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Saponites as New Generation Engineered Buffer Materials for Harsh Environments

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Abstract

Montmorillonite with an empirical formula of $Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$ is a di-octahedral smectite. Montmorillonite-rich bentonite is a primary buffer candidate for high level nuclear waste (HLW) and used nuclear fuel to be disposed in mild environments. In such environments, temperatures are expected to be ≤ 90ºC, the solutions are of low ionic strengths, and pH is close to neutral. Under the conditions outside the above parameters, the performance of montmorillonite-rich bentonite is deteriorated because of collapse of swelling particles as a result of illitization, and dissolution of the swelling clay minerals followed by precipitation of non-swelling minerals.

It has been well known that tri-octahedral smectites such as saponite, with an ideal formula of $Mg_3(Si, Al)_4O_{10}(OH)_2 \bullet 4H_2O$ for an Mg-end member (saponite-15A), are less susceptible to alteration under harsh conditions. Recently, Mg-bearing saponite has been favorably considered as a preferable engineered buffer material for the Swedish very deep holes (VDH) disposal concept in crystalline rock formations. In the VDH, HLW is disposed in deep holes at depth between 2,000 m and 4,000 m. At such deployment depths, the temperatures are expected to be between 100ºC and 150ºC, and the groundwater is of high ionic strength. The harsh chemical conditions of high pH are also introduced by the repository designs in which concretes and cements are used as plugs and buffers. In addition, harsh chemical conditions introduced by high ionic strength solutions are also present in repository designs in salt formations and sedimentary basins. For instance, the two brines associated with the salt formations for the Waste Isolation Pilot Plant (WIPP) in USA have ionic strengths of 5.82 $mol \bullet kg^{-1}$ (ERDA-6) and 8.26 $mol \bullet kg^{-1}$ (GWB). In the Asse site proposed for a geological repository in salt formations in Germany, the Q-brine has an ionic strength of ~13 $mol \bullet kg^{-1}$.

In this work, we present our investigations regarding the stability of saponite under hydrothermal conditions in harsh environments.

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Introduction

In a multiple component engineered barrier system (EBS) for a high-level nuclear waste (HLW)/spent nuclear fuel (SNF) repository, the buffer is an important component. The key functions of the buffer are to inhibit the penetration of groundwater into canisters/overpacks for HLW/SNF, and to retard the movement of radionuclides from canisters/overpacks to the surrounding environments, should canisters/overpacks be breached.

Montmorillonite with an empirical formula of $Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$ is a di-octahedral smectite. Montmorillonite-rich bentonite has been favorably considered as a buffer material for HLW/SNF owing to its high swelling and sorption properties and extremely low permeability. These favorable properties are expected to be reserved in mild environments. In such environments, the following key parameters are usually restrained in the disposal design concepts: (1) temperatures are expected to be $\leq 90^{o}C$; (2) the solutions are generally of low ionic strengths, and (3) pH is close to neutral. However, in many disposal design concepts, the conditions are usually outside the above mild environments. Under the conditions outside the above parameters, the performance of montmorillonite-rich bentonite is deteriorated because of collapse of swelling particles as a result of phase transformation to illite/chlorite, and dissolution of the swelling clay minerals followed by precipitation of non-swelling minerals.

It has been known that tri-octahedral smectites such as saponite, with an ideal formula of $Mg_3(Si, Al)_4O_{10}(OH)_2{\bullet}4H_2O$ for an Mg-end member (saponite-15A), are less susceptible to alteration under harsh conditions [1-2]. Recently, Mg-bearing saponite has been favorably considered as a preferable engineered buffer material for the Swedish very deep holes (VDH) disposal concept in crystalline rock formations [3]. In the VDH, HLW is disposed in deep holes at depth between 2,000 m and 4,000 m. At such deployment depths, the temperatures are expected to be between $100^{o}C$ and $150^{o}C$, and the groundwater is of high ionic strength [3]. The harsh chemical conditions of high pH are also introduced by the repository designs in which concretes and cements are used as plugs and buffers [4]. In addition, harsh chemical conditions introduced by high ionic strength solutions are also present in repository designs in salt formations and sedimentary basins. For instance, the two brines associated with the salt formations for the Waste Isolation Pilot Plant (WIPP) in USA have ionic strengths of 5.82 $mol{\bullet}kg^{-1}$ (ERDA-6) and 8.26 $mol{\bullet}kg^{-1}$ (GWB) [5]. In the Asse site proposed for a geological repository in salt formations in Germany, the Q-brine has an ionic strength of ~13 $mol{\bullet}kg^{-1}$[6].

In this work, we investigate the stability of saponite under hydrothermal conditions in harsh environments.

Method

In this work, we use both synthetic and natural saponite for our investigations. For synthesis of saponite, the chemicals used were ACS reagent grade chemicals. The synthesis of the starting material follows the procedure of Shao and Pinnavai [7] with some modifications. In the work of Shao and Pinnavai [7], the sources for Al, Mg, Na and Si, were $Al(NO_3)_3{\bullet}9H_2O$, $Mg(NO_3)_2{\bullet}6H_2O$, and water glass solution (containing 27 wt.% Si and 14 wt.% NaOH), respectively. In this work, the source for Si is $Na_2SiO_3{\bullet}9H_2O$, and NaOH was used to control the pH_m conditions. The other reagents are the same as those in Shao and Pinnavai [7]. Deionized water (DI) with >18.3 MΩ·cm used in the experiments was sparged with high purity Ar gas for a minimum of one hour to remove dissolved CO_2, following the procedure of Wood et al. [8] and Xiong [9]. The natural saponite was acquired from a commercial company.

In our experiments, we place certain amounts of saponite into Parr vessels with desired solid/liquid ratios. For the experiments with high ionic strength solutions, we use saturated NaCl brines which may represent the natural brines in salt formations such as ERDA-6 in the WIPP [5]. For the experiments with high pH, we use portlandite [$Ca(OH)_2$] to control the pH, as portlandite is expected to be present in cement seals and plugs. The Parr vessels are heated to the temperatures of interest ranging from 100°C to 200°C for certain periods of time. After that, the Parr vessels are cooled down to room temperature, and solid reaction products are separated from liquid by vacuum filtration. Solid reaction products are then dried at room temperature for at least overnight. The dried solid products are characterized by using XRD, XRF, etc.

Results

Our preliminary results suggest that Mg-rich saponite is stable in the temperature range we investigate in this study. Whitney [10] investigated the stability of K-saponite, Na-saponite and Ca-saponite in the temperature range from 300°C to 550°C. He concluded that K-saponite, Na-saponite and Ca-saponite are stable up to 400°C.

Summary

In this study, we investigate the stability of Mg-rich saponite from 100°C to 200°C. Our results suggest that Mg-rich saponite is stable in this temperature range. We are to further study the stability of Mg-rich saponite in multiple component brines that are expected to be present in various disposal design concepts including clay formations, crystalline rock formation, and salt formations. We are also to further study the stability of Mg-rich saponite, when it interacts with anticipated corrosion products from canisters/overpacks.

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References

[1] Eberl, D.D., Whitney, G. and Khoury, H., 1978. Hydrothermal reactivity of smectite. *American Mineralogist*, *63*(3-4), pp.401-409.

[2] Güven, N., 1990. Longevity of bentonite as buffer material in a nuclear-waste repository. *Engineering Geology*, *28*(3-4), pp.233-247.

[3] Yang, T., Pusch, R., Knutsson, S., and Liu, X.-D., WIT Transactions on Ecology and The Environment 180, 403-413 (2014).

[4] Wieland, E., Lothenbach, B., Glaus, M.A., Thoenen, T. and Schwyn, B., 2014. Influence of superplasticizers on the long-term properties of cement pastes and possible impact on radionuclide uptake in a cement-based repository for radioactive waste. *Applied geochemistry*, *49*, pp.126-142.

[5] Xiong, Y. and Lord, A.S., 2008. Experimental investigations of the reaction path in the $MgO–CO_2–H_2O$ system in solutions with various ionic strengths, and their applications to nuclear waste isolation. *Applied Geochemistry*, *23*(6), pp.1634-1659.

[6] W. Schuessler, et al., Materials Research Society Symposium Proceedings 663, 791 (2001).

[7] Shao, H. & Pinnavaia, T.J.,. Synthesis and properties of nanoparticle forms saponite clay, cancrinite zeolite and phase mixtures thereof. *Microporous and Mesoporous Materials* **133**, 10-17 (2010).

[8] Wood, S.A., Palmer, D.A., Wesolowski, D.J. & Bénézeth, P. The aqueous geochemistry of the rare earth elements and yttrium. Part XI. The solubility of $Nd(OH)_3$ and hydrolysis of Nd^{3+} from 30 to 290 °C at saturated water vapor pressure with in-situ pH_m measurement. In Hellmann, R. and Wood, S.A., ed., Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David Crerar, Special Publication 7, The Geochemical Society, pp. 229–256 (2002).

[9] Xiong, Y.-L. Thermodynamic properties of brucite determined by solubility studies and their significance to nuclear waste isolation. *Aquatic Geochemistry* **14**, 223–238 (2008).

[10] Whitney, G., 1983. Hydrothermal reactivity of saponite. *Clays and Clay Minerals*, *31*(1), pp.1-8.