

3-2 Understanding the Impact of Nitrates on Geological Disposal Systems

— Modeling of the Chemical Transition of Nitrates Accompanied by Corrosion of Carbon Steel —

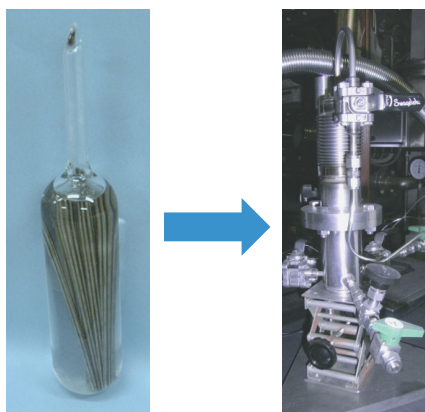


Fig.3-6 Reaction container (glass ampul) and apparatus for analysis of gas phase (ampul opening member)

Experimental apparatus for measuring gaseous reaction products during immersion of steel specimens in a test solution.

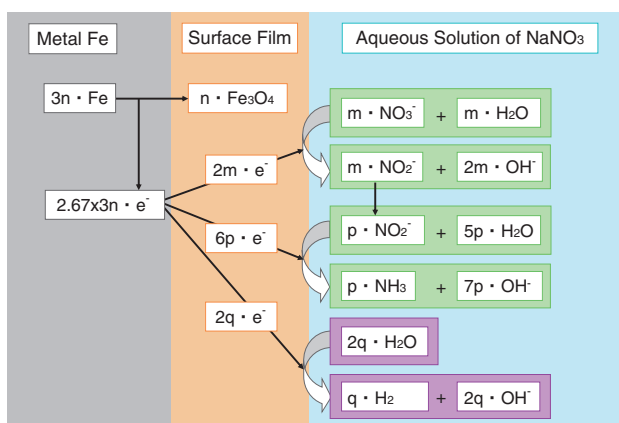


Fig.3-7 Conceptual model of nitrate evolution accompanied by corrosion of carbon steel

Chemical reaction scheme among nitrate ions, carbon steel (Fe), and water, including electron transfer.

A number of low-level radioactive wastes contain large amounts of nitrate salts. Nitrate ions are oxidizing species that can be reduced to nitrite and ammonia by the corrosion of metals inside a repository for radioactive wastes. It is possible that nitrate ions and their reduction products affect the mobilities of radionuclides owing to changes in their solubilities and sorption distribution coefficients. Therefore, estimation of the chemical evolution of nitrate ions accompanied by metal corrosion is necessary to assess the safety of repositories for the geological disposal of radioactive wastes.

Carbon steel, which is likely to be used extensively and disposed of in repositories, was immersed in a closed aqueous solution of NaNO₃ (Fig.3-6) to observe the chemical interaction between metal and nitrate ions. The experimental pH range of the NaNO₃ solution was 12.5~13.5, which was designed to simulate conditions imposed by the pore fluid of cementitious material. Despite the accelerated cathodic reaction due to the existence of nitrate and nitrite ions, the results of the immersion experiments showed no acceleration of the corrosion rate of carbon steel in this pH range. This implies that the system is controlled by an anodic reaction. The nitrate reduction accompanied by the corrosion of carbon

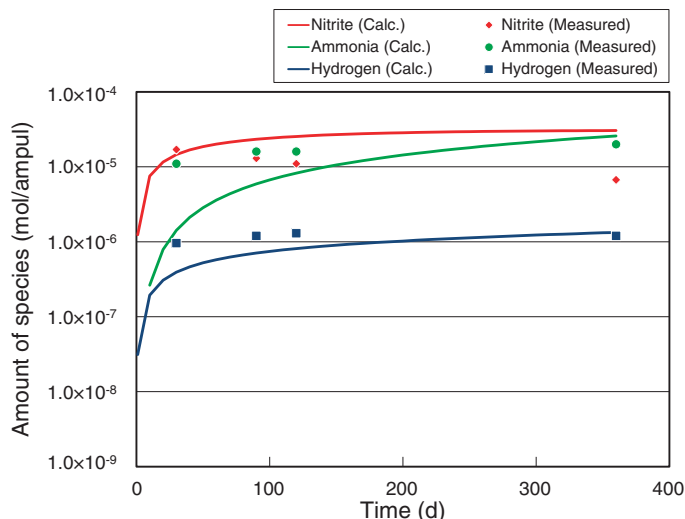


Fig.3-8 Variation of reaction products (NO₂⁻, NH₃, and H₂) with time in an ampul

Measured and calculated variation of reaction products at 323 K, pH 12.5, and 5.0 mol/dm³ of NaNO₃.

steel is considered to be a reaction series of $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3$. The nitrate reduction reaction competes with the water reduction (hydrogen evolution) reaction under the anodic controlled conditions. Therefore, the nitrate ions strongly reduce the hydrogen generation rate in a 1.0 mol dm⁻³ NaNO₃ solution.

Accordingly, the sum of the current of the reaction series $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3$ and that of the water reduction reaction was assumed to be balanced with the anodic current of carbon steel (conceptualized in Fig.3-7). Examples of the simulation results are shown in Fig.3-8. To develop a system for estimating nitrate impacts on the chemical conditions inside and outside of repositories for radioactive waste, this model will be combined with a model of nitrate chemical evolution caused by microbial activity and mineral reactions outside a repository.

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Reference

Honda, A. et al., Understanding and Modeling of Chemical Transition of Nitrate Accompanied with Corrosion of Carbon Steel under Hyper-alkaline and High Nitrate Concentration Conditions, Zairyo to Kankyo, vol.60, no.12, 2011, p.541-552 (in Japanese).