1.8.23

Effect of corroded engineering barrier on the alteration process of the spent fuel matrix under repository conditions

J. QUIÑONES[1], A.G. DE LA HUEBRA[1]
AND A. MARTINEZ-ESPARZA[2]

[1] Ciemat. SPAIN (javier.quinones@ciemat.es)
[2] ENRESA. SPAIN

The safety of all deep geological disposal designs for HLW are based on the existence of several engineering barriers. Those prevents the interaction between the groundwater with the matrix of the spent fuel. it is reasonable to foresee that with time evolution the corrosion of these barriers will be done and the groundwater will react with the matrix of the spent fuel. Practically, the most of the performance assessment exercises related to deep geological disposal safety and in the particular case of the groundwater – spent fuel matrix interaction, the influence of corroded engineering barriers is only taking into account for predicting the following topics: At which time the groundwater react the surface of the spent fuel and their influence on the chemical composition of the groundwater. In this work a different point of view of the problem is proposed, i.e., it attempts to resolve which will be the influence of the corroded materials on the leaching behaviour of the spent fuel, for example: changes on U solubility, precipitation or coprecipitation of new phases, retention process, etc. The present work was performed using as starting solution that emulate other one obtained by dissolution of a spent fuel pellet. This starting solution has bivalent, trivalent and tetravalent elements in molar fraction ratio similar to uranium analogous to which the radionuclides has in a spent fuel with a burnup of 40 MWd/kg U. This work presents the results obtained from coprecipitation experiments of uranyl solutions in presence of iron metallic and/or its alteration phases under synthetic bentonitic-granitic water. Experiments were performed under oxidising conditions at room temperature. The covered pH range was between 7.4 – 8.8. The evolution of the uranium concentration and the characterisation by XRD and SEM-EDS of the secondary phase formed are presented herein. The uranium concentration values reached were in the range of $2 \cdot 10^{-5} - 5 \cdot 10^{-4}$ mol·(kg of $H_2O)^{-1}$. In all cases, results from these experiments did not show evidence of a clear effect due to the presence of iron (metallic or previously corroded) in the uranium concentration. These data were similar to those obtained by coprecipitation in similar condition but in absence of iron material. Formation of Boltwoodite “$K_2(UO_2)_2(SiO_3)_2(OH)_2 \cdot 3H_2O$” in iron surface material was observed and characterised in all experiments. Based on the experimental data obtained (uranium concentration in solution and bulk solid phase characterisation) a thermodynamic model is proposed.

1.8.24

Long term hydration of nuclear waste glass

K. FERRAND, A. ABDELOUAS AND B. GRAMBOW

SUBATECH, Ecole des Mines de Nantes, 4 rue Alfred Kastler, 44307 Nantes, France
(grambow@subatech.in2p3.fr)

New observations on the role of water diffusion in the mechanism of glass dissolution in Si-rich solutions

The initial step of the nuclear waste glass/ water reaction is alkali release by exchange with hydrogen ions in presence of water molecules. The simultaneously occuring hydrolysis of iono-covalent bonds of the glass network becomes rate limiting after few hours. This is why most models for long-term nuclear waste glass corrosion ignore ion exchange and describe only the corrosion reaction. Leach tests in flowing Si-rich solutions, and post test FTIR characterisation of the solids now have shown that glass hydration/ion exchange becomes again rate limiting under conditions where the reaction rate decreases due to affinity reduction of surface reaction. The obtained water diffusion coefficients and activation energies were similar for nuclear waste glass, for alkali silicate glass and for obsidien.

The quantity of water molecules entering the glass is directly proportional to the release of alkali ions. The data indicate that the water uptake of the hydrated glass is governed by volume constraints in the glass structure.

Implications for long-term glass performance evaluations

Already after few years the diffusion of water molecules in the glass becomes very slow, and its contribution to the long-term release of radionuclides from glass will be low under open systems conditions. Nevertheless, if this process is ignored in the evaluation of experimental glass/water reaction data, errornenous parameters for long term prediction are obtained. Hence, understanding of the role of water diffusion is a prerequisite of long-term glass performance predictions.