Solubility of Nickel Ferrite ($NiFe_2O_4$) from 100 to 200°C

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Nickel ferrite is one of the oxides present on surfaces of the components of the primary circuit of pressurized water reactors (PWR). Its dissolution contributes to the release of nickel in the primary water, at the origin of the contamination phenomenon. A complete understanding of the behavior of nickel in the primary circuit must include solubility measurements of nickel oxides, including mixed oxides such as nickel ferrite.

The solubility of nickel ferrite was measured in a Hydrogen-Electrode Concentration Cell (HECC), which has been described in [1], at temperatures of 100°C, 150°C and 200°C and measured *in situ* pH between 4 and 5.25. The experimental solution was composed of HCl and NaCl (0.1 $mol.L^{-1}$). Based on previous studies ([2,3]), pure nickel ferrite was experimentally synthesized by calcination of a mixture of hematite Fe_2O_3 and bunsenite NiO in molten salts at 1000°C for 15 hours in air. The so obtained powder was fully characterized. After the experiment, the powder showed no significant XRD evidence of Ni(II) reduction. Nickel concentration was measured by atomic absorption spectroscopy and iron concentration was measured by UV spectroscopy. The protocol has been designed to enable the measurement of both dissolved Fe(II) and total iron [4].

The solution was slightly undersaturated relative to nickel oxide [1] and to both hematite and magnetite. The nickel/iron ratio indicated a non stoichiometric dissolution. The solubility measurements were compared with equilibrium calculations using the MULTEQ database. The solubility of nickel ferrite in a reducing acidic solution is reasonably well described by the available thermodynamic data.

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Alternative nitrogenases in terrestrial ecosystems?

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Recent studies have shown that molybdenum (Mo), which is used in the Mo-nitrogenase, can limit N_2 fixation in temperate and tropical ecosystems. This suggests that alternative nitrogenases, which use V or Fe in place of Mo, may contribute to N_2 fixation. The acetylene reduction assay (ARA) is commonly used to estimate N_2 fixation rates but requires the use of an adequate conversion ratio (R ratio = acetylene reduction/N_2 fixation). The theoretical value for R is 3-4, but measured values in the field range from less than 1 to more than 10. In this study, we show that even in pure cultures, the R ratio is variable and dependent on the culture growth phase. Nonetheless, low R values (below 2) can be consistently attributed to N_2 fixation by alternative nitrogenases. Interestingly, an analysis of the literature shows that low R ratios are measured almost exclusively in soils, and are not found in the surface oceans (where Mo is abundant, and alternative nitrogenases are unlikely to be important) or in plant symbions (which do not possess the genes for the alternative nitrogenases). The low R ratios may thus be indicative of alternative nitrogenases in soils. In a series of microcosm experiments with temperate soils from New Jersey, we were able to confirm that alternative nitrogenase genes were present, and expressed, even though N_2 fixation did not appear to be Mo-limited. The R ratios were low at the beginning of the incubations, suggesting that alternative nitrogenases contribute to the bulk to N_2 fixation in these samples. The R ratios also tended to increase over time, possibly reflecting depletion of the fixed carbon pool, or increased contribution from the Mo-nitrogenase. The possibility that alternative nitrogenases may contribute to N_2 fixation in systems that are not Mo limited is intriguing and deserves further investigation.

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