

Controls on Iron/Sulphur Ratios on Spoil Heaps and in Mineworkings

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Acidity and high iron co-kinetically controlled, equilibrium precipitation of secondary minerals is controlling the effluent concentrations of Fe and S, thus validating the use of equilibrium thermodynamic calculations. The second is that conclusions regarding mineral sources and sinks obtained from one site may be applied to other sites, providing the processes underlying the evolution of water chemistry are understood.

This study uses X-Ray Diffraction, Scanning Electron Microscopy and geochemical modelling to investigate sources and sinks for iron and sulphur in discharges from several well characterised coal mines and spoil heaps. Preliminary conclusions are validated by the examination of independently measured parameters affected by the dissolution/precipitation of particular minerals, such as alkalinity and concentrations generated by the oxidation of pyrite within spoil heaps and mine-workings present a considerable problem worldwide. The success with which discharges from these locations may be treated depends on the accuracy with which the discharge can be characterised in terms of the initial chemistry, the short term (seasonal) variability of water chemistry, and the long term evolution of dissolution rates of both acidity producing and acidity consuming minerals. One of the most important parameters in the characterisation of the discharges is the Fe/S ratio, which records the progress of the pyrite oxidation reaction. After the first stage of pyrite oxidation, the Fe/S ratio is, theoretically, 0.5 as all the iron released is dissolved as Fe^{2+} . Further oxidation will gradually decrease this ratio as the Fe^{2+} is transformed to Fe^{3+} and is precipitated as iron oxyhydroxides. Complications arise when other Fe and/or S bearing phases such as jarosites and schwertmannite begin to precipitate.

A high Fe/S ratio presents a challenge to the designer of effluent remediation in that there is a substantial reservoir of potential acidity present; this acidity is released upon oxidation and precipitation of the iron. A low Fe/S ratio, on the other hand, indicates that the iron has already been precipitated and hence further problems with acidity production are unlikely. However, sources and sinks for both iron and sulphur, and the controls on these sources and sinks must be understood in detail if the Fe/S ratio is to be used with confidence, as some iron "sinks" are temporary (e.g. readily soluble jarosites), and provide a reservoir of potential acidity which may be mobilised under certain conditions.

Plots of Fe against S concentrations for a wide range of spoil heaps and mine-workings from a number of coal-mining sites world wide exhibit systematic differences in Fe/S ratios for the two different types of site, with ratios from spoil heaps being substantially lower than those from minewater discharges. Two important inferences may be drawn from these observations. The first is that, although pyrite dissolution is pH. The work reveals that although Fe/S ratios are governed by mineral precipitation, rather than the source minerals, it is difficult to uniquely identify precipitating minerals using geochemical modelling alone, as there are a number of minerals which precipitate under similar conditions and have closely related effects on water chemistry. However, it is possible to identify mineral groups which affect water chemistry in specified ways, and to relate the likelihood of their precipitation to external factors such as oxygen access, the physical and chemical breakdown of clay minerals, and water saturation. This observation provides an important validation for the construction of a process-based method of predicting Fe/S ratios and other geochemical parameters of discharges from poorly characterised coal mines and spoil heaps.