Magnetite transformation to hematite under high H_2 pressure at 150 °C

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The mechanisms of dissolution/precipitation of magnetite are not well understood, in spite of many previous investigations. The major problem has been a lack of precise measurements of pH and H_2 pressure. Therefore, we have examined the magnetite solubility using an emf cell for H^+ concentration measurements and a Shaw membrane comprising Pd for H_2 pressure measurement.

The experiments were carried out by reacting submicron grains of pure magnetite with HTr (trifluoromethane-sulfonate($CF_3SO_3^-$)) - NaTr solutions (itnitial H^+ concentration = 0.001 – 0.02 m) at 150°C. Ar – H_2 mixture gas was used to pressurize the system (total pressure: 35 – 95 bar; P_{H2}: 5 – 50 bar). After the system reached a steady state at each pH (< 2 days), an aliquot of solution was withdrawn and the Fe^{2+} concentration was measured by ICP-AES. The residual solid after the experiment was analyzed using XRD and XPS.

Our results have revealed: (a) the magnetite solubility is significantly lower (by ~1.5 log unit) than those proposed by other researchers; (b) the solubility was independent of the H_2 pressure; (c) the residue contains appreciable amounts (~20%) of hematite formed as the result of magnetite dissolution; and (d) the surface of residual particles is primarily magnetite with small amounts of (< 5%) iron hydroxides. These results indicate that magnetite was transformed to hematite under high H_2 pressure and this reaction is independent of redox condition, as shown in the following reaction:

$$Fe_3O_4 + 2H^+ \rightarrow Fe_2O_3 + Fe^{2+} + H_2O \quad (1)$$

This leaching of Fe^{2+} from magnetite by acid solution is much faster than reduction of Fe^{3+} to Fe^{2+} at 150°C, allowing the formation of hematite even under reducing conditions.

The effect of iron on bentonite stability

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Several designs for high-level nuclear waste (HLW) repositories include steel waste canisters surrounded by bentonite backfill. The aim of this work was to investigate montmorillonite stability in the presence of native Fe, magnetite and aqueous solutions using thermodynamic modelling and hydrothermal experimentation. Thermodynamic models suggest that if pore waters are supersaturated with respect to magnetite in HLW repositories, Fe(II)-rich saponite is the most likely montmorillonite alteration product (if $f_{O_{2(g)}}$ values are significantly lower than magnetite-hematite equilibrium). Experimental starting mixtures included combinations of Na-montmorillonite, magnetite, native Fe, calcite, NaCl and $FeCl_2$ solutions that were reacted at 250ºC, $P=P_{water\ sat}$ for between 90 and 114 days. Products were analysed using XRD, FT-IR, TEM, ICP-AES and ICP-MS. In the hydrothermal experiments with NaCl solutions, native Fe oxidised to produce magnetite and montmorillonite was altered to Fe-rich smectite (initially Fe(II)-rich, transforming to Fe(III)-rich on exposure to atmospheric O_2). The Fe(III)-rich smectite exhibited only partial expansion after ethylene glycol solvation. TEM imaging suggests this may be due to the loss of some tetrahedral units from smectite layers, producing 7Å layers that become hydrogen bonded to adjacent sheets. Experiments where magnetite was included as the main source of Fe did not produce Fe-rich smectite. The addition of a small amount of calcite to the starting mixtures promoted the alteration of montmorillonite to analcime. Experiments with a high concentration of Fe^{2+} did not produce significant amounts of Fe-rich smectite, instead, a low intensity 7 Å peak was observed in XRD patterns. Thermodynamic models successfully predicted reaction pathways in the experiments.