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Technetium solubility during the onset of progressive anoxia

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Technetium-99 is a long lived radionuclide formed with high yield in nuclear reactors and is of concern because of its longevity and high environmental mobility under oxic conditions. It can occur in multiple oxidation states, and is highly mobile in its oxic form (as TcO_4^-), but is predicted to be scavenged to sediments in its reduced form (predominantly as Tc^{4+}). Here, we examine the behaviour of TcO_4^- in sediment microcosms spanning freshwater to saline conditions in relation to both the geochemical and microbiological changes that occur as anoxia develops. A cascade of terminal electron accepting processes developed in all microcosms. Tc removal from solution occurred during the metal reducing phase of anoxia, and was largely complete (>99%) by the onset of sulfate reduction. Tc was strongly bound to sediments and had a relatively low affinity for sediment organic matter (< 30%).

Microbial community analysis surprisingly revealed a similar and complex microbial population at all three sample sites. At the intermediate salinity site, Paull, a broad range of NO_3^-, Mn(IV), Fe(III) and SO_4^{2-} reducers were present in sediments and included a range of microbes with the potential to reduce Fe(III), and by inference, TcO_4^-. This study confirms that Tc removal to anoxic sediments can be mediated by microbial processes which are likely to involve reduction of TcO_4^- to insoluble Tc^{4+} in parallel with metal reduction.

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Evaluation of current Zr(IV) solubility data and their influence on the stability of aqueous and solid hydroxides

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In the frame of a current assessment of Zr(IV) thermodynamic data that we are performing on behalf of ANDRA, we have investigated the current Zr(IV) hydrolysis models under consideration. Several studies in the literature are devoted to study the solubility of Zr oxyhydroxides. Recent studies[1] evidenced that the Zr hydrolysis scheme is not able to explain $Zr(OH)_4(s)$ solubility in a wide pH range. Thus, an exhaustive study of the available data in the literature data has been conducted with the aim of proposing a set of species and associated formation constants able to explain the different experimental data so far published.

Two main different types of data differing in their solubility values can be distinguished. Data obtained under oversaturation conditions plot in the upper range of dissolved Zr(IV) concentrations (10^{-4}-10^{-2}M), while data obtained from undersaturation or using a smaller filter pore size give concentrations two orders of magnitude lower. This could indicate that the oversaturation data has been obtained either in the presence of less crystalline phase and/or that the predominant species are polynuclear hydroxo complexes.

The first hydrolysis constant of Zr(IV) was directly measured at different ionic strength [2][3][4]. A value of $\log\beta^{\circ}_{11}=0.27\pm0.13$ is calculated by the SIT approach. Literature solubility data is interpreted by fixing $\log\beta^{\circ}_{11}$ to the previous selected value and allowing the variation of the other hydrolysis constants. The solubility data not affected by the presence of polynuclear complexes have been adjusted by considering the species $Zr(OH)_n^{4-n}$ (n=0-6) and two solids of different crystallinity. When data is affected by Zr(IV) oxo or hydroxo polymerisation, the species $Zr_4(OH)_{15}^+$ and $Zr_4(OH)_{16}(aq)$ have been included in the thermodynamic model, and similar species are being considered within the frame of the OECD-NEA-TDB project [5].

References

[1] Källvenius, G., Ekberg,C., Albinsson, Y. and Brown, P.L. (2002). *Thesis*, Chalmers Uni Tech., Göteborg, Sweden.
[2] Davydov, Y.P. and Zabrodskii, V.N. (1987). *Vetsi Akad. Navuk BSSR, Ser. Khim. Navuk*, **2**, 3-8 in Russian.
[3] Ekberg, C., Brown, P., Comarmond, J and Albinsson, Y. (2001). *MRS* **663**, 1091-1099.
[4] Noren, B. (1973) *Acta Chem. Scand*. **27**, 1369-1384.
[5] Grambow, B. (2004) Pers. Comm.