



Consumption and diffusion of dissolved oxygen in sedimentary rocks



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ABSTRACT

Fe(II)-bearing minerals (e.g., biotite, chlorite, and pyrite) are a promising reducing agent for the consumption of atmospheric oxygen in repositories for the geological disposal of high-level radioactive waste. To estimate effective diffusion coefficients (D_e , in $\text{m}^2 \text{s}^{-1}$) for dissolved oxygen (DO) and the reaction rates for the oxidation of Fe(II)-bearing minerals in a repository environment, we conducted diffusion–chemical reaction experiments using intact rock samples of Mizunami sedimentary rock. In addition, we conducted batch experiments on the oxidation of crushed sedimentary rock by DO in a closed system.

From the results of the diffusion–chemical reaction experiments, we estimated the values of D_e for DO to lie within the range $2.69 \times 10^{-11} < D_e < 6.30 \times 10^{-11}$. Values of the second-order rate constant (k , in $\text{L mol}^{-1} \text{s}^{-1}$) were in the range $-3.66 < \log k < -2.83$ (from batch experiments) and in the range $-3.87 < \log k < -2.22$ (from diffusion–chemical reaction experiments). Many of these values are within the range of previously published rates for reaction between $\text{O}_{2(\text{aq})}$ and Fe(II) surface complexes. The average value for the total concentration of reactive sites was about $10^{-4} \text{ mol m}^{-2}$ from batch experiments. In contrast, the value of reactive sites estimated from the physical surface area was about $10^{-8} \text{ mol m}^{-2}$, indicating that the reaction within intact rock is limited to the sites that originally existed with accessible porosity for $\text{O}_{2(\text{aq})}$. This difference arises because the batch experiments used powdered samples, meaning that new sites which formed during milling were added to the original reaction sites. On the basis of these observations and interpretations, diffusion–chemical reaction experiments make it possible to determine the values of the kinetic parameter and diffusivity for an intact rock sample simultaneously.

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1. Introduction

Research into the geological disposal of high-level radioactive waste is currently being conducted in many countries. Understanding the transport of radionuclides is important when evaluating options for geological disposal. The transport of redox-sensitive radionuclides such as Np, Pu, Tc, and U, which are soluble and mobile under oxic conditions (e.g., Langmuir, 1997), needs to be considered at the construction and operational stages of a repository. Conditions in the deep underground are expected to be reducing (e.g., Iwatsuki and Yoshida, 1999; Sasamoto et al., 2004); however, underground conditions temporarily become oxic when atmospheric O_2 is introduced during the construction and operation of the repository. After the repository is backfilled, O_2 trapped in the underground dissolves into underground water. The dissolved O_2 (DO) is consumed by the inorganic (mainly Fe(II)) and organic redox buffers (Puigdomenech et al., 2001) as it diffuses into the rock matrix around the repository. To understand the timeframe until rocks and groundwaters around the repository become anoxic again, the kinetics and diffusion parameters for DO need to be determined. Therefore, it is important to understand the interactions

between reduced mineral phases and DO, as well as the diffusion of DO in the rock matrix.

Mineral phases such as Fe(II)-bearing minerals (e.g., biotite, chlorite, and pyrite) are present in granitic rocks and sediments, and these are therefore candidate host rock formations for the geological disposal of radioactive waste. The most abundant redox-buffering mineral in a granitic rock is typically biotite (e.g., Ishihara and Terashima, 1977). Chlorite is commonly present in hydrothermal veins and fault gouges (e.g., Manaka et al., 2012). Pyrite is ubiquitous in granitic rocks and sedimentary rocks (e.g., Terashima and Ishihara, 1984; Tada et al., 1992).

It is expected that DO trapped in the underground will be consumed by these reduced mineral phases. Many studies have been devoted to measure the oxidation rates of these minerals or rocks, including in the presence of water (e.g., White and Yee, 1985; White et al., 1985; Grenthe et al., 1992; Banwart et al., 1994; Rivas-Perez et al., 2003; Perez et al., 2005; Giménez et al., 2006; Manaka, 2009). However, most measurements have been performed on crushed rock rather than intact rock samples. The use of crushed rock raises the question as to whether the results are representative, such as whether: (i) there is a difference in the reactivity of the reaction sites between the crushed and intact rock samples or not; and (ii) new reaction sites are created by milling a rock sample. To our knowledge, few studies have determined DO consumption parameters using intact rock samples

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(e.g., Pirhonen and Pitkänen, 1991; Trotignon et al., 2002). Pirhonen and Pitkänen (1991) determined the reducing ability (redox capacity) of crystalline rocks and minerals in an aqueous granite solution. Trotignon et al. (2002) performed continuous DO, pH, and Eh monitoring experiments using cores sampled in boreholes and discussed oxidizing perturbations in deep crystalline rocks. However, estimations of DO diffusivity along with DO consumption parameters from intact rock samples have yet to be made.

This work deals with the difference in DO consumption rates between crushed and intact rock samples from the Mizunami underground rock laboratory. The DO consumption parameter and DO diffusivity in intact rock samples were estimated from reactive transport experiments. DO consumption parameters for crushed rocks were estimated using standard batch reaction methods. The difference between DO consumption parameters measured for crushed and intact samples is discussed and the results are compared with data from the literature. Given that DO diffusivities for saturated sedimentary rocks are not available from the literature, the measured data are compared with diffusivities of tritiated water (HTO). Finally, the dominant DO-consumers in the Mizunami sedimentary rocks are evaluated.

2. Materials and methods

2.1. Characterization and preparation of the sedimentary rock samples

The Mizunami underground laboratory site is located in the city of Mizunami, Gifu Prefecture, in central Japan. Around the site, Pliocene to Pleistocene rocks of the Seto Group (12–15 Ma) unconformably overlie Miocene sedimentary rocks of the Mizunami Group (27–15 Ma). The latter rocks, at depths of about 100–200 m, in turn unconformably overlie a basement of the Cretaceous Toki Granite (75 Ma; Sasao et al., 2006). The Mizunami Group is divided into the Toki Lignite-Bearing Formation, the Hongo Formation, and the Akeyo Formation, from bottom to top (Itoigawa, 1974). The upper part of the Mizunami Group (i.e., the Akeyo Formation) is composed of shallow-marine siltstone–sandstone alternations. In contrast, the middle and lower parts of the Mizunami Group (i.e., the Hongo Formation and the Toki Lignite-Bearing Formation, respectively) are composed of fluvial sediments.

The sedimentary rock samples were collected from borehole MSB-2, at depths of approximately 34, 35, 95, and 125 m. The samples from depths of 34 and 35 m belong to the Akeyo Formation of the Mizunami Group, and the samples from 95 and 125 m belong to the Toki Lignite-Bearing Formation of the Mizunami Group.

The samples were cored (diameter = 20 mm) parallel to the drill core axis. The cylindrical samples were then sliced to a thickness of about 3 mm. Before each run, the sliced coin-shaped samples were stored in distilled deionized water in a refrigerator to remove salt formed by evaporation at the sample surface during storage. The samples were then stored in a test solution in the refrigerator to prevent oxidation. The remains of the drilled cores were crushed and air-dried. Part of the air-dried sample remained in a massive state for determination of the physical characteristics of the sedimentary rock, and the other was powdered using a fully automatic pulverizer (HP-MS, Herzog). The powdered samples were stored in a desiccator containing an oxygen scavenger to prevent oxidation until the experiments were performed.

The porosities, bulk dry densities, and pore areas of the sedimentary rocks were measured by the mercury intrusion method (Autopore IV-9520, Micromeritics) using the massive remains of the drilled cores from which the samples were taken. The specific surface areas of the rock powders were measured with a Shimadzu TriStar 3000 analyzer using the BET method (Brunauer et al., 1938). Measurement of triplicate samples indicated a precision of better than 2.7%. A confidence level of 95% was adopted for the analyses. Table 1 summarizes these results.

The bulk-rock powders were analyzed with an X-ray powder diffractometer (MultiFlex, Rigaku) using monochromatic CuK α radiation operated at 40 kV and 40 mA, from 2° to 65°. The step size was 0.02° and the scan speed was 1° min⁻¹. The clay fractions (<2 μ m) of the sedimentary rocks were extracted using a conventional sedimentation method according to Stokes' Law. Clay identification and procedures were based on those reported by Wada (1966) and Shirozu (1988). For oriented aggregate mounts of the clay fraction of samples, clay mineral identification was confirmed by diagnosing the extent of d-spacing expansion and/or contraction, which is indicative of certain clay minerals during subsequent treatments. These treatments included air drying, ethylene glycol treatment, potassium saturation, and glycerol treatment after magnesium saturation. XRD patterns for clay fractions of samples were obtained with a Rigaku MultiFlex instrument operated at 40 kV and 40 mA from 2° to 20°, to determine the d-spacings in each sample. The step size was 0.02° and the scan speed was 0.5° min⁻¹.

Supplementary data files present the XRD patterns (Figs. A1 and A2) for the bulk-rocks and clay fractions of samples at each depth. These features are summarized in Table 2 and are consistent with the mineralogy reported by Iwatsuki et al. (1995). Focusing on the Fe(II)-bearing minerals associated with consumption of DO in the rocks, it is evident that smectite decreases with depth and hornblende is present at depths of >95 m. Furthermore, gypsum is present in samples at depths of <35 m.

Weight loss on ignition (LOI) was determined for each rock powder by means of whole-rock analysis. After determining LOI, the samples were analyzed for major elements at Activation Laboratories, Canada, using inductively coupled plasma–optical emission spectrometry (ICP–OES), apart from Fe(II), which was determined by titration. For the ICP–OES analysis, a Li metaborate/tetraborate fusion technique was used. Analytical errors were <0.01% (FeO is <0.1%).

The compositions of the sedimentary rock samples are listed in Table 3. In general, the oxides SiO₂, Al₂O₃, and LOI are dominant, and the sum of these oxides accounts for >80% of the samples. Variations in the contents of FeO, Fe₂O₃, and CaO were greater than those of the other oxides. FeO contents decreased from 3.2 wt.% (at 32.90–33.00 m) to 1.2 wt.% (at 125.00–125.13 m), but Fe₂O₃ contents increased from 1.7 to 3.2 wt.% over the same interval. The CaO contents varied among samples, but this variation was unrelated to depth.

Total sulfur and pyrite-sulfur contents in the rock powders were analyzed by the combustion–infrared absorptiometric method (e.g., Kakegawa et al., 1999). The powders were treated with 6 M HCl to remove most of the sulfate minerals. The residues were dried to form an acid-insoluble matter that is composed mainly of pyrite. The sulfate-sulfur content was calculated by subtracting the pyrite-sulfur content from the total sulfur content.

The variation in the total sulfur content was greater than that in the oxides. Total sulfur content decreased upward. The highest abundance of pyrite was 0.60 wt.% at 34.90–35.00 m, and the abundances at 32.90–33.00 m, 95.50–95.63 m, and 125.00–125.13 m were 0.37, 0.36, and 0.047 wt.%, respectively. Sulfate-sulfur was documented at 32.90–33.00 m and 34.90–35.00 m, which is consistent with the presence of gypsum indicated in the XRD analyses for these samples.

The total Fe(II) surface site concentrations at the start of the experiment (S_T), calculated independently using data from FeO titration, BET, and fusion ICP analyses of bulk-rock samples, are listed in Table 4. Perez et al. (2005) and Davis and Kent (1990) recommended a value of 2.31 sites per nm² when estimating surface sites in coin-shaped materials. Fe(II) surface site concentrations are calculated using this quantity and the measured data for Fe²⁺ concentration and surface area for each sample. This calculation yields estimates for $S_T \times$ solution volume (V)/sample surface area (SA) in the region of 10⁻⁸ mol m⁻².

2.2. DO consumption experiments on rock powder

Experiments were conducted on rock powders in an air-saturated carbonate-buffered (ASCB) solution (initial pH ~9.4). Fig. 1 shows a

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