

Overview of the clay-mineralogy studies presented at the ‘Clays in natural and engineered barriers for radioactive waste confinement’ meeting, Brussels, March 2015

M. VAN GEET^{1,*} AND R. DOHRMANN^{2,3}

¹ ONDRAF/NIRAS, Belgian Agency for Radioactive Waste and Enriched Fissile Materials, Avenue des Arts 14, 1210 Brussels, Belgium

² Landesamt für Bergbau, Energie und Geologie (LBEG), Stilleweg 2, D-30655 Hannover, Germany

³ Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Stilleweg 2, D-30655 Hannover, Germany

This special issue of *Clay Minerals* contains 13 full papers presented at the 6th conference on ‘Clays in natural and engineered barriers for radioactive waste confinement’ held in Brussels during 2015. The conference was organized by the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (ONDRAF/NIRAS) together with partner organizations ANDRA (France), COVRA (The Netherlands), NAGRA (Switzerland), NWMO (Canada), POSIVA (Finland) and SKB (Sweden) and a broad international scientific committee. Since 2002, this conference has developed into the most important event for scientists from the world over, dealing with the disposal of highly and long-lived radioactive waste. After each of these conferences, a special issue of a journal was published which focused on clay radioactive waste (radwaste), research which has contributed in a significant way to the outstanding scientific level of the research in this field (*e.g.* Landais & Aranyossy, 2011; Landais *et al.*, 2013; Norris *et al.*, 2014). Therefore, *Clay Minerals - Journal of Fine Particle Science*, is happy to be able to provide the present compilation of recent HLW-disposal research in clay mineralogy in an open access issue. Most of the 13 papers published in this special 2016 issue were taken from the session on alteration processes. Papers from this conference which focus on large-scale geological characterization, general strategies for clay-based disposal systems, geomechanics, or

mass and gas transfer will be published in a ‘Special Publication’ of the Geological Society of London.

Many countries have chosen to dispose of all or some of their radioactive waste in facilities constructed in stable geological formations. Geological disposal as a safe solution for the long-term management of radioactive waste is in line with international recommendations and practices. The development of a geological disposal facility at a specific site requires a systematic and integrated approach taking into account the characteristics of the waste to be emplaced, the enclosing engineered barriers and the host rock (the three characteristics together being referred to as the ‘geological disposal system’) and of the geological setting of the host rock. Three main rock types are usually considered for geological disposal: crystalline rocks, rock salt and clays. Each type includes bedrock formations with a relatively broad spectrum of geological properties. The engineered barriers contain different types of materials such as metals, concrete and natural materials like clay. In fact, clays have many interesting properties which are to be exploited in the development of most geological disposal systems. Clays are used both as host rock and as material for engineered barriers. Whatever their use, clays present various characteristics that make them high-quality barriers to the migration of radionuclides and chemical contaminants towards the surface environment. As host rocks, clays are also hydrogeologically, geochemically and mechanically stable over geological timescales, *i.e.* millions of years.

Each of the elements of the geological disposal system fulfils, separately or in complementary fashion,

* E-mail: M.VanGeet@nirond.be
DOI: 10.1180/claymin.2016.051.2.01

multiple safety functions. The ‘defence-in-depth’ principle requires multiple levels of protection, which are designed to enhance safety through their diversity and redundancy. It is the whole system that must be taken into account in safety assessments and not each system component individually.

Safety assessment is concerned with the post-closure performance and safety of a disposal system and is the means by which various lines of evidence, arguments and analyses for passive long-term safety, radiological and non-radiological, are identified and assessed critically. A safety assessment typically considers several different evolution scenarios, and different assessment cases for each scenario, where an assessment case is a specific realization of how the disposal system might evolve and perform over time within the corresponding evolution scenario.

Therefore, in the different national programs on geological disposal, research continues on the phenomenological description of the disposal system and its evolution in order to provide a description of the initial state of the disposal system at the time of emplacement of the first waste package and a description of the expected evolution of the system (see for example ONDRAF/NIRAS, 2013). The description of the expected system evolution includes the key thermal, hydraulic, mechanical and chemical (THMC) processes. The description of the expected evolution requires the identification and bounding of different possible alteration processes of all components (compare Sellin & Leupin, 2014, and Dohrmann *et al.*, 2013). Therefore, studies are conducted to either identify new alteration mechanisms (*e.g.* of smectites under the conditions expected) or to try to model specific alteration mechanisms (*e.g.* dissolution rates at high pH).

Kumpulainen *et al.* (2016, this volume) studied four of 31 compacted blocks made of MX-80 (LOT), Deponit CaN, and Friedland clays in the lower part of the alternative buffer material test (ABM-II) in Äspö, Sweden (blocks #2, 4-6). The authors identified changes in exchangeable cation population, accumulation of water-soluble SO_4 , Ca, K and Mg, a decrease in poorly crystalline iron oxides, accumulation of total Mg, Ca and S, and a decrease in Na and K with increasing distance from the heater towards the rock. At the heater boundary, accumulation of Fe, decrease in Si and Al, precipitation of gypsum and anhydrite, dissolution of cristobalite and feldspars, and indications for the formation of trioctahedral clay minerals was found. They observed an increase in exchangeable Ca, and decrease in Na, Mg and K without cation exchange capacity (CEC) change. No horizontal elemental profiles could be identified.

Geochemical evolution of Wyoming bentonites (MX80) under thermo-hydraulic gradients were also studied by Gómez-Espina & Villar *et al.* (2016, this volume). They tested compacted 20 cm-long cylinders in thermo-hydraulic (TH) cells with hydration from the top and heat (30 and 140°C) from the bottom simulating the conditions of a sealing material in a nuclear waste repository. The authors identified gradients along the column with respect to the physical state (water content, dry density) and geochemistry of the bentonite leading to gypsum dissolution, carbonate precipitation, smectite dissolution and possibly bentonite erosion. The CEC decreased towards the heater and ion exchange occurred while solutes were transported along the columns confirming the results of large-scale field tests of bentonites in crystalline rocks.

From the perspective of long-term safety, the question of illitization of bentonite in a geological disposal environment must be raised because Cs sorption in such a barrier system might be important. Ishidera *et al.* (2016, this volume) studied diffusion and the retention behaviour of Cs in illite-added compacted montmorillonite. This group used the fine fraction (Kunipia-F) of the Japanese bentonite, Kunigel V1 (Kunimine Industry Co. Ltd., Japan) and added purified illite which was obtained from a shale rock containing 85% illite (Rochester, USA) by elutriation. Illite is known for its large sorption capacity for Cs due to the presence of the so-called Frayed Edge Sites (FES) which have the positive effect that although illitization reduces the swelling capacity of the clay, it may also increase the sorption capacity of Cs.

Using MX80 from the ABM test, Järvinen *et al.* (2016, this volume) developed a ‘squeezing’ method for analysing compacted bentonite porewater. These treatments usually lead to pronounced artifacts, such as mixing of the different pore-water types, dissolution of the accessory minerals and cation exchange reactions. The authors tried to overcome these problems by combining squeezing methods, chemical analyses, microstructure measurements and geochemical modelling, applying four different maximum pressures. They showed that 35 wt.% of the water collected originated from the interlamellar (IL) pores and that this ratio was constant over the applied pressure range of 60–120 MPa. The authors concluded that limited space for anions in non-IL water affects the chemical activities of the anions and should be taken into account in modelling.

The microstructure of MX80 bentonites compacted to different densities and saturated with water and NaCl solution was analysed by Matuszewicz *et al.* (2016, this volume) using X-ray scattering measurements. The

authors showed that different treatment of the bentonite samples can lead to different structural features particularly for samples of low dry densities (0.7 and 1.0 g/cm³) whereas at intermediate dry density the effects measured were small and increased again at 1.7 g/cm³. They concluded that more research is necessary to understand the relationship between different preparation procedures and resulting differences in the clay microstructure.

Molecular dynamics (MD) calculations were used by Seppälä *et al.* (2016, this volume) to investigate the swelling properties of montmorillonites with different layer charges and interlayer cationic compositions. The authors obtained self-diffusion coefficients of interlayer water and cations in different montmorillonites. The coefficient increased with increasing water content and with decreasing layer charge; the modelled swelling behaviour of K-montmorillonite contradicts the experimental observations, however, where K acts as a swelling inhibitor which was caused by the system setup, leaving room for further improvements.

Another large-scale underground test site in crystalline rock but with groundwater of low ionic strength in Grimsel, Switzerland, is the Full-scale Engineered Barriers Experiment (FEBEX) using bentonite obtained in the Cortijo de Archidona deposit (Almería, Spain). Erosion of bentonite may be very significant in terms of long-term safety and relevant research was supported by the European Commission under the BELBaR project (Bentonite Erosion: effects on the Long term performance of the Engineered Barrier and Radionuclide Transport). Within this framework Mayordomo *et al.* (2016, this volume) investigated the size distribution of bentonite colloids upon fast disaggregation in low ionic-strength water. These authors confirmed that disaggregation of bentonite colloids is promoted effectively by decreasing ionic strength. The process is not fully reversible, however, and initial stable hydrodynamic diameter is not recovered, even at lower ionic strength and in the absence of bivalent cations. Single-Particle Counter measurements indicated that fast and extensive dilution of aggregated colloids to low ionic strength provided smaller colloids.

The FEBEX bentonite was also studied by Fernández *et al.* (2016, this volume) who investigated C-S-H or C-A-S-H phases observed in bentonite–cementitious interface materials sampled from various existing experiments with different scale size, time and experimental conditions. Precipitation of C-A-S-H was observed in all experiments. The most representative C-S-H phase from the montmorillonite–cement interface reactivity was Al-tobermorite. The authors

found evidence for the intercalation or association of montmorillonite and C-A-S-H phases at the pore scale.

Another important material is the Chinese reference Gaomiaozi bentonite (GMZ) and little is known about the reactions of this bentonite in highly alkaline environments induced by cementitious materials in the repository. Chen *et al.* (2016, this volume) used this bentonite, which contains ~7 wt.% cristobalite, a mineral which is known to react in high-pH solutions (*cf.* Karnland *et al.*, 2007; using MX80 bentonite). As expected, dissolution and changes in microstructure were also observed in this bentonite.

MX80 from the ABM test was used by Grolimund *et al.* (2016, this volume) in a pioneering study of the impact of Ti corrosion on compacted MX80 bentonite. This is relevant for the alternative Swedish and Finnish repository design, KBS-3H, where horizontal emplacement of copper canisters–bentonite modules surrounded by a titanium shell is foreseen. The authors showed that Ti in the MX-80 bentonite might occur in the clay structure, presumably in the octahedral sheet, whereas in other natural bentonites, Ti often occurs as free oxide. The Grolimund *et al.* group performed hydrothermal tests at 200°C using synthetic montmorillonite and showed that under alkaline conditions, limited alteration was observed, including the formation of trioctahedral clay minerals and zeolite; these changes occurred independently of the addition of Ti, however. In batch tests conducted at 80°C the authors found evidence that Ti was incorporated in a neoformed phyllosilicate structure.

Kunipia-F was used in for high-pH alteration experiments by Sawaguchi *et al.* (2016, this volume) who investigated the effects of activity of OH[−] and temperature on the dissolution of montmorillonite in the range of 0.10–1.0 mol dm^{−3} OH[−] and 50–90°C. The dissolution rate of montmorillonite was greater in compacted montmorillonite than in compacted sand–bentonite mixtures which was explained by considering a decrease in *a*OH[−] in the mixtures accompanied by dissolution of accessory minerals such as silica.

Yamaguchi *et al.* (2016, this volume) studied high-pH systems with and without contact with compacted Kunigel V1 bentonite. Alteration of cement–bentonite interfaces and accompanying changes in the diffusivity of tritiated water were investigated experimentally using intact hardened cement–paste specimens. The modelling procedure for the simultaneous alteration and diffusion experiments needs to be verified in the future. Finally, Kaufhold & Dohrmann (2016, this volume) give an overview on the assessment of parameters to distinguish more suitable from less

suitable bentonites for use in HLW disposal concepts. The authors identify 10 key issues used to discuss bentonite specification. Swelling pressure and thermal conductivity depend more on processing and production than on the origin of the bentonite. For some of the key issues, in contrast, significant effects of the type of bentonite were found, indicating possible specifications, the most important being the absence of reactive phases such as organic matter, pyrite or gypsum. The structural Fe content of the smectites should be small and, depending on the canister material, a large layer-charge density of the swelling clay minerals may lead to less corrosion at iron–bentonite interfaces.

The collection of different topics presented here proves the diversity of HLW-repository research and identifies bentonite studies as important topics. Our understanding of all of the topics presented in this special issue and investigated elsewhere still requires more work. After visiting Belgium for the first time in 2015, NAGRA will organize the 7th conference on ‘Clays in natural and engineered barriers for radioactive waste confinement’ in 2017 in Davos, Switzerland.

REFERENCES

- Chen B., Guo J. & Zhang H. (2016) Alteration of compacted GMZ Bentonite by infiltration of alkaline solution. *Clay Minerals*, **51**, 237–247.
- Dohrmann R., Kaufhold S. & Lundqvist B. (2013) The role of clays for safe storage of nuclear waste. pp. 677–710 in: *Developments in Clay Science, Vol. 5B, Handbook of Clay Science, Techniques and Applications* (F. Bergaya and G. Lagaly, editors). Elsevier, Amsterdam.
- Fernández R., Ruiz A.I. & Cuevas J. (2016) Formation of C-A-S-H phases from the interaction between concrete or cement and bentonite. *Clay Minerals*, **51**, 223–235.
- Gómez-Espina R. & Villar M.V. (2016) Time evolution of MX-80 bentonite geochemistry under thermo-hydraulic gradients. *Clay Minerals*, **51**, 145–160.
- Grolimund D., Wersin P., Brendlé J., Huve J., Kiviranta L. & Snellman M. (2016) Interaction of titanium with smectite within the scope of a spent fuel repository: A spectroscopic approach. *Clay Minerals*, **51**, 249–266.
- Ishidera T., Kurosawa S., Hayashi M., Uchikoshi K. & Beppu H. (2016) Diffusion and retention behaviour of Cs in illite-added compacted montmorillonite. *Clay Minerals*, **51**, 161–172.
- Järvinen J., Matuszewicz M. & Itälä A. (2016) The composition of pore water in compacted MX-80 bentonite. *Clay Minerals*, **51**, 173–187.
- Karland O., Olsson S. & Nilsson U. (2007) Experimentally determined swelling pressures and geochemical interactions of compacted Wyoming bentonite with highly alkaline solutions. *Physics and Chemistry of the Earth*, **32**, 275–286.
- Kaufhold S. & Dohrmann R. (2016) Distinguishing between more and less suitable bentonites for high-level radioactive waste. *Clay Minerals*, **51**, 289–302.
- Kumpulainen S., Kiviranta L. & Korkeakoski P. (2016) Long-term effects of Fe-heater and Äspö groundwater on smectite clays: Chemical and hydromechanical results from in-situ alternative buffer material (ABM) test package 2. *Clay Minerals*, **51**, 129–144.
- Landais P. & Aranyosy J.-F. (2011) Clays in natural and engineered barriers for radioactive waste confinement. *Physics and Chemistry of the Earth, Parts A/B/C*, **36**, 1437.
- Landais P., Kaufhold S. & Dohrmann R. (2013) Overview of the clay mineralogy studies presented at the ‘Clays in natural and engineered barriers for radioactive waste confinement’ meeting, Montpellier, October 2012. *Clay Minerals*, **48**, 149–152.
- Matuszewicz M., Pulkanen V.-M. & Olin M. (2016) Influence of the sample preparation on MX-80 bentonite microstructure. *Clay Minerals*, **51**, 189–195.
- Mayordomo N., Deguedre C., Alonso U. & Missana T. (2016) Size distribution of FEBEX bentonite colloids upon fast disaggregation in low ionic strength water. *Clay Minerals*, **51**, 213–222.
- Norris S., Bruno J., Cathelineau M., Delage P., Fairhurst C., Gaucher E.C., Höhn E.H., Kalinichev A., Lalioux P. & Sellin P. (2014) *Clays in Natural and Engineered Barriers for Radioactive Waste Confinement*. Geological Society, London, Special Publications, **400**, doi:10.1144/SP400.43.
- ONDRAF/NIRAS (2013) ONDRAF/NIRAS Research, Development and Demonstration (RD&D) Plan for the geological disposal of high-level and/or long-lived radioactive waste including irradiated fuel if considered as waste, State-of-the-art report as of December 2012. ONDRAF/NIRAS, report NIROND-TR 2013-12E.
- Sawaguchi T., Tsukada M., Yamaguchi T. & Mukai M. (2016) Effects of OH⁻ activity and temperature on the dissolution rate of compacted montmorillonite under highly alkaline conditions. *Clay Minerals*, **51**, 267–278.
- Seppälä A., Puhakka E. & Olin M. (2016) Effect of layer charge on the swelling of Na⁺, K⁺ and Ca²⁺ montmorillonites: DFT and molecular dynamics studies. *Clay Minerals*, **51**, 197–211.
- Sellin P. & Leupin O. (2014) The use of clay as an engineered barrier 1 in radioactive waste management – a review. *Clays and Clay Minerals*, **61**, 477–498.
- Yamaguchi T., Sawaguchi T., Tsukada M., Hoshino S. & T. Tanaka (2016) Mineralogical changes and associated decrease of n tritiated water diffusivity after alteration of cement-bentonite interfaces. *Clay Minerals*, **51**, 279–287.