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Evolution of the redox potential in the corrosion system

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The knowledge of chemical conditions, especially of redox potential, inside waste packages with radioactive wastes is important for determination of radionuclides speciation and their leaching rate after failure of waste packages. Conditions inside waste packages will be determined primarily by the reactions of thermodynamically unstable iron with groundwater penetrating into waste packages and by the nature of the iron corrosion products formed. The main corrosion products of iron corrosion are Fe (II) ions, hydrogen and products of reactions of these species with species presented in water flowing into waste packages. The composition of water will correspond to the composition of ground water affected by other engineered barriers.
The rate of the corrosion reaction, the rate of oxidation and hydrolysis of Fe2+ and the rate of the formation of precipitation products will govern the development of Eh inside waste packages. One possibility of estimating chemical conditions in such complex systems is to use advanced geochemical models. A great disadvantage of these models is that a lot of important input data must be estimated. This can lead to great uncertainty about the real conditions inside waste packages.
The main aim of this work was therefore to measure redox potential (Eh) in simplified systems simulating the conditions inside waste packages and the effect of iron corrosion on Eh development inside waste packages after ingressions of groundwater. The results can then be used to validate geochemical models.
The corrosion systems consisted of the carbon steel plates and the synthetic bentonite porewater. The apparatus was put into anaerobic box (O2 < 0.1 ppm), where redox potential was measured by platinum and gold electrode. The corrosion rate of carbon steel was determined during experiment by measuring hydrogen evolution and then from weight loss of samples.
The results show that the values of the redox potential during the experiments firstly sharply decrease and then slowly increase. Opposite behaviour was observed at measuring pH, where values of pH first slightly increased and then slowly decreased. The concentration of Fe3+ ions after the experiments was negligible in comparison with Fe2+ concentration. The corrosion rate at 50 ℃ was almost constant during corrosion experiment, while the corrosion rate at 60 and 70 ℃ was very fast at the beginning of corrosion, but then significantly slowed down. It seems that the effect of temperature on corrosion rate is affected by the nature of corrosion products formed on the surface of metal.
The experiments provide useful information about evolution of the redox potential and other parameters which can be expected inside waste packages with radioactive wastes, but time of the experiments carried our so far was relatively short (30 days). In the future, long-term experiments must be performed under various conditions to verify the results obtained.

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