

Oxidation Kinetics of Tetrathionate at Low pH: Implications for Pyrite Oxidation Mechanisms and Microbial Ecology in Acid Mine Drainage Environments

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The oxidation kinetics of tetrathionate ($S_4O_6^{2-}$) is being studied in a series of laboratory experiments under conditions similar to those found in acidic mine drainage sites, including the Iron Mountain Superfund Site in northern California, USA. Several researchers have confirmed the occurrence of intermediate sulphur oxyanions in the course of pyrite oxidation over a wide range of pH values (Goldhaber, 1983; Moses et al., 1987; Schippers et al., 1996). At lower pH ranges, the concentration of these intermediate sulphur oxyanions decreases as the stable end product of the reaction, sulphate, increases. Luther (1987) proposed a mechanism for the oxidation of pyrite by ferric iron, resulting in thiosulphate ($S_2O_3^{2-}$) detaching from the pyrite structure. Subsequently, several researchers (Williamson and Rimstidt, 1993; Xu and Schoonen, 1995) investigated the stability of thiosulphate with respect to ferric iron complexation, acid dissociation, and pyrite surface catalysis. At the conditions of low pH and high ferric iron concentrations common in acidic mine drainage environments, it is reasonably expected that the majority of thiosulphate in solution would oxidise to tetrathionate. Schippers et al. (1996) studied the stability of tetrathionate at pH 1.9 and determined that it was stable in low pH, ferric iron solutions, but the oxidation to sulphate was catalysed by pyrite. To our knowledge, Schippers et al. (1996) is the only study of tetrathionate stability under these conditions to date, and there has been no attempt to quantify the rates of oxidation for this species. Quantification of the rate of formation and oxidation of tetrathionate under relevant conditions is critical for evaluating the kinetics and mechanisms of oxidation pathways. The presence of sulphur oxyanions in solutions generated by the oxidation of sulphide minerals must be supported by a relevant investigation of the stability of those species and the mechanisms by which they form and are oxidised. In addition, observed spatial and temporal changes in microbial ecology at the Iron Mountain Mine site may be intimately linked to the mechanism and rate of sulphur oxidation in different environments. It is the goal of this research to quantify the rate of polythionate oxidation at low pH, and to use kinetic data for intermediate sulphur oxyanions to analyse the oxidation pathway in sulphide and elemental sulphur oxidation. Batch experiments investigating the stability of tetrathionate have been carried out to evaluate reactivity towards molecular oxygen and ferric iron in solution over a pH range of 0.5 to 2.2 and a temper-

ature range of 4 to 70 C. Sample aliquots were measured for polythionate concentration by an ion-pairing technique utilising an isocratic elution of 1:3 acetonitrile:water containing 3.0 mM tetrabutyl ammonium hydroxide as an ion-pairing reagent with a Dionex Series 500 ion chromatograph and an IonPac NS1 column. Experiments involving oxygenated solutions containing no ferric iron exhibited no measurable reaction over several weeks. Solutions containing ferric iron from 0.5 to 20mM that were de-oxygenated with N_2 and sealed in plastic reaction vessels at 25°C also exhibited no measurable reaction over several weeks. Oxygenated solutions containing ferric iron were reactive and exhibited degradation of the tetrathionate with a proportional decrease in ferric iron to ferrous iron with a half-life of approximately 300 hours. Sulphate was the only product detected by subsequent ion chromatographic analyses using conductivity and UV detection by isocratic elution with a carbonate/bicarbonate eluent and an IonPac AS14 column. In situ solution Raman experiments also identified only sulphate as a product of the oxidation experiments. Homogeneous reaction experiments over a range of conditions expected in acidic mine drainage environments indicate that tetrathionate may be oxidised at low pH by dissolved oxygen in the presence of ferric iron, which acts as a catalyst. The ferric iron may be subsequently reduced in the oxidation of tetrathionate reaction products. Several experiments are underway to further quantify the reaction kinetics of the homogeneous reactions, the catalytic effect of pyrite, and the rate which micro-organisms may oxidise tetrathionate.

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