

# Ferric oxyhydroxide in underground geological environments and high-level radioactive waste disposal: influence on siting and site characterization

Hidekazu YOSHIDA<sup>(1)</sup>

(1) Nagoya University, Furo-cho, Chikusa, Nagoya, 464-8601 Japan  
E-mail:dora@num.nagoya-u.ac.jp

## Abstract

Ferric oxyhydroxide in the underground geological environments is an important factor that may influence the long-term natural barrier function with respect to nuclide migration, in scenarios for the geological disposal of high-level radioactive wastes (HLW). Here, examples of Ferric oxyhydroxide seen in the underground environment of Japan were reviewed in order to: 1) evaluate suitable repository depths that will need to be characterized; and 2) assess how Ferric oxyhydroxide will need to be treated in nuclide migration scenarios at a future repository site. The Ferric oxyhydroxide examined provide the following insights into the features relevant to site characterization and the rock's barrier function: 1) Ferric oxyhydroxide has been formed along the connective fracture network that extends from the surface, but there is a certain depth limit of oxidation due to geochemical buffering by redox reactions; 2) Past Ferric oxyhydroxide will remain even after the environment returns to a reducing condition; 3) Ferric oxyhydroxide produced in the rock matrices, however, can contribute to retarding nuclide migration by sorbing radionuclides and clogging micro-pores. The evidence shows that Ferric oxyhydroxide formed in the geological environment may influence on the siting as well as the geosphere barrier function in and around repository caverns for the disposal of HLW constructed in the deep geological environment of Japan.

**Keywords:** Ferric oxyhydroxide, barrier function, radioactive waste, geological disposal

## 1. Introduction

When siting and site characterization a deep geological repository for long-lived radioactive wastes within fractured host rocks is conducted, it has to be characterized that oxidizing surface water will not penetrate to repository depth along water conducting fractures and not seriously influence on the barrier system established (NUMO, 2002).

In Japan, presently fundamental studies are being carried out in order to develop a technical basis for disposal of vitrified radioactive waste (HLW), although no host rock and specific site has been selected (Committee for Geological Stability Research, 2011). Within the scope of characterization,

understanding the influence of Ferric oxyhydroxides development into the host rock along the water conducting fractures from the surface to repository depth is recognized as a key issue to evaluate for the future site characterization (e.g. Hofman, 1999; Yoshida, 2012; Yamamoto et al., 2013; Fig.1). In particular, to characterize the processes that control the rate and depth of oxidizing water penetration into the host rocks can be used to establish general criteria for recognizing host rock bodies to evaluate the suitability or unsuitability as host rocks for repository (Miller et al., 2000) within the orogenic environment of Japan.

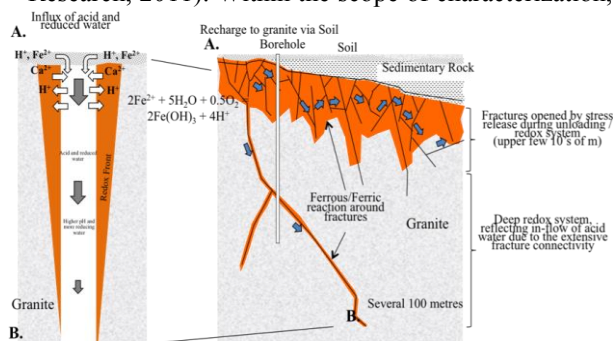


Figure 1. Penetration of redox front in granitic rock and associated chemical buffering processes (After Yamamoto et al., 2013)

## 2. Studied materials & methodology

To evaluate long-term influence of Ferric oxyhydroxides for the barrier function of repository system, analogous natural evidence of Ferric oxyhydroxide formation in both crystalline rock and sedimentary rock have been investigated (e.g. Oono & Yoshida, 2015; Yoshida et al., 2003; Yamamoto et al., 2013).

For the crystalline rock analysis, DH-5R1 deep borehole (depth of 530m) drilled by Japan Atomic Energy Agency (JAEA) close to the Underground Research Laboratory Site (MIU site) was studied

(Akagawa et al., 2006; Yamamoto et al., 2013). This granitic rock named Toki Granite is a stock-type pluton and is composed of Ryoke-type granite that is recognized as typical of Mesozoic ones distributed in Japan. Studied Ferric oxyhydroxides formed in redox front developed along fractures was identified at the depth of about 210m of drilled core as shown in Figure 2. The redox front developed is seen along the groundwater conducting fracture with the depth of several cm into the matrices.

For the sedimentary rock, drilled cores excavated in Shimanto Belt, what we call, accretionally complex distributed in southern part of Kyushu Island was studied. The site drilling was carried out to investigate for hydraulic dam construction. The Shimanto belt consists of calcareous sandstone and mudstone intercalated. Redox front is seen in the fracture developed mainly in the calcareous sandstone and the feature is quite similar of the crystalline rock (Oono & Yoshida, 2015).

Detailed morphological, mineralogical and geochemical analysis were conducted in both type of rocks by rock thin section, Scanning Electron Microscopy (SEM) and X-ray fluorescence spectrometer (XRF) respectively.

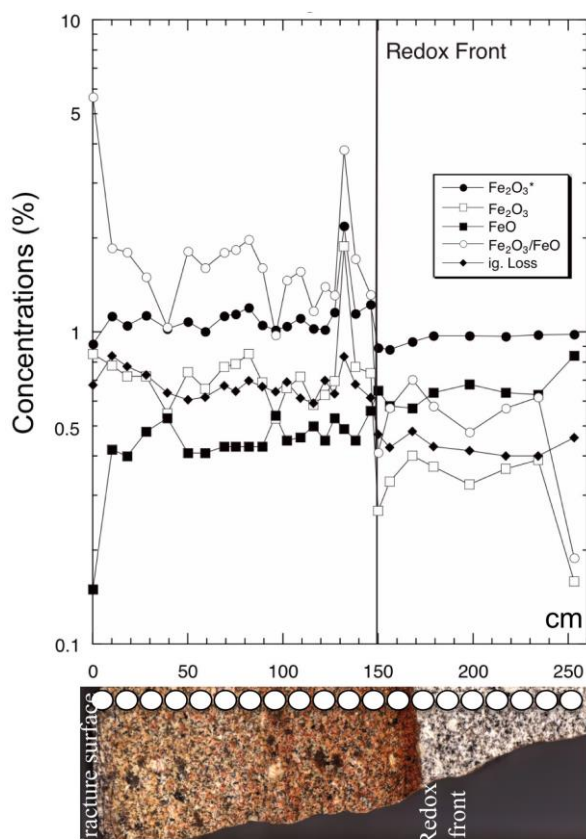


Figure 2. Elemental distribution across redox front. An example from Toki granitic rock (Modified from Yamamoto et al., 2013)

### 3. Results and discussions

#### 3.1 Microscopic morphological features

Optical microscopic observations in both crystalline rock and calcareous sandstone revealed that Ferric oxyhydroxides are mainly distributed at the grain boundaries (Fig. 3) and also in the micro fracture developed in feldspar and quartz grains. This feature suggests that the Fe (Ferrous iron) content water has been impregnated into the micro pore or fracture connected from water conducting major fracture by diffusion. In particular, Ferric oxyhydroxides are highly concentrated in micro pores of feldspar grains in crystalline rock or calcareous matrix of sandstone probably due to high pH conditions generated by buffering of Ca dissolution from feldspar with penetrated groundwater as well as diagenetic calcite filled in grain boundary. This geochemical interaction is an important process of Ferric oxyhydroxides formation in host rock as described in 3.3.

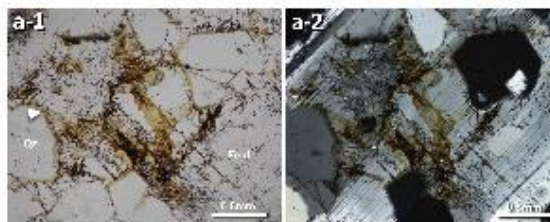


Figure 3. Fe oxyhydroxides in rock matrices. An example from Toki granitic rock. Qz: Quartz, Feld: Feldspar. a-1:Open, a-2:under cross polar. (modified from Yamamoto et al., 2015)

#### 3.2 Geochemical characteristics of redox front

Profiles of selected elements across the redox front developed in crystalline rock are shown in Figure 5. Elemental distribution clearly shows that Ca is depleted from the redox front towards the fracture surface. Such CaO loss commonly occurred during low-temperature water-rock interaction by preferential leaching of Ca from feldspar and hornblende in crystalline rock and calcite precipitated in grain boundary of sedimentary rock as well. Ca is a very common element containing all kind of rocks and the result shows that the buffer reaction with Ca dissolution from rock forming minerals is quite effective process to control the impregnated Fe into the rock matrices and also form Ferric oxyhydroxides to fill the micro pore.

Geochemical analysis revealed that uranium also has been moved from the water conducting fracture into the rock matrices and concentrated at the Ferric oxyhydroxide concentrated redox front. Akagawa et al. (2006) shows that the uranium was co-precipitated with Ferric oxyhydroxides during the uranium migration. This strongly suggests that precipitated Ferric oxyhydroxides in rock matrices could play a role of 'barrier' materials by its sorptive function for radionuclides and might also be influence on the solubility of uranium by redox reaction (Baertschi et al., 1991; Drake et al., 2009).

These kinds of elemental migration from the

ground water conducting fracture surface into the vicinity rock matrices has been taken into account as an analogue of 'matrix diffusion' considered as an important process of nuclide retardation in safety assessment of repository host rocks (Alexander et al., 1990; Grisak et al., 1980).

### 3.3 Redox front formation in rock matrices

Within both characteristics of Ferric oxyhydroxide developed along the water conducting fracture in crystalline rock and sandstone (sedimentary rock), pH buffering process of impregnated groundwater from the surface was a key function of development of redox front i.e. Ferric oxyhydroxides precipitation in rock matrices. This is due to the dissolution of Ca contained minerals such as feldspar and calcite in grain boundary formed during diagenesis of sedimentary rock.

Relatively acidic and reducing surface (Kamioka, 1991) is readily generated with the reaction of organic rich surface soil through and after impregnated into the bed rock in Japan. The impregnated surface water has been buffered thereafter during transport through flow-path fractures and reacted with the vicinity rock forming minerals. This means that the reaching depth of redox front is considered to have certain limit depend on the rock types containing Ca in host rocks.

### 3.4 Application to HLW disposal

Natural evidence shows that redox front can be developed inevitably in the bed rocks along ground water conducting fractures. When developing safety case for a future repository, it is important to provide evidence that redox front at certain depth is not indicative of presently oxidizing conditions. It is also necessary to show that future oxidizing environment could not propagate downwards to the level of waste emplacement for safety assessment timescale.

The observations and analysis carried out for understanding redox front development and influence of oxyhydroxides on barrier function show that there is certain limit of redox front development through fractures. In particular, natural feature implies that dissolved oxygen has been consumed by water/rock interactions as it diffuses into the rock matrices during downward groundwater flow through fractures. The downward depth is also related to the uplifting rate of the area. In Japan, no candidate host rock type has not been selected and many areas of country has a rate of less than 1 mm/a. Nevertheless, it is important to build confidence that redox fronts will not be penetrated to repository depths in the future. In particular, several observations shown here revealed that calcareous bed rock can be more effectively buffered penetrated acidic surface water to retain Ferric oxyhydroxides in shallower depth from the surface. This feature can be used for the knowledge

of some criteria to select suitable depth of the repository when future candidate site and host rock will have been selected.

## 4. Conclusions

The work presented here tries to focus on the influence of Ferric oxyhydroxides inevitably encountered in the certain depth of probably any types of host rocks for HLW waste repository. The results show several important general implications for HLW disposal summarized as follows:

1) Even if in the site characterization redox front with Ferric oxyhydroxides identified at depth of a possible HLW repository, it does not mean that the host rock has lost the barrier function and unsuitability for repository site.

2) The pH-buffering of the host rocks (particularly Ca rich minerals) limits the extent to which certain elements such as Fe even if conditions do become oxidizing.

3) Ferric oxyhydroxides formed in the redox front during ancient process could contribute to the barrier function of the biosphere by radionuclide sorbing.

This kind of analogous data can be used in the development of scenarios for the future evolution of site for HLW waste repositories. In particular, the observations help to build confidence in the ability of the geosphere to resist changes to redox conditions as might be caused by uplift or increased recharge due to climate change in orogenic field of Japan.

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