

Thermodynamic and structural models of pollucite-analcime solid solutions

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Pollucite (nominally $\text{CsAlSi}_2\text{O}_6$) is an important rock-forming mineral in Cs-enriched pegmatites and is a common product of hydrothermal alteration of radioactive waste. The tetrahedral framework of pollucite is isostructural with the analcime (which contains Na, H_2O in place of Cs). Solid solution between these minerals is well known, but controversy exists as to whether natural parageneses exhibiting exsolved Na- and Cs-rich phases reflect the presence of a solvus in this system. Analysis of ^{29}Si MAS NMR spectra for analcime-structure materials clearly indicate the presence of at least two analcime polymorphs distinguished by differing degrees of short-range Si-Al disorder [1,2], with natural pollucite exhibiting Si-Al disorder consistent with the more disordered ("high") analcime found in experimental syntheses and Si-deficient igneous rocks. "Low" analcimes formed in pegmatitic and hydrothermal environments exhibit less Si-Al disorder. Pollucite thus forms a solid solution with "high analcime", and the exsolution of separate pollucite and analcime phases observed in natural parageneses is not due to a solvus; rather, it reflects decomposition during cooling of high analcime-pollucite solid solutions into separate pollucite and "low analcime" phases. These observations are the basis for a new thermodynamic model of pollucite-analcime solid solutions that explicitly considers both Si-Al substitution (using athermal interaction parameters [1,2]) and Cs-Na, H_2O mixing, which appears to be ideal [3] (thus ruling out a solvus in this system). Thermodynamic properties derived from calorimetric data and equilibrium observations are used to calculate the compositions of high analcime-pollucite solid solutions as a function of temperature, pressure and the composition of coexisting phases (including low analcime).

References

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Chemical environment at waste package surfaces in a high-level radioactive waste repository

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We have conducted a series of deliquescence, boiling point, chemical transformation, and evaporation experiments to determine the composition of waters likely to contact waste package surfaces over the thermal history of the repository as it heats up and cools back down to ambient conditions. In the above-boiling period, brines formed by the deliquescence of salts found in dust will be characterized by high nitrate to chloride ratios that are stable to higher temperatures than previously predicted. Current high-temperature Pitzer models capture dry-out conditions but not composition for NaCl-KNO₃ brines, and they fail to predict dry-out conditions for NaCl-KNO₃-NaNO₃ brines. Chemical transformations appear to be important only for pure calcium- and magnesium-chloride brines at temperatures greater than 120°C. This stems from a lack of acid gas volatility in NaCl/KNO₃ based brines and by slow CO₂ (g) diffusion in alkaline brines. This suggests that Yucca Mountain corrosion models based on bulk solution experiments over the appropriate composition, temperature, and relative humidity range can be used to predict corrosion in thin brine films formed by salt deliquescence.

In contrast to the above-boiling period, the below-boiling period is characterized predominately by NaCl based brines with minor amounts of K, NO₃, Ca, Mg, F, and Br at less than 70% relative humidity formed by the evaporation of pore water that has dripped onto the waste package surface. These brines are identified as sulfate and bicarbonate brines by the chemical divide theory. Nitrate to chloride ratios are strongly tied to relative humidity and halite solubility. Once the relative humidity is low enough to produce brines saturated with respect to halite, then NO₃:Cl increases to levels that may inhibit corrosion. In addition to the more abundant NaCl-based brines some measured pore waters will evaporate towards more corrosive NaCl-CaCl₂ brines.