Pore space property of clay in the forms of gelled and compacted

*Hisao Satoh[1], Yuki Araki[2], Ken Nagashima[3]

1. Naka Energy Research Laboratory, Mitsubishi Materials Corporation, 2. Department of Physical Sciences, College of Science and Engineering, Ritsumeikan University, 3. The Institute of Low Temperature Science, Hokkaido University

Context: Rock and clay are still major constructive materials in the modern ages even for the underground facilities such as radioactive waste repository, due to its long-term robustness. The chemical and mineralogical robustness should be promised by its very low reactivity. Until recently, there are many studies developing the geochemical and engineering models to validate the safety of waste disposal, because the repository has buffer clay as engineered barrier. Dissolution of clay minerals is the first priority information. Direct measurement revealed that dissolution rate of clay is extremely lowered by effective surface area at the reactive (hk0) edge (ESA) exposed to the pore solution as a function of density [1]. Recently, we have successfully formulated the effective ESA as the function of density involving isotropic-nematic transition [2]. Step-interaction also affect the dissolution kinetics [1, 3] which is sometimes explained by the step-dynamic law such as the BCF theory [4]. Explaining the relationship between dissolution and its resultant degradation in water-stopping property such as hydraulic conductivity is required to validate the feasibility in engineered barrier system. Very recently, we have developed an atomistic scale method to evaluate the surface property of hydration structure of clay in groundwater directly [5].

Methods: We used FESEM to observe pores in clay rocks from Tsukinuno mine (Kunimine Industries Co., Dr. M. Itoh, Pers. Comm.). The tomographic observation was also made on this clay with micro X-ray CT (Fig. 1). Direct dissolution measurement by interferometry had been carried out on a purified separate from same clay rock (Kunipia P) under various compaction conditions [1, $<1E-12\ mol/m^2/s$]. To understand the connection between hydraulic property and dissolution, we applied surface force measurement with FM-AFM [6]. This method can realize force curve measurement which reflects interaction between hydrated clay surface and ambient water. The force curve scanning can visualize 3-D development of electric double layer (EDL) over the interface (a few nm). This is a new direct measurement estimating hydraulic property at the very nano-scale pores. Based on the step-dynamics and hydration structure with EDL, we can evaluate evolution of actual pore size during alteration process.

Results and Discussion: Groundwater has passed though these pores while the clay-rock is underlying at the mine. Pores as interstitial space surrounded by clay grains are the flow-path. The actual space is limited by the EDL as well as clay density. FM-AFM exhibited that the EDL over the clay surface is not constant [5], so that the water-path in the compacted clay should be very complicated. Generally, it is understood that the hydraulic conductivity varies as the function of clay density. The density cannot affect only the exposed area of the clay edge at which dissolution mainly occurs [2], but also the hydraulic property by the variety of the EDL in compacted clay. If the clay contains other secondary minerals such as zeolite or silica, the EDL of pores should be changed.

Until now, there are many macroscopic data about clay hydraulic measurements. Realistic pore observation of natural clay-rock can be currently achieved only by FM-AFM and nano-scale tomography. For better safety management, we need to proceed such a bottom-up approach to explain the large scale phenomena concerning migration issues about waste disposal.

References: [1] Satoh et al. (2013) Clay Min., 48, 285-294.; [2] Terada et al. (2017) Mat. Res. Exp. 6(3) 035514.; [3] Satoh et al. (2007) Am. Min., 92, 503-509.; [4] Burton et al. (1951) Phil. Trans. Royal Soc. London, 243, 299; [5] Satoh et al. (2019), Abst. Migration 2019; [6] Araki et al. (2017) Surf. Sci, 665 32-36.

Figure 1. Micro XCT images of gelled (a, wet) and compacted (b, dry) montmorillonite clay.

Keywords: clay, EDL, hydraulic conductivity