water, after cooling, and at pH intervals up to the endpoint). Calculated acidities were also computed for each stage based on pH and dissolved metal concentrations. Hot and calculated net acidity results showed poor agreement for some waters. Mn removal after Hot Acidity titration ranged from 0 to 96%, thus the reliability of the Hot Acidity to account for Mn acidity is not clear. Up to 27% of Ca+Mg decreases were not explained by dilution, thus Ca and Mg apparently contributed acidity. Up to 80% of SO₄ decreases were not explained by accounting for dilution and H₂SO₄ addition. Both of these phenomena are contrary to predictions based on geochemical computer modeling, and both can impact treatment planning and costs.

Additional Key Words: calculated and measured acidity.

¹ Presented at the 2005 National Meeting of the American Society of Mining and Reclamation, Breckenridge CO, June, 19-23 2005. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

² Carl S. Kirby, Associate Professor, Department of Geology, Bucknell University, Lewisburg PA 17837, 570-577-1385, kirby@bucknell.edu; Brent Means, Hydrogeologist, U.S. Office of Surface Mining, 415 Market Street, Harrisburg, PA 17011 bmeans@osmre.gov