

Shinkolobwe (Zaire)

Description: The Shinkolobwe deposit is a uranium orebody located in Zaire which has been used to study UO_2 dissolution under oxidising conditions which may exist within the near-field due to processes such as radiolytic oxidation (Finch and Ewing, 1989). The deposit weathers under oxidising conditions in a monsoonal-type environment where rainfall is above 1 m/year. At Shinkolobwe, the uraninite is coarsely crystalline and lacks many of the impurities (e.g. thorium and rare earth elements) found in other uranium deposits. This lack of impurities led Finch and Ewing (1989) to suggest that the thermodynamic stability of the Shinkolobwe uraninite may closely approximate spent fuel. Over 50 secondary uranyl phases were identified from the alteration of uraninite at this site. It was concluded that uraninite transforms to Pb-U oxide hydrates and then to uranyl silicates if sufficient silica is present in the system.

The conditions at Shinkolobwe are very different to the reducing environment expected in most deep, water saturated repository near-fields. As such, the Shinkolobwe natural analogue is more relevant to either the US Yucca Mountain repository or a spent fuel repository that has become oxidising due to groundwater radiolysis. In an expansion of the Shinkolobwe study, Finch and Ewing (1991) listed the most important uranium deposits around the world and also provided a comprehensive catalogue of the uranyl minerals that have been identified at each locality. The extent to which this information can be of direct use in performance assessment is yet to be established.

In a review of uranium minerals at various ore deposits, including Shinkolobwe, as possible natural analogues for the alteration of spent fuel, Finch and Ewing (1991) discussed radiolysis but also concluded that no known studies, at that time, adequately address the significance of this process. These authors, however, did note that the natural occurrence of some uranium peroxides, specifically studtite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$) and metastudtite ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$), indicate the existence of highly oxidising conditions which may result from radiolysis in the geological environment.

In the same study, Finch and Ewing (1991) report that these minerals occur at the Shinkolobwe mine in Zaire, although this line of inquiry has not been taken any further. Hofmann (1996) reports that these minerals also occur at Menzenschwand in Germany. In both locations, studtite is associated with primary pitchblende and secondary uranyl silicates in near-surface weathering environments. Radiolysis may only be responsible for peroxide formation, while uranium oxidation is most likely the result of interaction with the atmosphere.

The identification of radiolysis at a range of geological environments and chemical conditions, suggest that radiolysis is a common feature in nature in systems where natural high-radiation fields occur. It is probable, therefore, that the radiolytic processes that would occur in a repository would be identical in mechanism to those observable in natural systems. Only the rates of radiolysis might be different due to the different radiation fields in a HLW or spent fuel repository compared to a uranium orebody.

However, there are indications that radiolysis may occur in nature at locations without particularly high radiation fields. Hofmann (1992) discusses the common occurrence of reduction spots (local reduction phenomena) in red bed sediments without any evident source of reductants. These have been interpreted as the result of porewater radiolysis followed by catalysed reduction of trace elements by H_2 .

Position(s) in the matrix tables: Near-field matrix, radionuclide release from barriers (Dissolution), Wasteform (Spent fuel).

Limitations: The monsoonal-type climate and high rainfall means that the hydrochemical environment at Shinkolobwe is different to that expected within a repository near-field.

Quantitative information: None known

Uncertainties: Differences in the geochemical conditions in the ore body compared to those envisaged in a repository near-field.

Time-scale: Geological.

PA/safety case applications: None identified.

Communication applications: None identified.

References:

Finch RJ and Ewing RC (1989) Alteration of natural UO₂ under oxidising conditions from Shinkolobwe, Katanga, Zaire: a natural analogue for the corrosion of spent fuel. SKB Technical Report, TR 89-37, SKB, Stockholm, Sweden.

Finch RJ and Ewing RC (1991) Uraninite alteration in an oxidising environment and its relevance to the disposal of spent nuclear fuel. SKB Technical Report, TR 91-15, SKB, Stockholm, Sweden.

Hofmann BA (1996) Natural analogues of radiolytic processes. In: H von Maravic H and J Smellie (eds) Natural analogue working group, sixth meeting, Santa Fe, September 1994. CEC Nuclear Science and Technology Report, EUR 16761, 175-184, CEC, Luxembourg.

Hofmann BA (1992) Isolated reduction phenomena in red beds: a result of pore water radiolysis? In: YK Kharaka and AS Maest (eds) Proceedings of the 7th International Symposium on Water-Rock Interaction, 503-506.

Added value comments: None identified.

Potential follow-up work: Further studies on the importance and influence of radiolysis would be of use.

Keywords: Near-field, radionuclide release, spent fuel dissolution, radiolysis

Reviewers and dates: Gavin Thomson, Enviro Consulting (January 2005)