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Thermodynamic Properties of Layered Iron Silicates in Steel-Bentonite Interactions

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Steel and bentonite will be used in the geological disposal of vitrified HLW in Japan. Precipitation of layered iron silicate minerals are an expected consequence of steel-bentonite interactions on relevant timescales. However, there is a lack of reliable thermodynamic properties of layered iron silicates for them to be included in reactive transport simulations.

In the present study, fifteen calibration minerals were used to define a polyhedral model [1] that provided estimates for the missing Gibbs free energy of formation ($\Delta_f G^o$) of layered iron silicates. Entropy (S^o) and heat capacities (C_p) were estimated by additive methods. Enthalpy of formation ($\Delta_f H^o$) could then be calculated. Molar volumes (V^o) were calculated from lattice parameters reported in the literature. These methods were carefully used to maintain internal consistency with the JAEA thermodynamic database for geochemical reactions (https://migrationdb.jaea.go.jp).

The polyhedral model resulted in a maximum 0.1% error in estimates for the known $\Delta_f G^o$ values of the fifteen calibration minerals. Using the polyhedral model with estimation of S^o and C_p, and calculation of $\Delta_f H^o$ and V^o, a full suite of thermodynamic properties was derived for the layered iron silicates berthierine, cronstedtite, greenalite, minnesotaite, and odinite (Table 1).

These thermodynamic properties were tested in a reactive transport simulation of steel-bentonite interaction. Steel corrosion formed magnetite and siderite, montmorillonite and chalcedony in Kunigel V1® dissolved and sepiolite and greenalite (Table 1) precipitated at the steel-bentonite interface.

More detailed studies on the thermodynamic properties of the minerals siderite, sepiolite and greenalite, and their use in reactive transport simulations is ongoing.

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[1] Chemark & Rimstidt (1989), American Mineralogist 74, 1023-1031.

Table 1: Thermodynamic properties of layered iron silicates.

Mineral	$\Delta_f G^o$ [i]	$\Delta_f H^o$ [i]	S^o [ii]	C_p^o [ii]	V^o [iii]
Berthierine	–828.9	–901.0	72.3	71.4	104.9
Cronstedtite	–626.8	–698.4	73.5	83.2	110.9
Greenalite	–718.5	–789.7	72.6	74.1	115.0
Minnesotaite	–1070.1	–1153.4	83.5	88.5	147.9
Odinite	–827.3	–902.2	58.3	66.9	107.8

[i] kcal/mol, [ii] cal/K/mol, [iii] cm^3/mol.