Pyrite dissolution in acidic media.

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Oxidation of pyrite in aqueous solutions in contact with air (oxygen 20%) was studied at 25℃ using short-term batch experiments. Fe^{2+} and SO_4^{2-} were the only dissolved Fe and S species detected in these solutions. After a short period, $R = [S]_{tot}/[Fe]_{tot}$ stabilized from 1.25 at pH = 1.5 to 1.6 at pH = 3. These R values were found to be consistent with previously published measurements (as calculated from the raw published data). This corresponds to a non-stoichiometric dissolution ($R < 2$) resulting from a deficit in aqueous sulphur. Thermodynamics indicate that S(-I) oxidation can only produce $S^0(s)$ and SO_4^{2-} under these equilibrium conditions. However, Pourbaix diagrams assuming the absence of SO_4^{2-} indicate that $S_2O_3^{2-}$ and $S_4O_6^{2-}$ can appear in these conditions. Using these species the simplest expected oxidation mechanism is

$$FeS_2(s) + 1.5\ O_2 \rightarrow Fe^{2+} + S_2O_3^{2-}$$

followed by

$$S_2O_3^{2-} + 1.2\ H^+ \rightarrow 0.4\ S^0(s) + 0.4\ S_4O_6^{2-} + 0.6\ H_2O,$$

and finally

$$S_4O_6^{2-} + 3.5\ O_2 + 3\ H_2O \rightarrow 4\ SO_4^{2-} + 6\ H^+$$

possibly in several steps.
The overall reaction is

$$FeS_2(s) + 2.9\ O_2 + 0.6\ H_2O \rightarrow Fe^{2+} + 0.4\ S^0(s) + 1.6\ SO_4^{2-} + 1.2\ H^+,$$

consistent with R = 1.6. In the most acidic (pH = 1.5) conditions, SO_2 formation is expected as an intermediate step in the oxidation of $S_4O_6^{2-}$ to SO_4^{2-}. Emission of $SO_2(g)$ would result in $R < 1.6$, again consistent with experimental observations. The above multistep mechanism, based on known aqueous redox chemistry of sulphur species, accounts for the deficit in aqueous sulphur noticed in all published experimental observations. The intermediate species cannot be detected, and this is consistent with calculated concentrations being below the detection limits. Under non-acidic conditions, $S_2O_3^{2-}$ can be detected, but evaluation of the dissolution mechanism is hindered by precipitation of Fe(III) as iron oxyhydroxides.