Redox transformations of iron in extremely low pH environments: Environmental and industrial implications

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Iron is a particularly important microbial resource in extremely acidic (pH <3) environments, where it serves not only as a micronutrient, but also as a major electron donor and/or acceptor. This is due primarily to the much greater stability of ferrous iron (even in oxygen-saturated liquors) and solubility of ferric iron in extremely acidic compared to neutral pH waters. Many different species of acidophilic prokaryotes are known to either catalyze the dissimilatory oxidation of ferrous iron or the dissimilatory reduction of ferric iron, while some can do both, depending on the prevailing environmental conditions.

Measurements of specific rates of iron oxidation by acidophilic bacteria have revealed significant differences between species. In general, specialized chemolithotrophs, such as Leptospirillum spp., exhibit significantly faster rates than more generalist mixotrophic and heterotrophic species, such as Sulfobacillus spp. and Ferrimicrobium acidiphilum. Measurement of specific rates of dissimilatory reduction of soluble ferric iron by Acidiphilium cryptum str. SJH have shown that these are often much greater than values recorded for neutrophiles. Rates of reductive dissolution of ferric minerals by acidophilic bacteria appear to depend on the relative acid-solubilities of the former. Acidophilic ironreducing bacteria appear to use the often small amounts of ferric iron in solution, thereby causing the equilibrium between mineral-phase and solution-phase iron to move in the direction of the latter. Reductive dissolution (and concommitant release of associated metals and metalloids) of a wide range of ferric iron minerals, including jarosites, schwertmannite and goethite, has been demonstrated in vitro.

Recent developments that harness redox transformations of iron for industrial applications include remedation of mine waters using the recently characterised species *Ferrovum myxofaciens*, and the extraction of nickel from oxidized ores by causing the reductive dissolution of goethite. The latter represents a major development in 'biomining'.

Oxygen isotope exchange between H₂O and super critical CO₂: Lab experiments and field evidence

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Traditionally, the application of stable isotopes in Carbon Capture and Storage (CCS) projects has focused on δ^{13} C values of CO_2 to trace the migration of injected CO_2 in the subsurface. More recently the use of δ^{18} O values of both CO₂ and reservoir fluids has been proposed as a method for quantifying in situ CO2 reservoir saturations due to oxygen isotope exchange between CO2 and H2O and subsequent changes in $\delta^{18}O_{\rm H2O}$ values in the presence of high concentrations of CO2. To verify that oxygen isotope exchange between CO2 and H2O reaches equilibrium within days, and that $\delta^{18}O_{H20}$ values indeed change predictably due to the presence of CO₂, a laboratory study was conducted to measure the isotope composition of H₂O, CO₂, and dissolved inorganic carbon (DIC) at representative reservoir conditions (50°C and 19 MPa) and varying CO₂ pressures. Results obtained showed that δ^{18} O values of CO₂ were on average $36.4 \pm 2.2 \% (1\sigma, n = 15)$ higher than those of water at all pressures up to and including reservoir pressure (19 MPa), in excellent agreement with the theoretically predicted isotope enrichment factor of 35.5 % for the experimental temperature of 50°C. Since the fraction of oxygen sourced from CO₂ is related to the total volumetric saturations of CO₂ and water as a fraction of the total volume of the system, we conclude that changes in δ^{18} O values of reservoir fluids can be used to calculate reservoir saturations of CO₂ in CCS settings given that the δ^{18} O values of CO₂ and water are sufficiently distinct. This was confirmed by field data obtained from eight observation wells at the Pembina Cardium CO₂ Monitoring Pilot in Alberta (Canada). Arrival of injected CO₂ caused changes in the δ^{18} O values of reservoir fluids of up to 4 ‰, as well as increasing DIC, Ca and Fe concentrations in the reservoir fluids.

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