

Estimating the formation and dissolution of ferrihydrite nano-particles in Mayak

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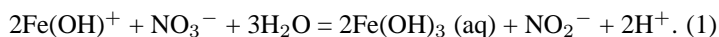
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For the safety assessment of the geological disposal of high-level nuclear wastes we have to estimate how radionuclides transport in the near and far fields of a disposal site. When estimating the radionuclide transport, we need to take into account the effect of nano-particles because much radionuclides transport in groundwater with nano-particles.

Outline of the formation mechanism of ferrihydrite proposed here is as follows. The original groundwater in the host rock of Mayak contained much dissolved iron, most of which was divalent. When the groundwater was mixed with the effluent from the reprocessing plant, most divalent iron was oxidized to trivalent by nitrate ion in the effluent. Although the dissolved iron content was still high, the solubility of ferrihydrite decreased with decreasing divalent iron, thus the groundwater became supersaturated with ferrihydrite, and ferrihydrite nano-particles formed in the groundwater.

The concentration of dissolved iron in the original groundwater of Mayak is estimated as follows. Because the host rocks of Mayak are igneous and metamorphic, they must contain magnetite (Fe_3O_4). Thus, the iron content in the Mayak groundwater is equal or close to the solubility of magnetite. The solubility of magnetite as a function of $\log P_{\text{O}_2}$ at pH 7. The pH is set to seven because the pH of Mayak groundwater is between 5.85 and 8.12. The solubility of magnetite is $10^{-0.3} \text{ Fe mol L}^{-1}$ when $\log P_{\text{O}_2} = -89.0$, and $10^{-3.5} \text{ Fe mole L}^{-1}$ when $\log P_{\text{O}_2} = -70.2$.

Nitrate ion (NO_3^-) can oxidize the divalent iron ($\text{Fe}(\text{OH})^{2+}$) to trivalent. The concentration of nitrogen species (NO_3^- , NO_2^- , N_2 , and NH_4^+) dissolved in an aquatic solution that is equilibrated with atmospheric nitrogen gas ($P_{\text{N}_2} = 0.78 \text{ bar}$). Note that the relative concentrations of nitrogen species do not change even if the P_{N_2} changes. The $\log P_{\text{O}_2}$ can be buffered at -37.8 with NO_3^- and NO_2^- if the sufficient NO_3^- and NO_2^- exist in the solution. Because the $\log P_{\text{O}_2}$ buffered by NO_3^- and NO_2^- is higher than the $\log P_{\text{O}_2}$ buffered by divalent and trivalent iron species, the NO_3^- can oxidize the divalent iron $\text{Fe}(\text{OH})^{2+}$ with the following reaction:



This equation shows that most divalent iron is oxidized if the concentration of NO_3^- is higher than half of the concentration of divalent iron. Because the groundwater within 2 km from Lake Karachai contains $10^{-0.9}$ to $10^{-1.4} \text{ mole L}^{-1}$ of NO_3^- , these nitrate can oxidized the $10^{-0.6}$ to $10^{-1.1} \text{ mole}$ of divalent iron.

The groundwater became super-saturated with ferrihydrite after most divalent iron was oxidized to trivalent. The solubility of ferrihydrite is $10^{-6.5} \text{ mole L}^{-1}$ when most dissolved iron is trivalent. If the mixing ratio of the effluent to the original Mayak groundwater is one, the concentration of dissolved iron in the mixed groundwater is between $10^{-0.6}$ and $10^{-3.8}$, which is super-saturated with ferrihydrite. Even if the mixing ratio is 100, the concentration is $10^{-2.6}$ and $10^{-5.8}$, which is still supersaturated with ferrihydrite. Although the mixed groundwater is supersaturated with ferrihydrite and goethite (FeOOH), only ferrihydrite forms and goethite does not. This is because the nucleation or crystal growth of goethite is extremely slow.

We have shown that ferrihydrite forms when divalent irons in groundwater are oxidized by nitrate. This process is particularly important when the high-level nuclear waste and TRU (trans-uranium) waste are deposited in a same site as planned in Japan because TRU waste contains much nitrate.