Solubility limitation of contaminant trace metals: an assessment for nickel in sulphidic groundwaters

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Trace metal concentrations in groundwaters are controlled by a number of mechanisms, such as complexation, adsorption, ion exchange and precipitation of solid phases. Solubility limitation by solid phases is a process which is much relied upon in performance assessment of radioactive waste repositories. The calculation of realistic solubility limits for a specific trace metal requires that the chosen solubility-limiting mineral may form under the relevant geochemical conditions (pressure, temperature, water composition, redox state), that the solubility of the mineral is reliably known, that all relevant aqueous complexes involving the trace metal are accounted for, and that the corresponding complexation constants are reliably known.

Calculated solubility limits may be in serious error if any of these basic requirements are not respected (as is too often the case). This will be shown for the solubility of Ni in sulphidic groundwaters which is of relevance to the planned Swiss repository for low- and intermediate-level radioactive waste at Wellenberg.

Solubility limiting minerals

Given the measured total sulphide content of about 10^{-4} mol/L for groundwaters at Wellenberg, it is not unreasonable to consider sulphide minerals as potential solubility limiting solids for Ni. The formation of endmember Ni- or Fe-Ni-sulphide minerals seems to be exceedingly rare in low-temperature sulphidic environments and only millerite (NiS) was reported to have formed authigenically in surficial anoxic-sulphidic waters (Ferris *et al.*, 1987), contrary to the other low-temperature Ni- or Fe-Ni-sulphide minerals (vaesite, bravoite and violarite) which are mainly known from weathering environments. The remaining Ni- or Fe-Ni-sulphide minerals (heazlewoodite, godlevskite, polydymite, and pentlandite) are high-temperature phases and therefore irrelevant for solubility limitation in groundwaters. Thus, millerite is the most likely member of the Ni- and Fe-Ni-sulphide mineral group that may limit the solubility of Ni in sulphidic groundwaters. Trace concentrations of Ni, however, may also be limited by coprecipitation with ubiquitous Fe-sulphide minerals such as amorphous FeS, mackinawite, greigite, or pyrite.

Solubility data

Published solubility products for NiS differ by many orders of magnitude (values for log K at 25°C listed in the IUPAC database vary from -17.7 to -27.7) and none of them were derived from measurements of sufficient quality to warrant the calculation of trustworthy solubility limits. The study of coprecipitation of trace elements with Fe-sulphide minerals is still in its infancy and defies quantification (with the sole exception of mackinawite for which experimental data on coprecipitation of Ni and other trace metals were provided by Morse and Arakaki, 1993).

Metal-sulphide complexation

Ni-solubility may be significantly influenced by the formation of Ni-sulphide complexes. Unfortunately, these are very poorly studied. According to the Irving-Williams order, the stability of Ni-complexes is roughly comparable to the stability of Zn-complexes. Therefore, the effect of Ni-sulphide complexation on the aqueous solubility of Ni can be estimated by analogy with Zn. Daskalakis and Helz (1993) studied the solubility of sphalerite (ZnS) at 25°C, 1 atm, pH from 2 to 9 and total sulphide concentrations from 10^{-1} to $4{\cdot}10^{-4}$ M. Their experiments indicated the existence of several Zn-sulphide complexes: $Zn(HS)_2^0$, $Zn(HS)_4^{2-}$, $ZnS(HS)^-$, and $ZnS(HS)_2^{2-}$. Calculated solubility curves for a pH of 8.5 (where $ZnS(HS)^-$ is dominant) are shown in Fig. 1 from which it is clear that, at higher sulphide concentrations, the neglect of Zn-sulphide complexes may lead to a severe underestimation of Zn-solubility by several orders of magnitude. A similar behaviour can be expected for Ni.

Ni-solubility in low-temperature sulphidic environments

It adds to the credibility of thermodynamically calculated solubility limits if it can be plausibly shown that the solubility of the element is actually limited by the proposed solid in comparable natural environments.

Judging from the analyses of Ni in natural sulphidic environments (reducing continental groundwaters, anoxic fjords and ocean basins), it appears that the total concentration of Ni is no way related to the total sulphide concentration and to date, no study of sulphidic aqueous environments has been found that convincingly demonstrated the concentration of dissolved Ni to be limited by equilibrium with any sulphide minerals.

Conclusions

There are indications that millerite may be formed in sulphidic groundwaters. Thermodynamic data for millerite, however, are in a dismal state and there is virtually no data on Ni-sulphide complexation. The effect of Ni-sulphide complexation on the aqueous solubility of Ni may be estimated by analogy with Zn. Field data on Ni-solubility in sulphidic waters give no indication of solubility limitation by sulphide minerals.

At the present state of knowledge, therefore, solubility limitation of dissolved Ni by sulphide minerals cannot be relied upon in safety assessments for radioactive waste repositories.

References

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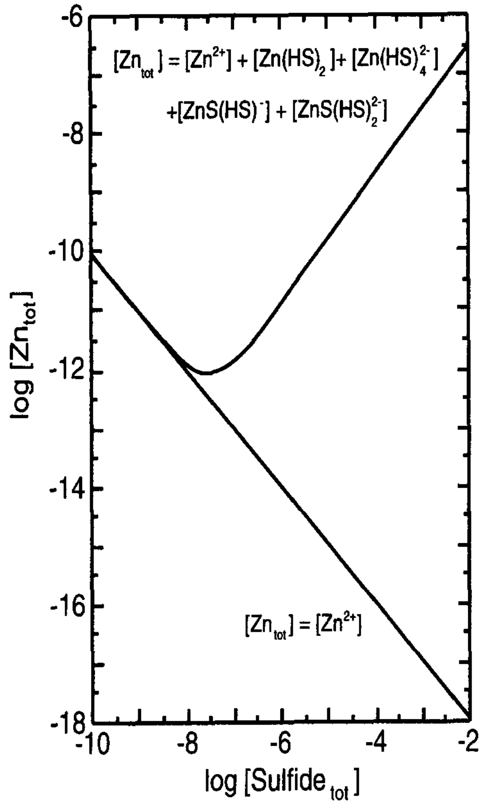

FIG. 1. Solubility of sphalerite (ZnS) at 25°C, 1 bar and pH 8.5, based on the experimental data by Daskalakis and Helz (1993). The upper curve shows the solubility of Zn if Zn-sulphide complexes are considered, while they are neglected in the lower curve. In the absence of reliable data for Ni, it is reasonable to assume that Ni-solubility is limited by Ni-sulphide minerals in a similar manner.