

The influence of cyanide complexation on the speciation of radionuclides

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The problem

Prussian Blue, $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, and related compounds like $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ are used as caesium ion exchangers in decontamination procedures of liquid radioactive waste. The used ion exchangers are conditioned as cementitious waste form for interim storage and are foreseen to become part of the radioactive waste in an underground repository.

The high pH cement pore water of the conditioned waste form will readily dissolve all forms of Prussian Blue and will release the complexed caesium and, in addition, hexacyanoferrate(II) $[\text{Fe}(\text{CN})_6]^{4-}$. This anionic complex itself is of no importance in performance assessment of a repository.

In the dark $[\text{Fe}(\text{CN})_6]^{4-}$ is stable for thousands of years under alkaline conditions (pH > 8). By contrast, UV irradiation, and even diffuse daylight, cause rapid photodecomposition of hexacyanoferrate and the concomitant release of free cyanide (Meeussen et al., 1992). Unfortunately, nothing is known about the effects of gamma-irradiation in the near-field of a repository on the stability of hexacyanoferrate.

If $[\text{Fe}(\text{CN})_6]^{4-}$ decomposes, free cyanide is released which forms very strong complexes with some metal cations. In fact, this property of (alkali) cyanides has been utilised for about 100 years in the leaching of precious metals such as gold and silver from ores. The possibility of "radionuclide leaching" from the repository is an unresolved problem.

The solution

In a detailed case study (Hummel, 2001) I assumed as a worst case scenario the instantaneous and complete dissolution and decomposition of $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ in a cementitious environment (pH 12.5, $I = 0.3 \text{ M}$) to free cyanide.

Critical examination of published thermodynamic data and subsequent analyses of chemical equilibrium systems revealed that all radionuclides belonging to the class of "hard acceptors" (e.g. Cs, Sr, Ra, Th, U, Np, Pu, Am, Cm) are not affected by cyanide complexation. Radionuclides belonging to the class of "soft acceptors" (Pd, Ag) and "borderline" metals (Co, Ni, Tc, Cd, Pb) are affected to a various degree by cyanide complexation: (1) No influence of cyanide on speciation and solubility of Tc, Cd and Pb is expected for the specified scenario. (2) Strong complexation and extensive cyanide leaching is expected for Ni, Co, Pd and Ag. These elements need special attention in performance assessment.

References

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Use of stable isotopes to evaluate the fate of chlorinated hydrocarbons in the subsurface

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Natural occurring biodegradation can play an important role in contaminant attenuation in the subsurface. However, assessing biodegradation under field conditions is often complicated by interactions of physical, chemical and microbial processes and the presence of multiple sources of contamination or contaminant mixtures. Analysis of isotope ratios of contaminants is a potentially sensitive method to gain insight into contaminant transformation. The method relies on the frequent occurrence of a kinetic isotope effect during biodegradation of organic compounds, which leads to a characteristic shift of the isotope ratio of the compound (isotope fractionation). A strong carbon isotope fractionation has been observed during biodegradation of various chlorinated hydrocarbons by different degradation mechanisms such as reductive dechlorination of chlorinated ethenes (Hunkeler et., 1999) or aerobic oxidation of 1,2-dichloroethane (Hunkeler and Aravana, 2000). In contrast, to transformation processes, physical processes usually have only a small or no effect on isotope ratios of chlorinated hydrocarbons.

The presentation provides an overview about isotope fractionation during transport and transformation of aliphatic chlorinated hydrocarbons, discusses quantitative aspects of isotope fractionation and illustrates the application of the approach with a case study.

References

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