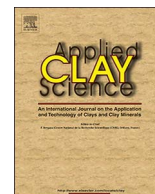




Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Mobility and reactivity of sulphide in bentonite clays – Implications for engineered bentonite barriers in geological repositories for radioactive wastes

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ARTICLE INFO

Keywords:

Asha
Bacteria
Calcigel
Diffusion
Montmorillonite
MX-80
Sulphate
Sulphur

ABSTRACT

Bentonite clays will be used as barriers in geological repositories for radioactive wastes. Anoxic conditions will prevail in such repositories, and the presence of sulphide-producing bacteria in commercial bentonites and deep groundwater environments is well established. In this study, sulphide was found to reduce ferric iron in bentonites denoted Asha, MX-80 and Calcigel under the formation of elemental sulphur, ferrous iron and iron sulphide. These reactions rendered an immobilisation capacity of the clays that was 40 $\mu\text{mole sulphide (g clay)}^{-1}$ or more, depending on the load of sulphide, and type of clay. In addition, the effective diffusion coefficients for sulphide in Asha bentonite, compacted to saturated wet densities of 1750 kg m^{-3} and 2000 kg m^{-3} , were determined to $2.74 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $6.60 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, respectively. The found immobilisation effect can reduce the mass of sulphide that corrode metal canisters over repository life times, but the concomitant reduction of ferric iron may be problematic due to the destabilizing effect of ferrous iron on dioctahedral smectites such as montmorillonites.

1. Introduction

Bentonites rich in swelling montmorillonite are used to construct engineered barriers in geological repositories for low- intermediate- and soon also high-level radioactive wastes. While there are several low- and intermediate-level repositories in operation around the world, high-level repositories are still in planning or under construction. Various types of metal containers, made of iron or copper will be used to encapsulate the wastes. Sulphide is in general corrosive to these metals, and safety cases for radioactive waste disposal must, therefore, evaluate the risks involved with sulphide corrosion (e.g. King et al., 2011). The inorganic reduction of sulphate to sulphide is kinetically hindered at normal pressure and temperature (Cross et al., 2004). The main source of sulphide in geological repository environments is, therefore, past and present microbial reduction of sulphate to sulphide. Sulphide-producing bacteria (SPB) have been found in most commercially available bentonites (Masurat et al., 2010; Svensson et al., 2011), and they frequently occur in deep geological formations and deep groundwater (e.g. Moser et al., 2005; Pedersen et al., 2014). The dissociation constant for $\text{HS}^-/\text{H}_2\text{S}$ is $10^{-6.98}$ (Richard and Luther, 2007). The pH of groundwater in repository environments, and in clay pore water is buffered above 7, which means that sulphide mainly will be

present as HS^- when pH approaches 8 or higher.

Microbial sulphide-producing activity in compacted clays was recently investigated as a function of clay type, saturated wet density, and geomechanical stress (Bengtsson and Pedersen, 2016; Bengtsson and Pedersen, 2017). The registered sulphide-producing activity generally decreased with increasing stress and density. The sulphide-production was analysed as formation of radioactive Cu_2^{35}S on copper discs, and as decrease in concentration of sulphate in pore water. A discrepancy was observed as the decrease in pore water sulphate concentration was larger than the modelled decrease based on the amount of Cu_2^{35}S on the copper discs. It was proposed that the investigated clays, to some extent, immobilised HS^- (Bengtsson and Pedersen, 2016; Bengtsson and Pedersen, 2017). A similar effect was recently observed elsewhere for Wyoming MX-80 clay (Stone et al., 2016). Such effect was also noticed in diffusion experiments where HS^- break-through was delayed compared to what was expected for monovalent anions (Eriksen and Jacobsson, 1982).

Sulphide produced by SPB has been shown to reduce ferrihydrite to ferrous iron in bioreactors (Hansel et al., 2015). The process of anaerobic reduction of ferric iron with H_2S produced by SPB to ferrous iron and S_8 is known to occur in marine (Richard and Luther, 2007), and subsurface sediments (Kwon et al., 2014). This process has been

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Received 20 February 2017; Received in revised form 5 June 2017; Accepted 5 July 2017

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connected to a microbial cryptic sulphur cycle (Holmkvist et al., 2011). In analogy, it can be hypothesized that a similar process can occur in bentonite. That hypothesis was recently tested on illite-smectite minerals, and it could not be falsified (Liu et al., 2012). The results showed that bio-reduction of structural ferric iron to ferrous iron by SPB was positively correlated with the amount of smectite and surface area. Taken together, the above cited literature suggests that sulphide can reduce ferric iron to ferrous iron in bentonites with the concomitant reduction of sulphide to elemental sulphur. It has been demonstrated that dioctahedral smectites are destabilized by ferrous iron (Lantenois et al., 2005). Bentonites to be used in engineered barriers contain ferric iron both in accessory minerals, and to a small extent also in the montmorillonite. If sulphide can reduce ferric iron in bentonite to yield ferrous iron and sulphur, it may explain the observed immobilisation effects described for sulphide in experiments with activity of SPB in compacted bentonites (Bengtsson and Pedersen, 2016; Bengtsson and Pedersen, 2017). Such process may be detrimental to the bentonite due to the destabilizing effect of ferrous iron on montmorillonite (Bradbury et al., 2014; Soltermann, 2014).

In this study, the reactivity of sulphide with ferric iron in suspensions of Wyoming MX-80, Asha and Calcigel bentonite clays in water was studied. The immobilisation of sulphide by the clays, and the formation of ferrous iron and elemental sulphur as a function of sulphide concentration was quantified. In addition, the apparent diffusion coefficients of H^{35}S^- in iron rich Asha bentonite at two saturated wet densities, 1750 and 2000 kg m^{-3} , were determined. Possible implications for engineered barriers in radioactive waste repositories are discussed.

2. Materials and methods

2.1. Bentonites

Three bentonite types were used in the study. They were Wyoming MX-80, Asha and Calcigel which were supplied by Swedish Nuclear Fuel and Waste Management CO. The mineral compositions of these clays were previously characterised in detail (Table 1) (Herbert and Moog, 2002; Karnland, 2010; Sandén et al., 2014). The element composition was analysed with inductively coupled plasma sector field mass spectrometry (ICP-SFMS) after sintering and dissolution in diluted

Table 1

Average results from the XRD analyses of mineral compositions of the MX-80 ($n = 6$), (Karnland, 2010), Asha ($n \geq 5$) (Karnland, 2010; Sandén et al., 2014) and Calcigel ($n = 2$) (Herbert and Moog, 2002) and the element composition of the bentonite materials expressed as weight percent of major element oxides of dry mass after sintering and analysis on ICP-SFMS. LOI denotes the percent mass loss due to ignition. n: number of independent samples.

Component	MX-80	Asha	Calcigel
<i>Minerals</i>			
Montmorillonite	81	82	66
Muscovite	3.4	1.9	14
Plagioclase	3.5	0.82	3
Pyrite	0.6	0.66	0
Quartz	3.0	1.2	8.2
Other	8.5	13.4	8.8
<i>Elements</i>			
SiO_2	61.2	45.5	56.6
Al_2O_3	18.4	16.9	17.8
CaO	1.15	2.85	1.69
Fe_2O_3	4.15	13	6.11
K_2O	0.599	0.128	1.55
MgO	2.02	2.34	2.92
MnO	0.0146	0.112	0.085
Na_2O	1.56	1.3	0.251
P_2O_5	0.0541	0.0954	0.0531
TiO_2	0.148	1.03	0.402
Loss of ignition	5.9	9.5	7

nitric acid (ALS Scandinavia, Luleå, Sweden). MX-80 and Asha are sodium bentonites with five times more Na_2O compared with Calcigel. Asha distinguished from the other clays by a larger amount of iron and Calcigel distinguished from the other clays by a smaller amount of montmorillonite, 66%. MX-80 and Asha bentonites contained approximately 80% montmorillonite.

2.2. Preparation of clay suspensions

The water contents of the clays were determined before the preparation of clay suspensions. Duplicate clay samples were placed in aluminium bowls and heated for 24 h at 105 °C. An average of the weight difference before and after the heating was registered as the water content of each bentonite clay batch and was used to calculate the dry weight in gram of the clays. The water content of the clays were 6.8% for Asha, 8.8% for MX-80 and 8.8% for Calcigel. All clay weights in this paper are dry weights without water.

Clay suspensions were prepared inside an anaerobic box with an atmosphere of 97% N_2 and 3% H_2 , $\text{O}_2 < 1$ ppm (Coy Laboratory Products, Grass Lake, MI, USA). Series of 50 mL glass injection bottles (No 772, Nordic Pack, Nykvarn, Sweden) with 0.5 g of the respective clay were mixed with 17 mL deoxygenated Analytical Grade Water (AGW), sealed with butyl rubber stoppers (Bellco Glass, Inc., Vineland, NJ, US, no. 2048-117800), and crimped with aluminium seals (Bellco, no. 2048-11020). Sealed injection bottles were removed from the anaerobic glove box and immediately evacuated two times down to < 2.0 kPa. The bottles were filled with 120 kPa scientific N_2 between evacuations. Following the second evacuation, bottles were left at 120 kPa.

2.3. Addition of Na_2S

Stock solutions of Na_2S were prepared to give a range of amounts of sulphide per gram clay; from 50 $\mu\text{mol Na}_2\text{S (g clay)}^{-1}$ up to 320 $\mu\text{mol Na}_2\text{S (g clay)}^{-1}$, analysed amounts are given in the results section. The stock solutions were prepared by dissolving $\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$ under N_2 -infusion in 50 mL O_2 -free AGW. When dissolved, the solutions were transferred with N_2 -flushed syringes into O_2 -free 100 mL injection bottles (Nordic Pack, No 1500) that were sealed with butyl rubber stoppers and crimped with aluminium seals. The obtained concentrations of the stock solutions were analysed with CuSO_4 according to Widdel and Bak (1992). Series of injection bottles with clay suspensions and blank injection bottles with only water were added with 1 mL of the respective stock solutions, agitated and left to incubate for 24 h.

2.4. Adjustment of pH with buffer and HCl

The pH of the clay suspensions was adjusted for 24 h after addition of Na_2S with two different methods. A buffer method used a citric acid + Na_2HPO_4 mix to obtain three different pH values in the clay suspensions: pH 7 was obtained by addition of 2 mL buffer with 0.065 M citric acid and 0.872 M Na_2HPO_4 , pH 5 with 2 mL of 0.243 M citric acid and 0.514 M Na_2HPO_4 and pH 2.6 with 2 mL of 0.446 M citric acid and 0.108 M Na_2HPO_4 . A HCl method comprised addition of a 2 M solution of HCl in AGW to reach pH lower than 3 in clay suspensions. However, they were first adjusted to pH 2.6 with the buffer method and then purged for volatile H_2S (see Section 2.5) before further pH adjustment. The injection bottles were agitated after pH adjustment and the pH values were analysed on withdrawn aliquots with a pH meter (Scott, mod. CG 843P, VWR International AB, Stockholm, Sweden) equipped with a Hamilton electrode (Polilyte lab temp DIN, product no 242058/01, Genetec, Sweden).

2.5. Analysis of volatile H_2S

The pH adjusted clay suspensions were left for 24 h before analysis

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