

Overview of the clay mineralogy studies presented at the ‘Clays in natural and engineered barriers for radioactive waste confinement’ meeting, Montpellier, October 2012

P. LANDAIS^{1,†}, R. DOHRMANN^{2,3,*} AND S. KAUFHOLD³

¹ French National Agency for Radioactive Waste Management, 1/7 Rue Jean Monnet, 92290 Châtenay-Malabry cedex, France, ² Landesamt für Bergbau, Energie und Geologie (LBEG), Stilleweg 2, D-30655 Hannover, Germany, and ³ Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Stilleweg 2, D-30655 Hannover, Germany

(Received 12 April 2013)

The present special issue of *Clay Minerals* contains 19 full papers of scientific studies presented at the 5th conference on “Clays in natural and engineered barriers for radioactive waste confinement” held at Montpellier 2012. Since 2002, ANDRA, the French National Radioactive Waste Management Agency, developed this conference into the most important event for all kinds of scientists from all over the world dealing with the disposal of highly and long-lived radioactive waste (HLRW). With these conferences, ANDRA contributed significantly to the outstanding scientific level of European research in this field. Therefore, *Clay Minerals* is happy to be able to provide the present compilation of recent HLRW disposal research articles in clay mineralogy. The 19 papers published in this special Montpellier 2012 issue were classified according to different areas within the field of HLRW disposal research. Notably, the assignment of a study to one of the classes was not always easy because many studies provide information of, and for, different aspects of HLRW disposal research. Papers from this conference which focus on topics such as large-scale geological characterization, geomechanics, or

mass and gas transfer will be published in a Geological Society Special Publication book.

For long-term safety assessment of the multi-barrier systems two main topics have to be addressed. First, the different possible alteration processes of all components have to be identified and understood. Therefore, studies are conducted to either identify new alteration mechanisms (e.g. of smectites under the conditions expected) or to try to model special alteration mechanisms (e.g. dissolution rates at high pH). Secondly, possible routes of migration of radionuclides through the barrier have to be understood. All of the first six studies dealt with **alteration and migration using either experiments conducted in underground rock laboratories (URLs) or natural analogues**.

1) Aertens *et al.* (2013) compared the results of tracer migration experiments in the URL Mol in Belgium with laboratory tests. In their study they show how the diffusion coefficients of different tracers can be modeled. They present models which were able to explain both the laboratory and in-situ derived values.

2) Watson *et al.* (2013) investigated the 15–20 year-old interface of a cement filled bore hole in a clay formation in the industrial analogue for cement-clay interaction at Tournemire, southern France with respect to a possible alteration of the clay minerals caused by the alkaline plume derived from the cement. Their QPAC based model, which

* E-mail: reiner.dohrmann@lbeg.niedersachsen.de

† Present address: BRGM, 3 avenue Claude Guillemin, BP 36009, 45060 Orléans cedex 2, France
DOI: 10.1180/claymin.2013.048.2.00

consisted of ion exchange and surface complexation, was able to explain the main features observed at the Tournemire site as porosity variations and precipitation of secondary minerals.

3) Similarly to the former authors, Yamaguchi *et al.* (2013a) developed a model for the prediction of alteration reactions at the clay concrete interface. Their PHREEQC based model proved most of the experimentally observed reactions to involve formation of carbonates and CSH phases as well as dissolution of quartz and formation of porosity but was not able to predict the clay dissolution and gypsum formation. This model, therefore, will be further improved.

4) Kaufhold *et al.* (2013) investigated one block of each different clay material used in the first package of the Äspö hard rock laboratory ABM-test (alternative buffer material test). They found the different materials to have reacted differently and finally summarized all alteration mechanisms as Fe-, C_{org}, C_{inorg}, SO₄-accumulation and mineral dissolution. Of particular interest is the possible formation of trioctahedral domains in some clays which was found by XRD (*d*₀₆₀ shift) and IR (appearance of 680 cm⁻¹ band) and which correlated well with an increase of MgO concentrations at the interface to the heat source.

5) In the second part of the ABM study, Dohrmann *et al.* (2013) focused on the exchangeable cation population before and after the heating period. Surprisingly, the cation population changed significantly towards a more-or-less average interlayer composition. Na-rich bentonites adsorbed Ca and Mg and Ca- or Ca-Mg-rich materials adsorbed some Na. The authors concluded that the whole package seems to be influenced by the groundwater which was added from a water tank at the experiment site, enabling at least partial equilibration between the different blocks

6) Alexander *et al.* (2013) investigated one of the few natural analogues in which bentonite is and was in contact with alkaline waters. Such a site can be found on Cyprus. The authors identified a minimal volumetric reaction of the bentonite and the formation of palygorskite.

A further challenge in HLRW-related clay research is the improvement of the characterization of the materials. In this respect the microstructure represents an outstanding case because it is considered to be the reason for many unexplained differences between chemically similar clays and, on the other hand, is difficult to determine.

Microstructure investigations also appear to be necessary for understanding complex and coupled mechanisms which are supposed to occur during repository evolution. In the present issue two studies focused on the **clay microstructure investigation**.

7) Muurinen *et al.* (2013) investigated the microstructure by NMR and SAXS and hence distinguished stacks with interlayer water and water bound to external surfaces. The dry density was varied and chloride porosity measurements were performed additionally. The number of layers per stack was used as fitting parameter to derive a model being able to explain all measured results.

8) Matusiewicz *et al.* (2013) used similar methods as Muurinen *et al.* (2013) but instead considered a Ca-montmorillonite. They confirmed the conclusions drawn by Muurinen *et al.* (2013) in that different methods yield similar water distributions.

Laboratory tests, in contrast to the investigation of natural analogues and large scale tests, are advantageous in that it is possible to fix and vary single parameters and, hence, specifically investigate **alteration processes in bentonite buffer systems**.

9) Itälä *et al.* (2013) investigated the effect of CO₂ on the pH of compacted bentonite. They showed that the measurement of the pH even inside the solid compacted bentonite is possible. Generally, a decrease of the pH value upon introduction of CO₂ was found which to its full extent could not be explained by their model.

10) Satoh *et al.* (2013) studied the dissolution rate of montmorillonite in-situ, i.e. within a compaction cell and at different compaction pressures. Using this device they proved two orders of magnitude lower dissolution rates of montmorillonite compared to the suspended state. Also an effect of the compaction on the dissolution rate was found which, however, was restricted to dry densities below 1 Mg/m³. Accordingly compaction reduces the dissolution rate but not above 1 Mg/m³.

11) Similarly to the authors above, Myllykylä *et al.* (2013) also investigated the dissolution of montmorillonite but focused on the effect of different exchangeable cations (Na or Ca). The log rates in mol/g/s varied between -10.6 and -12.1. These values were calculated based on the amount of dissolved silica.

12) Heikola *et al.* (2013) also studied the dissolution of a Na- and a Ca-bentonite. The pH was varied between 8 and 12, hence simulating pore

waters affected by cement. The pH buffering capacity of the bentonite decreased the pH particularly at the beginning of the experiments. While some Si was found in the solution of the different experiments detectable amounts of dissolved Al were only found in the pH 12 experiments.

13) In their study, Ishii *et al.* (2013) attempted to couple hydraulic/mechanical phenomena and chemical analysis of bentonite alteration. They found the “dissolution of montmorillonite” to be suppressed near the cementitious material but they also identified issues which still have to be resolved for a comprehensive modelling.

14) In the frame of long term tests with different temperatures and time (up to 150°C for 18 months) Valter & Plötze (2013) concluded a high mineralogical stability. Apart from some Ca intercalation into the previously Na-saturated bentonite, a decrease of the water uptake capacity was found which could, at least partly, be explained by the cation exchange. However, also smectite aggregation processes were supposed to cause the changes.

A particular challenge of HLRW repository research is the assessment of coupled processes such as the effect of smectite dissolution on the swelling pressure and/or hydraulic conductivity. In this respect both **thermo-hydro-mechanical and chemical processes in the engineered barrier system** have to be considered.

15) In the early phases of a repository, when hydraulic gradients are expected to be more significant than in the long run, piping, which is the local erosion of bentonite, may play a role. Considering the Japanese case (70 mass% Kunigel + quartz) Suzuki *et al.* (2013) proved that such pipes, which were at least partially filled with quartz, could be sealed by swelling of bentonite if the inflow rate is low (0.1 ml/min).

16) Svoboda (2013) investigated the swelling of bentonite gels into fissures of different aperture. He found a linear relation of the penetration depth of the tested bentonite with the aperture (fissure width) and could relate the overall swelling ability to the penetration depth.

17) Using ESEM and digital image correlations techniques Wang *et al.* (2013) proved the anisotropic swelling of the Callovo-Oxfordian clay on a micro-scale. Increasing the relative humidity in the electron microscope clearly revealed that the anisotropic swelling can be explained by the preferred orientation of particles.

18) Yamaguchi *et al.* (2013b) investigated the changes of the hydraulic conductivity of sand-bentonite mixtures upon introduction of an alkaline solution (NaOH) at elevated temperature (80–90°C). They found a significant increase of the hydraulic conductivity and in some experiments a decrease of the montmorillonite content.

19) Sawaguchi *et al.* (2013) investigated the diffusion of Cs, Np, Am, and Co in compacted sand-bentonite mixtures. By comparing the concentration gradients of both adsorbed and bulk Cs they assumed surface diffusion to play a major role with respect to the Cs migration.

The collection of different topics presented in the present issue proves the diversity of HLRW repository research. Of course the understanding of all topics presented here and investigated elsewhere (such as corrosion or detachment of colloidal particles) still requires more work. At the same time more studies focusing on the complex connection of different processes are expected to be required (e.g. change of pH → change of adsorption properties → change of microstructural arrangement → change of swelling pressure → change of hydraulic conductivity). This may be a challenging future task for all HLRW scientists.

Although ANDRA will not continue to organize this conference series, ONDRAF has agreed to organize the 6th conference on “Clays in natural and engineered barriers for radioactive waste confinement” in 2015 in Brussels, Belgium.

REFERENCES

- Aertsens M., Maes N., Van Ravestyn L. & Brassinnes S. (2013) Overview of radionuclide migration experiments in the HADES Underground Research Facility at Mol (Belgium). *Clay Minerals*, **48**, 153–166.
- Alexander W.R., Milodowski A.E., Pitty A.F., Hardie S.M.L., Kemp S.J., Rushton J.C., Siathas A., Siathas A., MacKenzie A.B., Korkeakoski P., Norris S., Sellin P. & Rigas M. (2013) Bentonite reactivity in alkaline solutions: interim results of the Cyprus Natural Analogue Project (CNAP). *Clay Minerals*, **48**, 235–249.
- Dohrmann R., Olsson S., Kaufhold S. & Sellin P. (2013) Mineralogical investigations of the first package of the alternative buffer material test – II. Exchangeable cation population rearrangement. *Clay Minerals*, **48**, 215–233.
- Heikola T., Kumpulainen S., Vuorinen U., Kiviranta L. & Korkeakoski P. (2013) Influence of alkaline (pH 8.3–12.0) and saline solutions on chemical, miner-

- ological and physical properties of two different bentonites. *Clay Minerals*, **48**, 309–329.
- Ishii T., Yahagi R., Owada H., Kobayashi I., Takazawa M., Yamaguchi K., Takayama Y., Tsurumi S. & Iizuka A. (2013) Coupled chemical-hydraulic-mechanical modelling of long-term alteration of bentonite. *Clay Minerals*, **48**, 331–341.
- Itälä A., Järvinen J. & Muurinen (2013) CO₂ effect on the pH of compacted bentonite buffer on the laboratory scale. *Clay Minerals*, **48**, 277–284.
- Kaufhold S., Dohrmann R., Sandén T., Sellin P. & Svensson (2013) Mineralogical investigations of the first package of the alternative buffer material test – I. Alteration of bentonites. *Clay Minerals*, **48**, 199–213.
- Matusewicz M., Pirkkalainen K., Liljeström V., Suuronen J.-P., Root A., Muurinen A., Serimaa R. & Olin M. (2013) Microstructural investigation of calcium montmorillonite. *Clay Minerals*, **48**, 267–276.
- Muurinen A., Carlsson T. & Root A. (2013) Bentonite pore distribution based on SAXS, chloride exclusion and NMR studies. *Clay Minerals*, **48**, 251–266.
- Myllykylä E., Tanhua-Tyrkkö M., Bouchet A. & Tiljander M. (2013) Dissolution experiments of Na- and Ca-montmorillonite in groundwater simulants under anaerobic conditions. *Clay Minerals*, **48**, 295–308.
- Satoh H., Ishii T. & Owada H. (2013) Dissolution of compacted montmorillonite at hyperalkaline pH and 70°C: *in situ* VSI and *ex situ* AFM measurements. *Clay Minerals*, **48**, 285–294.
- Sawaguchi T., Yamaguchi T., Iida Y., Tanaka T. & Kitagawa I. (2013) Diffusion of Cs, Np, Am and Co in compacted sand-bentonite mixtures: evidence for surface diffusion of Cs cations. *Clay Minerals*, **48**, 411–422.
- Suzuki K., Asano H., Yahagi R., Kobayashi I., Sellin P., Svemar C. & Holmqvist M. (2013) Experimental investigations of piping phenomena in bentonite-based buffer materials for an HLW repository. *Clay Minerals*, **48**, 363–382.
- Svoboda J. (2013) The experimental study of bentonite swelling into fissures. *Clay Minerals*, **48**, 383–389.
- Valter M. & Plötze M. (2013) Characteristics of variably saturated granular bentonite after long-term storage at near-field relevant temperatures. *Clay Minerals*, **48**, 343–361.
- Wang L.L., Bornert M., Chanchole S., Yang D.S., Héripé E. Tanguy A. & Caldemaison D. (2013) Micro-scale experimental investigation of the swelling anisotropy of the Callovo-Oxfordian argillaceous rock. *Clay Minerals*, **48**, 391–402.
- Watson C., Savage D., Wilson J., Benbow S., Walker C. & Norris S. (2013) The Tournemire industrial analogue: reactive transport modelling of a cement-clay interface. *Clay Minerals*, **48**, 167–184.
- Yamaguchi T., Kataoka M., Sawaguchi T., Mukai M., Hoshino S., Tanaka T., Marsal F. & Pellegrini D. (2013a) Development of a reactive transport code MC-CEMENT ver. 2 and its verification using 15-year *in situ* concrete/clay interactions at the Tournemire URL. *Clay Minerals*, **48**, 185–197.
- Yamaguchi T., Sawaguchi T., Tsukada M., Kadowaki M. & Tanaka T. (2013) Changes in hydraulic conductivity of sand-bentonite mixtures accompanied by alkaline alteration. *Clay Minerals*, **48**, 403–410.