Incorporation of radionuclides in hydroxycarbonate and hydroxychloride green rust

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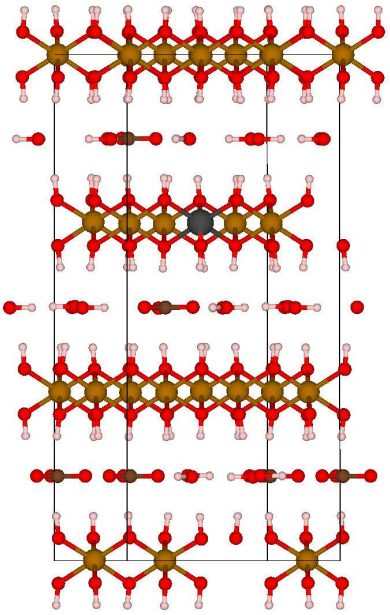

Figure 1: GR(CO_3^{-2}) .

Deep geological disposal is considered a prime solution for the safe management of high-level nuclear waste (HLW), such as spent nuclear fuel and waste from fuel reprocessing. In such deep facilities, the HLW will be confined in steel canisters which are foreseen to be surrounded successively by man-made (engineered) and natural (host rock) barriers.
Over extended period of time, ground water may reach the canisters which will corrode, resulting in the formation of secondary Fe phases and the establishment of reducing conditions. Typical corrosion products are mixed-valent Fe minerals [Fe^{II}/Fe^{III}] such as magnetite and green rust (GR). These mixed-valent iron minerals have received a significant amount of attention over recent decades, especially in the environmental sciences and play an important role regarding the mobility, toxicity, and redox transformation of organic and inorganic pollutants, such as radio nuclides.

In this study we focus on the incorporation of radio nuclides in hydroxycarbonate GR(CO_3^{-2}) $[Fe_4^{II}\ Fe_2^{III}\ (OH)_{12}]^{2+}\cdot[(CO)_3^{(-2)}\cdot 3H_2\ O]^{2-}$ and hydroxychloride GR(Cl^-) $[Fe_3^{II}\ Fe^{III}\ (OH)_8]^{+}\cdot[(Cl)^-\cdot 3H_2O]^-$. We present density functional (DFT+U) calculations on both systems. From a theoretical side the presence of mixed-valence iron [Fe(II)-Fe(III)] ions in the brucite-like layers exhibits a major challenge. We find that the DFT+U method is very capable to determine the structural parameters as well as the magnetic properties of GR(CO_3^{-2}) and GR(Cl^-). In a second step we studied the incorporation of radionuclides, such as Ln^{3+}, An^{3+} and Iodide (I^-) into GR and compared with available experimental data [1,2].

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