

# Computational modelling of uranium incorporation into goethite ( $\alpha$ -FeOOH)

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The UK has been utilising nuclear power since 1956 and this has led to a build-up of nuclear waste, particularly high-level waste, which requires a cost effective, long-term storage solution to ensure important radionuclides and contaminated materials are not released into the environment. Currently, the UK and other nations around the globe have identified that a Geological Disposal Facility (GDF) may be the best long-term disposal route. Within a GDF, corrosion of stainless-steel leads to the formation of iron (oxyhydr)oxide minerals, particularly ferrihydrite. Through the interaction between uranium and transforming ferrihydrite, uranium can be incorporated into the mineral structure of goethite. There is limited information on the REDOX (electron transfer) reactions that occur between iron minerals and key actinides, but it has been shown that Fe (II) minerals (green rust and magnetite) can reduce U(VI) to its less mobile (V) state.[1] Experimentally it has been found that both U(VI) and U(V) can be incorporated into goethite, however, there is a conflict about how the uranium incorporates at an atomic level. [1,2]

Computational modelling using the Periodic Electrostatic Embedded Cluster Method (PEECM) is being used to help clarify how uranium incorporates into the [010] surface of goethite, and how iron vacancies and water may affect this incorporation. PEECM utilises point charges to reduce the computational cost, whilst maintaining long range electrostatic interactions. Within the PEECM, there is a quantum mechanically treated embedded section, shown in Figure 1, using Density Functional Theory to model the interactions of uranium and other actinides within the mineral structure. Two positions within the embedded cluster have been identified to incorporate the uranium in the surface and near-surface of the [010] goethite structure. These positions would both be included within the near-surface region (first 2 nm below the surface) that was identified by Stagg et al. as the region uranium incorporates into.[1] To test the effect of iron vacancies on uranium incorporation, three different iron vacancy models have also been developed, testing the effect of iron vacancy distance on uranium incorporation. Finally, the surface was also solvated to determine the effect of solvation on uranium incorporation and how this may affect the interactions between the incorporated uranium species and the goethite mineral structure.

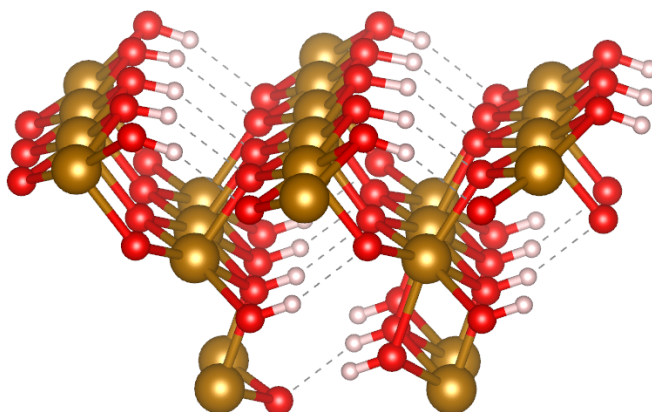


Figure 1: Embedded quantum mechanically treated [010] goethite surface used in PEECM calculations.

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[1] O. Stagg, et al., "Fe(II) induced reduction of incorporated U(VI) to U(V) in goethite", *Environment science and technology*, 55, 16445-16454. (2021)

[2] M. S. Massey, et al., " Competing retention pathways of uranium upon reaction with Fe(II)", *Geochimica et Cosmochimica Acta*, 142, 166-185. (2014)