Comparison of thermodynamic data for aqueous species with focus on hyperalkaline conditions

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Introduction and objective

Presently, geochemical databases lack agreement on thermodynamic properties for a substantial number of aqueous species and minerals. Some discussion of thermodynamic data can be found in the literature for minerals and solid phases (e.g. Arthur *et al.*, 2005), but not much attention has been paid to aqueous species.

The objective of this study is to address the thermodynamic properties of aqueous species with emphasis on major components relevant for hyperalkaline conditions. For this purpose, the most commonly used and accessible thermodynamic databases have been treated in similar fashion. Six databases were included: llnl-EQ3/6, minteq, phreeqc, wateq4f, JAEA and NAPSI.

Method and results

Pertinent temperature dependent thermodynamic data for 66 aqueous species were evaluated. The equilibrium constant for species association (log K at 25 ºC), ΔH_R and the temperature dependence of log K (analytical expressions where available) were taken for each species and each database. The data bases were first brought to a common format in terms of basis species. Results for log K up to either 100 ºC or 300 ºC (extrapolated by Van't Hoff, or given by analytic expressions) were graphically compared relative to the value at 25 ºC, and in absolute terms. Select literature sources and the HKF/SUPCRT model were used in addition to try and resolve some of the discrepancies.

Discussion

The results point at some obvious short comings, limitations and discrepancies, but some of the interpretation is limited by the absence of an absolute reference. Modelling calculations on alkaline systems using different databases and including select solid phases are recommended for a more practical comparison, and this work is currently in progress.

This research project is associated with the Grimsel Test Site (CH) and supported by Nagra (CH), POSIVA (SF) and JAEA (JP).

References

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Passivating layer formation during glauconite dissolution: implications for mineral sequestration of CO_2

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The kinetic of glauconite dissolution in the pH range from 2 to 10 (T= 25ºC) has been determined from flow-batch reactor experiments. The textural and microstructural aspects induced by the dissolution process have also been characterized by XRD, HREM and BET. As a result of this analysis it is shown that, in acid conditions, glauconite is slightly more soluble than other silicates ubiquitous in sediments. The dissolution mechanism is incongruent at very acid pH values and tends to be congruent for intermediate and neutral values. Microstructural analysis show that kinetic factors are strongly influenced by structural factors. Dissolution of glauconite takes place in two steps involving, first, the disorder of tetrahedral and octahedral layers and, second, the release of cations to the solution, this process being controlled by the rate of liberation of the interlayer cation (K^+). As a consequence, an amorphous phase is formed that evolves compositionally to a more silica-rich end-member. The reactive surface is reduced during this process, giving rise to the formation of a passivating layer that has considerable influence on the dissolution rate. These experimental results have been used to analyze, by geochemical modelling, the response of glauconitic sediments during carbonation reactions.

References

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