

Aquatic chemistry and thermodynamics of radionuclides: applications to repository science and environmental studies

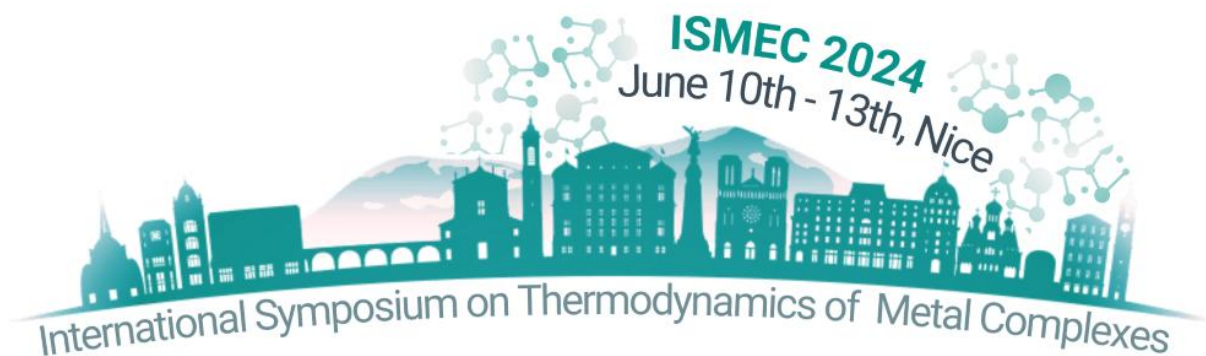
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Safety concepts regarding the disposal of nuclear waste in underground repositories generally rely on a combination of engineered and geological barriers that minimize the potential release of radionuclides from the containment-providing rock zone and transport through the biosphere. The presence of water (*e.g.*, groundwater and pore water of repository rocks), however, can alter the engineered barrier system, dissolve radionuclides, and facilitate radionuclide transport that, over millennia, may allow small fractions of water-soluble radionuclides to permeate to the biosphere. Thus, while barrier systems aim to prevent or hinder water from contacting the waste, the possible intrusion of aqueous solutions must be considered for several safety case scenarios impacted by the long-term evolution of a repository.

Solubility and sorption phenomena arise as important processes controlling the chemical behavior of radionuclides and other key elements relevant to such repositories and their safety assessment. For many radionuclides, solubility limits are reached only after release from the disposed waste products close to the disposal locations, where the expected maximal concentrations are highest. It is then often the solubility of a secondary phase, precipitated after the dissolution of a primary phase in the waste matrix, that controls the maximum transportable radionuclide concentration close to the disposal location. Complexation with inorganic and organic ligands present in the waste, in the technical barriers or in the intruding groundwater may also contribute to radionuclide mobilization.

In the context of nuclear waste disposal, actinides represent the main contributors to the radiotoxic inventory in a repository in the long term. Because of their specific electronic configuration, several oxidation states of actinides (+III to +VII) can exist in aqueous solution. This imposes a differential chemical behaviour as a function of the boundary redox conditions. Beyond the actinides, an accurate description of the aquatic chemistry of fission (*e.g.*, ^{99}Tc , ^{79}Se , ^{93}Zr , ^{129}I) and activation (*e.g.*, ^{63}Ni , ^{94}Nb) products is also relevant in specific repository concepts, involving both high level (HLW) and low and intermediate level (L/ILW) radioactive wastes. Moreover, research in the context of repository science extends beyond the radionuclides, for instance including chemotoxic elements expected in the repository (*e.g.*, Be) or key major elements like Fe, which is massively present in the repository (*e.g.*, as



container material, for construction purposes, etc.) and will strongly impact the redox boundary conditions.

In this contribution, examples on recent studies at KIT–INE on the radionuclide solubility, complexation and thermodynamic description will be presented, including actinides (^{242}Pu , ^{237}Np), fission and activation products (^{99}Tc , $^{95,93}\text{Nb}$) and chemotoxic elements (^9Be). In connection with these experimental studies, this contribution will make the link with the comprehensive reviews dedicated to the aquatic chemistry and thermodynamics of radionuclides and other elements of relevance in the context of nuclear waste disposal, a series of reference volumes developed within the Thermochemistry Database project of the Nuclear Energy Agency (NEA-TDB) of the OECD (e.g., [1-3]). These critical reviews summarize the very significant progress achieved in this field within the last decades, whilst highlighting data gaps and most relevant limitations in the existing thermodynamic models.

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