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The Effects of pH on Surface-Catalysed Oxidation of Aqueous Fe(II)

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A steady state geochemical model has been developed to assist in understanding the affects of pH on surface-catalysed oxidation of aqueous Fe(II) by O_2(aq) from ferruginous mine water discharges using engineered reactors with high specific-surface area filter media. Surface catalysed oxidation occurs due to accelerated oxidation of Fe(II)(aq) when absorbed on precipitated iron(III) oxyhydroxide mineral surfaces. Limited field data for the treatment of a mine water discharge were available for model development and assessment of possible parameter values. The model includes solution and surface speciation equilibrium, oxidation kinetics of dissolved and adsorbed Fe(II) species and mass transfer of O_2(g). Figure 1 shows iron removal as a function of adsorption capacity (surface area to total water content) for the simulated treatment of 4 currently unregulated mine water discharges in the UK, River Hipper, Thurcroft Colliery, Dunston Colliery, and Allen Spaw (Banks., et al 1997). Modelled results show that iron removal efficiency decreases with decreasing pH and alkalinity. The extent of removal by surface-catalysed oxidation is complicated by the effect of the resulting acidity generation on pH, and the resulting effect of pH on the adsorption of Fe(II). This is demonstrated dramatically by the enormous increase in adsorption capacity required for 100% removal of iron from the River Hipper (pH 3.81, [Fe(II)]=67.3mg/L), compared with that for drainage from Thurcroft Colliery spoil deposits (pH 6.76, [Fe(II)] = 18.2mg/L). The impact of acidity and pH on iron removal is also demonstrated by the results for Dunston Colliery (pH 6.3, [Fe(II)] = 10.6mg/L) and Allen Spaw discharge (pH 6.5, [Fe(II)] = 15mg/L). For these, 80% removal is achieved at relatively low adsorption capacity (10-06M), but complete removal requires an adsorption capacity that is an additional 4 orders-of-magnitude greater (10-02M). This increase corresponds directly to increases in acidity due to increased rates of iron oxidation and precipitation. The extent of Fe(II) adsorption on iron oxides depends strongly on pH, decreasing steeply as pH drops into the near-acid pH region. The pH where this decrease in adsorption occurs is termed the adsorption edge and generally falls in the range 5<pH<6 for Fe2+ adsorption on Iron(III) oxide. The oxidative precipitation of iron oxide mineral can drive the reactor pH to values below the adsorption edge for Fe(II), thereby severely limiting Fe(II) adsorption and the rates of surface-catalysed oxidation. Thus, there is a diminishing return on increasing the engineered adsorption capacity in a reactor if there is insufficient alkalinity in the discharge to prevent a drop in pH to values below the adsorption edge.

Banks, D. Burke, S. and Gray, C., *The hydrogeochemistry of coal mine drainage and other ferruginous waters in North Derbyshire and South Yorkshire, UK. Quarterly Journal of Engineering Geology*, **30**, 257-280, (1997).

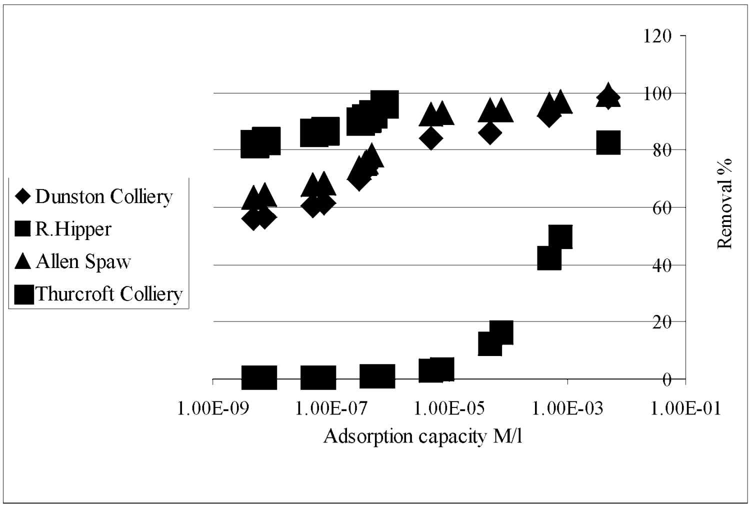

Figure 1: Iron removal as a function of adsorption capacity