State of Science Review: Natural Organic Matter in Clays and Groundwater

NWMO TR-2014-05 **February 2014**

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ABSTRACT

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Abstract

The Canadian concept for a deep geological repository (DGR) involves multiple barriers to contain and isolate used nuclear fuel, including an engineered barrier system (EBS). One of the major features of the EBS is a 100% highly compacted bentonite clay buffer between the used fuel container and the host rock. Properties of the bentonite buffer include: i) high sorption capacity, which impedes radionuclide movement; ii) low permeability, which inhibits groundwater flow; iii) low water activity, which prevents microbial activity; iv) high swelling capacity, which provides support to the surrounding rock and container; and v) thermal conductivity capable of transmitting heat to the surrounding rock. This report summarizes the current understanding of natural organic matter (NOM) in bentonite clay being considered for use in a DGR and its potential influence on long-term performance. Since groundwater in the repository host rock will saturate the bentonite buffer, the current understanding of NOM in groundwater in crystalline and sedimentary rocks was also reviewed.

NOM in the bentonite buffer is recognized as one of the largest inputs of organic matter into the repository, although the total amount of NOM will be low. Previous studies focusing on characterization of NOM in clays and groundwater are summarized within this report. To date, mostly low-resolution techniques were used to characterize NOM and the information gained did not provide much insight into the composition and potential reactivity of NOM in a repository environment. Two main NOM considerations for a repository have been identified. The first is the potential for NOM in bentonite to serve as a substrate for microbial growth and activity. The second is the potential for NOM in bentonite to form complexes with radionuclides, which could increase or decrease their mobility. To further assess the potential and implications of these processes, application of higher-resolution techniques would provide more detailed information about NOM to determine its structure and potential reactivity.

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1. INTRODUCTION

The Canadian DGR concept for used nuclear fuel involves multiple barriers to ensure the long-term safety of humans and the environment (NWMO, 2005). The multiple protective barriers proposed in Canada’s DGR concept include both naturally-occurring (geologic) and engineered (the used nuclear fuel containers and surrounding clay buffer, seal and backfill materials) components. Overall, the concept entails a network of tunnels and placement rooms located approximately 500 m below ground level in either an appropriate crystalline or sedimentary rock formation, connected by a shaft to the surface. An example of the multibarrier system conceptual design under consideration for a deep geological repository for Canada’s used nuclear fuel is shown in Figure 1.

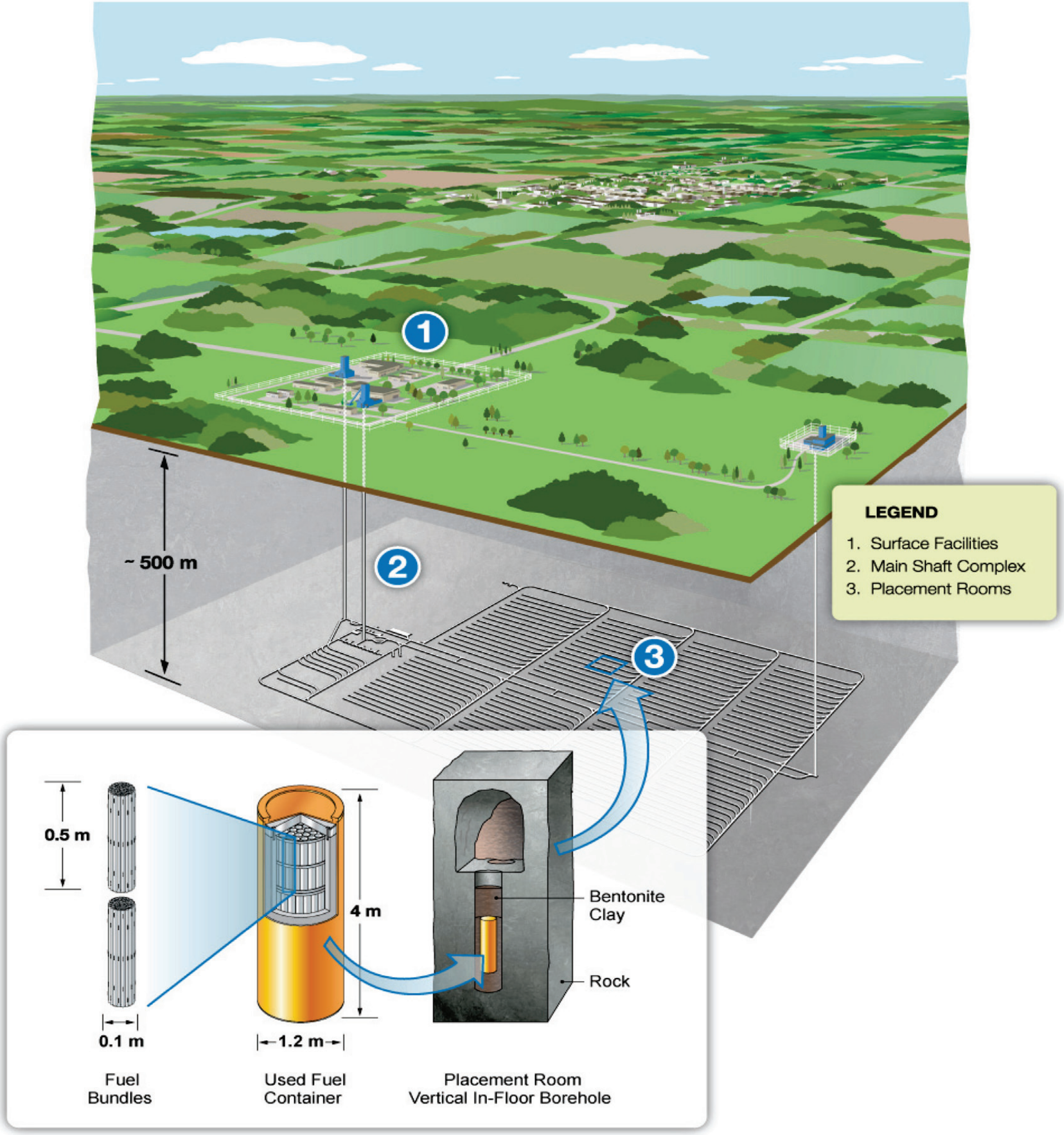

Figure 1: Deep Geological Repository Conceptual Design (Villagran et al., 2011)

The host rock can provide a natural barrier to radionuclide migration via retardation as a result of sorption to mineral surfaces or diffusion into the rock matrix via pores or micro fissures. The current understanding of sorption of radionuclides under the saline conditions expected in a Canadian DGR in crystalline or sedimentary rock is reviewed by Vilks (2009; 2011). The engineered barrier system (EBS) involves the use of a long-lived used fuel container (UFC) surrounded by 100% highly compacted bentonite. The main function of the buffer is to protect the UFC (Karnland, 2010) by preventing infiltration of groundwater (SKB, 2006; Wilson et al., 2011). The ideal buffer material will also support the UFC while having a small pore structure that will minimize microbial activity and promote radionuclide retardation (Kiviranata and Kumpulainen, 2011).

Bentonite clay has been chosen as the buffer material for many DGR concepts. It is primarily composed of montmorillonite, a smectite mineral with negatively charged surfaces and large interlayer spacing (Keto, 2003). These negatively charged surfaces have a high sorption capacity for cationic radionuclides (Bors et al., 1999; Kozai, 1998) although anionic radionuclide mobility will be unaffected. The large interlayer spacing also allows for several layers of water to penetrate between clay units (Hicks et al., 2009) giving the clay a high swelling capacity (Keto, 2003). Even under very high pressure conditions, at least two layers of water will fit within the interlayer space (Grauer, 1990). This will ensure that any gaps around the UFC are filled once the barrier has been in contact with groundwater for sufficiently long to saturate the bentonite clay (Mariner et al., 2011), thereby providing support for the UFC as well as separation from the surrounding environment. Bentonite also has high thermal conductivity once saturated (Ye et al., 2010) as well as being very mechanically stable (Hicks et al., 2009). Furthermore, bentonite can be a self-healing material when the rate of erosion is less rapid than the rate of clay swelling (Mariner et al., 2011). High density bentonite clay will also have sufficiently small pore sizes to discourage unwanted microbial activity in the buffer vicinity (Stroes-Gascoyne et al., 2010). These properties make bentonite an ideal candidate for the buffer material in the DGR.

Physical properties of bentonite including thermal, hydraulic and mechanical properties, swelling ability and cation exchange capacity have been well characterized by the NWMO and other management organizations who are responsible for the disposal of used nuclear fuel (Keto, 2003; Villagran et al., 2011; Wilson et al., 2011). However, not much is known about the composition of the natural organic matter (NOM) associated with bentonite (Hallbeck, 2010). NOM is found ubiquitously in the environment and is the collective term for the group of biologically derived organic compounds at different stages of biological oxidation (Baldock and Skjemstad, 2000). The composition of NOM in bentonite clay may vary depending on the source of the clay. For instance, bentonite clays found in Wyoming were formed during the Cretaceous period while European bentonites were mostly formed later during the Tertiary period (Keto, 2003). MX-80 bentonite mined by the American Colloid Company in Wyoming has long been the reference clay in the Swedish concept for sequestration of used nuclear fuel (Svensson et al., 2011) and is also the main clay being considered by the NWMO (Villagran et al., 2011). However, information regarding NOM composition within other clay deposits is also important for understanding the fundamental variability in composition that can occur both within and between clay deposits. Composition of NOM in the deep groundwater that will eventually infiltrate the repository also requires characterization (Pedersen and Ekendahl, 1990) since it will saturate the bentonite clay barrier.

In this review, we provide an overview of the presence of organic matter expected in the DGR and its potential influence on long-term performance. Previous research conducted to characterize NOM in bentonite and other clays as well as in groundwater is reviewed and recommendations for future work to characterize NOM in clay and groundwater are proposed.

2. THE GEOCHEMICAL SETTING IN THE REPOSITORY

Groundwater in the sedimentary (Michigan Basin) and crystalline (Canadian Shield) rock environments in communities engaged in the Canadian site selection process is expected to be anaerobic and saline at repository depth. Gascoyne et al. (1987) investigated the saline brines found within several Precambrian plutons of the Canadian Shield and identified a chemical transition at around 300 m depth marked by a uniform, rapid rise in total dissolved solids (TDS). For example, pore fluids observed to drain from the unfractured rock matrix in the former AECL underground research laboratory in Manitoba had a TDS of ~90 g/L (Gascoyne, 2004) and salinities greater than 200 g/L as TDS have been documented in Canadian Shield mines (Frape and Fritz, 1982). At depths relevant to the repository, this salinity is mainly due to Ca^{2+}, Na^{+} and Cl^{-} ions (Villagran et al., 2011). As such, high salinity waters may limit the swelling ability of sodium bentonite (Karnland, 1997; Savage, 2005) and thus a restriction has been made by SKB that the Swedish repository will not be built in a location in which the salinity exceeds 100 g/L (Andersson et al., 2000). Due to this restriction, most of the studies concerned with processes occurring in the repository have not considered salinities on the order of 100 g/L. These conditions may be present in the Canadian sites being considered for the repository, and thus testing of the high salinity case is currently ongoing by researchers at the NWMO (Villagran et al., 2011). Similarly, high salinity is expected in porewaters from potential Canadian sedimentary host rocks at repository depth, where elevated total dissolved solids (TDS) of 200 to 400 g/L have been measured (Hobbs et al., 2011; NWMO, 2011).

The presence of NOM in clay is another factor to consider in the DGR. Until recently, organic matter has been defined as being composed of humic and non-humic substances. Non-humic substances include compounds such as carbohydrates, proteins, peptides, amino acids, fats and waxes. Humic substances are operationally defined based on their solubility in acids and bases (Figure 2) and are found in soils and sediments and the atmosphere. Humin is the fraction of humic substances that is insoluble in both acidic and basic solutions. Humic acid and fulvic acid can be separated from humin by dissolution in a basic solution and then further separated by acidifying the resulting solution to precipitate the humic acid (Sparks, 2003). However, a recent review by Schmidt et al. (2011) describes how humic substances are now thought to be composed of organic biomolecules derived from plant, microbial and anthropogenic sources that have undergone varying extents of decomposition. Schmidt et al. (2011) also address the long-term persistence of these compounds in the environment which may be as long as thousands of years. Recalcitrance of NOM in the environment has long been thought to be a chemical process based on the structure of the compounds in question. However, evidence now shows that physical protection of these compounds through processes such as sorption to soil minerals also plays an important role in their environmental persistence (Schmidt et al. 2011).

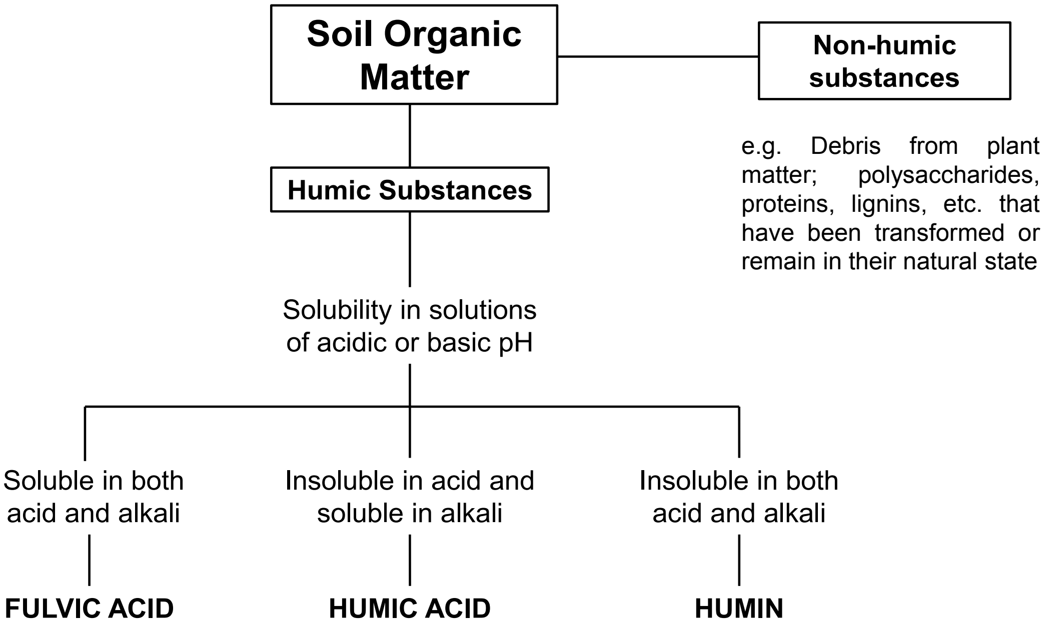

Figure 2: Operational Definition of Organic Matter Components (Adapted from Sparks, 2003)

NOM has been extensively studied in air, water, soils and sediments but not much is known about its composition in clays or in the deep subsurface (Hallbeck, 2010; OECD/NEA, 2012), making its long term behaviour in clays or in the deep subsurface more difficult to predict (Karnland, 2010). In terrestrial environments, clay particles provide many sorption sites for NOM which may stabilise organic matter by offering physical protection against biological attack (Baldock and Skjemstad, 2000). Organic matter sorbs to mineral surfaces through ligand exchange, cation bridging, anion exchange, cation exchange, van der Waals interactions or hydrophobic bonding (Feng et al., 2005). Interactions between NOM and mineral surfaces will depend upon the availability of oxygen-containing functional groups in the organic matter. These interactions will be dependant on pH and have been shown to decrease with increasing pH (Salman et al., 2007).

2.1 POSSIBLE SOURCES OF NATURAL ORGANIC MATTER IN THE DEEP GEOLOGICAL REPOSITORY

The main sources of NOM in the DGR will be introduced during construction of the repository (Humphreys et al., 2010). A summary of the source and composition of these materials is provided in Table 1 (Hallbeck, 2010). The input of organic materials during the construction of the DGR from most of the sources will be unavoidable. The impact from human activities such as tobacco products and urination in the vicinity of the repository can be minimized but other potential sources such as building materials may introduce NOM to the DGR (Hallbeck, 2010).

A recent review of the Swedish repository design identified the buffer and backfill materials as contributing the highest amount of NOM to the repository system (OECD/NEA, 2012). High levels of radiation have been shown to degrade NOM through cleavage of main or side chain bonds in organic macromolecules (Schäfer et al., 2009), potentially releasing smaller organic molecules through this process. Temperatures in the range of 60-90ºC may also cause NOM to be released from bentonite clay (Vilks et al., 1998) thus making it more susceptible to these degradation processes.

Table 1: Summary of Principal Organic Materials that May be Present in the Geological Repository (Hallbeck, 2010)

Category	Source	Organic Materials
Ventilation Air	Seeds	Carbohydrates, proteins, lipids
	Pollen grains	Cellulose, cartinoids, lipids, phylate
	Spores	Similar to seeds and pollen grains
	Dust	A wide array of biomolecules (from living organisms)
Construction Materials	Concrete	Additives will degrade to low molecular weight organics
	Asphalt	Bitumen (from binding agent)
	Bentonite clay	Organic matter (environmental contamination)
	Wood	Cellulose, lignin and tannins
Diesel, Emissions and Other Vehicle Pars	Diesel	Alkanes, polycyclic aromatic hydrocarbons, alkyl-benzenes, unsaturated aliphatic hydrocarbons, sulphur
	Emissions	Incomplete combustion products
	Rubber tires	Polycyclic aromatic hydrocarbons
Human Activities	Tobacco products	Propylene glycol, nicotine, other alkaloids, plant cell wall materials
	Skin and hair	Keratin, protein compounds
	Clothes	Synthetic fibres, cotton
	Urine	Urea, creatinine, ammonia, uric acid, amino acids
	Plastics and paper	Polyethylene terephthalate, polyethylene, polyvinyl chloride, polypropylene, polystyrene, cellulose
Blasting and Rock-drilling	Blasting	Paper and plastic materials, nitrate
	Rock-drilling	Hydrocarbons

2.2 IMPLICATIONS OF NATURAL ORGANIC MATTER FOR THE ENGINEERED BARRIER SYSTEM

Potential processes that can occur within the EBS involving NOM are summarized in the following sections.

2.2.1 Complex Formation of Radionuclides with Natural Organic Matter

Groundwater will eventually saturate and pass through the bentonite barrier, coming into contact with the UFC. One of the functions of the EBS is to sorb radionuclides in the event that they are released from the UFC. Due to the high affinity of negatively charged bentonite interlayers for cations, cationic radionuclides will be sorbed onto bentonite and are not expected to diffuse through the bentonite barrier (Keto, 2003). The anaerobic conditions that are eventually expected to prevail in the repository (Villigran et al., 2011) will enhance adsorption of radionuclides to the bentonite (Mariner et al., 2011). However, the presence of other materials such as NOM in the repository may decrease the ability of the bentonite barrier to sorb radionuclides due to competition for sorption sites. Interaction of radionuclides with materials sorbed to the clay may also have the opposite effect of immobilizing these contaminants.

Dissolved NOM is commonly found in natural waters with concentrations below 1 mg/L to 10 mg/L but may also be present in waters with concentrations of as much as 100 mg/L (Moulin and Moulin, 1995). Water-extractable NOM present in the bentonite clay itself could also contribute to the amount of dissolved NOM in porewater in the vicinity of the used fuel container. Formation of complexes between dissolved NOM and radionuclides can impact radionuclide mobility (Claret et al., 2003; Moulin and Ouzounian, 1992). For the formation of these complexes to occur, sorption of radionuclides to dissolved NOM must occur more readily than sorption to bentonite clay (Wold and Eriksen, 2000). This may be the result of partial saturation of the sorption sites on the bentonite buffer by radionuclides that had been released from the copper canister at an earlier point or by other materials present in the repository.

Sorption of cationic species to components in NOM is dependent upon the available functional groups of NOM. Oxygen-containing functional groups such as carboxyl, hydroxyl and phenolic groups are normally identified as the main binding sites for radionuclides in NOM (Pedersen, 1996). For instance, Schmeide et al. (2011) found that both Am^{3+} and UO_2^{2+} form complexes with carboxyl groups in NOM dissolved in porewater, thereby decreasing sorption of these radionuclides onto clay from the Opalinus formation. As long as the NOM in question remains in solution, these complexes could be released into the surrounding groundwater. Complex formation with dissolved NOM has been widely observed with actinides such as uranium (Moulin and Ouzounian, 1992; Nagasaki, 2001; Vazquez et al., 2008; Mukai et al. 2005) as well as other cations such as copper (Anirudhan and Suchithra, 2010), nickel (Mäkelä and Mannien, 2009) and iron (Ephraim et al. 1990). NOM that does not contain these reactive sites may be transformed through chemical and physical processes that could increase its reactivity with radionuclides. For example, Lehman and Mills (1994) demonstrated that decomposition of dissolved NOM by microbes may produce byproducts capable of forming soluble organometallic complexes with copper that exhibit increased mobility compared to copper alone which could also result in diffusion of these complexes into groundwater.

Sorption of cationic radionuclides such as UO_2^{2+} to bentonite has also been shown to be dependent upon pH and ionic strength of groundwater. An increase in the binding constants of these reactions is observed with increasing ionization of NOM (Olofsson and Allard, 1983). This is because carboxylic and phenolic groups in NOM become deprotonated at high pH and act as binding sites for metal cations (Yoshida and Suzuki, 2006). Because of this, the sorption affinity of bentonite for radionuclides in the presence of NOM may be increased at low pH and decreased at high pH (Nagasaki, 2001; Ren et al., 2010; Wang et al., 2009; Yang et al., 2009). In a study of the sorption of NpO_2^+ to clay in the presence of NOM, a pH of 8 was found to be the turning point where the organic matter started to hinder sorption of NpO_2^+ (Niitsu et al.

1997). The mobility of these organic matter-radionuclide complexes also increases with increasing pH compared to the radionuclides alone (Vazquez et al., 2008). An increase in the ionic strength of the solution decreases the ability of the bentonite clay to sorb radionuclides (Chen et al. 2011; Wang et al. 2009) which may also contribute to an increase in the mobility of these complexes. The pH and ionic strength of the groundwater that penetrates the repository are important factors to consider as they will be capable of changing the interactions of dissolved NOM with both the radionuclides and the bentonite barrier.

The most common anionic radionuclides, $^{129}I^-$ and $^{36}Cl^-$, will not be sorbed to bentonite clay or dissolved NOM in the same way as the cationic species which suggests that they may be much more mobile than their cationic counterparts. However, Lee et al. (2001) have found evidence that there may be some interaction between $^{36}Cl^-$ and the low molecular weight fraction of NOM. They postulate that this may be due to the presence of different functional groups compared to the high molecular weight fraction of NOM (Lee et al., 2001). This theory has not yet been tested and the explanation for this observation is still unknown. The mobility of these complexes through the bentonite clay barrier also has yet to be tested.

It has also been reported that bentonite may act as an effective filter for dissolved NOM (SKB, 2010). Lauber et al. (1998) found that dissolved NOM extracted from clay in concentrations ranging from 0.1–6.11 ppm C as well as dissolved NOM present in the incoming Mont Terri groundwater in concentrations ranging from 10–38.4 ppm C did not reduce the sorption of Eu^{3+} to a cation exchange resin. When using Aldrich humic acid dissolved in water, they observed a decrease in sorption by a factor of approximately 1000 but concluded that the concentration of organic matter found in the clay and groundwater was too low to have the same result (Lauber et al., 1998). Glaus et al. (2005) found that the water-extractable organic matter from clay only slightly decreased sorption of actinides implying that the water-extractable fraction of NOM present in the clay did not effectively sorb radionuclides. Ozaki et al. (2003) studied association of Am^{3+} and Cm^{3+} with biopolymers including cellulose, chitin and chitosan and observed a delay in the migration of these radionuclides. The conflicting results presented so far in the literature do not provide a clear insight into the role of dissolved NOM in the transport of radionuclides in bentonite in the DGR.

Some laboratory studies have reported that dissolved NOM is able to pass through compacted bentonite and that radionuclides may be transported with NOM as complexes (Wold, 2003). Wold and Eriksen (2007) demonstrated an increase in apparent diffusivity of Co^{2+} and Eu^{3+} through compacted bentonite in the presence of dissolved soil humic standard from the International Humic Substances Society. In the field, Kersting et al. (1999) reported the dissolved NOM-facilitated transportation of Pu through groundwater over distances as great as 1.3 km with groundwater flow velocities ranging from 1 to 80 m/yr over a period of 40 years. Radiocesium ($^{137}Cs^+$) has also exhibited increased mobility through clay-rich soils after binding with dissolved NOM in 100 g/L solutions of these soils (Nakamaru et al., 2007).

The studies discussed in this section were generally conducted in low ionic strength conditions. This is not representative of the high salinity groundwater conditions that may be present in a Canadian DGR (Frape and Fritz, 1982; Hobbs et al., 2011). The ionic strength of the groundwater in which these interactions are taking place is an important factor for the complex formation between dissolved NOM and radionuclides. A review of studies using higher salinity conditions by Vilks (2011) found that elements sorbed by coulombic attraction such as Cs^+, Sr^{2+} and Ra^{2+} have reduced sorption in high salinity conditions. Czerwinski et al. (1996) also observed a decrease in the loading capacity of humic acid for actinides with increasing ionic strength. With the presence of other ions such as Na^+ and Ca^{2+} competing with radionuclides for NOM sorption sites, an increase in the concentration of these ions would result in a decrease in the complexes formed between radionuclides and NOM.

2.2.2 Role of Microbes in the DGR

As discussed in Section 2.1, the DGR will not be a sterile environment following construction and emplacement of the used nuclear fuel (Hallbeck, 2010). Microbes may survive in an environment provided that their water, nutrient and energy requirements are met and that they can tolerate the elevated temperature, radiation and salinity conditions (Stroes-Gascoyne and West, 1997). Organic matter present in the repository or in the bentonite clay itself may be available for microbial use provided that it is composed of compounds that are easily broken down by microbes (Oscarson et al., 1986). Microbiological considerations relevant to a DGR for used nuclear fuel are reviewed by Sherwood Lollar (2011) and Wolfaardt and Kober (2012) and summarized here.

Microbial activity in the DGR may lead to microbiologically influenced corrosion of the UFC (Stroes-Gascoyne and West, 1997). In addition, microbial respiration may produce gas bubbles in the clay which have the potential to create preferential pathways for gas and fluid migration in the EBS (Nirex, 2006; Moulin and Ouzounian, 1992; Stroes-Gascoyne and West, 1997). However, it has also been suggested by Yang et al. (2007) that microbes may play an important role in the consumption of dissolved oxygen, a possible corrosion-causing agent in the DGR. Dissolved oxygen may be present in small voids in the buffer and backfill materials and may be consumed by geochemical and microbial processes (Yang et al., 2007). As such, current research has identified both advantages and disadvantages of microbial activity in the DGR and further investigation is required to elucidate the composition of NOM in bentonite clay deposits, and its likelihood to serve as a microbial substrate.

Stroes-Gascoyne et al. (2010) determined that a dry density of 1.6 g/cm^3 is necessary to ensure that the activity of water (the amount of unbound, available water) in the buffer is low enough to inhibit microbial activity. The high density of bentonite, which should limit microbial activity, will also reduce the rate of production of copper sulphide by sulphate reducing bacteria (SRB). A highly salinity (>100 g/L) environment will also suppress most microbial activity (Stroes-Gascoyne et al., 2002) by maintaining the desired low activity of water of <0.96 (Stroes-Gascoyne et al., 2010). Finally, in highly compacted bentonite clay, the voids are not considered to be large enough to allow large populations of microbes to survive (Wilson et al., 2011). Nutrient availability in the DGR is also an important consideration with respect to microbial activity. While a nutrient-poor environment is expected in the DGR host rock (Stroes-Gascoyne and Gascoyne, 1998), construction and operation activities have the potential to introduce organics and nutrients (Hallbeck, 2010; Stroes-Gascoyne and Gascoyne, 1998).

Although the proposed repository conditions should minimize microbial activity in the highly compacted bentonite, it is possible that activity may occur at the interfaces or in areas where the density is not maintained (Stroes-Gascoyne et al., 2011). Analysis of both buffer and backfill materials has identified populations of heterotrophic aerobes, anaerobes and SRB with increased quantities of microbes at interface locations (Stroes-Gascoyne, 2010).

Microbes can also interact with radionuclides causing changes in their mobility. These interactions may include processes such as redox reactions or methylation that change the chemical properties of the radionuclide, thereby varying its mobility. In a more indirect way, microbes can alter redox conditions and produce degradation products through consumption of NOM. Bacteria growing in biofilms may decrease the mobility of radionuclides through adsorption onto cell surfaces, intracellular uptake or via microbially mediated precipitation. These biofilms are not likely to occur in the buffer due to small pore sizes but may be found in interfaces between EBS components, for example between the host rock and backfill (Humphreys et al. 2010; Pedersen et al., 1991).

3. CHARACTERIZATION OF NATURAL ORGANIC MATTER IN CLAY

Characterization of NOM in bentonite clay will provide important information about whether complex formation with radionuclides or microbial activity will occur in the DGR. As mentioned earlier, bentonite clay will be one of the major inputs of NOM into the DGR during emplacement of used nuclear fuel although the total amount of NOM in the repository will be small (Hallbeck, 2010). The research performed to date to elucidate the origin and structure of NOM in bentonite and other clays does not provide all of the information required to make conclusions about the fate of this organic matter in the DGR. This work will be summarized and implications for the repository will be discussed.

3.1 SUMMARY OF PREVIOUS NOM CHARACTERIZATION RESEARCH

Although many countries identify bentonite clay as a potential candidate for the buffer material in their DGR concepts, the majority of studies which focus on NOM in clay are concerned with deposits that are being considered as host rock for a DGR. The Callovo-Oxfordian (COx) clay-rich sedimentary rock formation in France and the Opalinus Clay formation in Switzerland are both being considered as potential host rock for construction of a DGR (Johnson et al., 2002). The host rock in these formations has been the subject of many studies including some characterization of NOM found in these clays.

A summary of studies that have focused on characterizing NOM in bentonite and other clay deposits is provided in Table 2. Most studies have used low-resolution techniques such as ultraviolet-visible spectroscopy (UV/VIS) and Fourier transform infrared spectroscopy (FT-IR) that are useful for elucidating functional groups or relative amounts of humic and fulvic acid in the sample.

Overall, the information provided by these studies indicates that the NOM found in bentonite and other clays has some oxygen-containing functional groups. The presence of these groups indicates that NOM may be able to form complexes with radionuclides. However, the low amount of water-extractable organic carbon relative to the total amount of organic carbon in the clay indicates that much of the NOM in the clays is not removed by extraction with water.

Table 2: Natural Organic Matter in Bentonite and Other Clays

Reference	Sample	Extractant	Extraction Method	Analysis Method	Findings
Vilks et al. (1996)	Avonlea bentonite	DI[1] H_2O or 0.4N NaOH, resin to extract humics	500 g clay in 1500 mL water, shake for 24h then centrifuge	Acid-base titration	Functional groups: carboxylic acids, B-dicabonyls, enols, alcohols, phenolic acids
Lauber et al. (1998)	Opalinus Clay	DI H_2O	S:L[2] ratio of 100 g/L or 1000 g/L, shaken for 7 days then centrifuged	Carbon analyzer, UV/VIS[3]	[DOC[4]] = 4.62 - 18.84 ppm, fraction of humic and fulvic acid
Glaus et al. (2005)	Opalinus Clay	DI H_2O	S:L ratio of 1000 g/L, shaken for 7 days then centrifuged	UV/VIS	Relative amounts of humic and fulvic acid
Claret et al. (2003)	COx argillite clay rock	Biomarker methods			Oxfordian series: terrestrial biomarkers, Callovo series: marine biomarkers
Claret et al. (2005)	Opalinus Clay and COx argillite Clay rock	0.5N NaOH under Ar	International Humic Substances Society protocol	UV/VIS, AFFFF[5], NEXAFS[6]	Functional groups: C=C, phenol, aliphatic, carboxyl, carbonyl
Courdouan et al. (2007)	Opalinus Clay	DI H_2O or 0.1M NaOH or synthetic porewater	S:L ratio of 500 g/L, 1000 g/L, 1500 g/L or 2000 g/L, shake for 1-10 days then centrifuge	TOC[7], LC-OCD[8], HPLC[9] NEXAFS and FT-IR[10]	[DOC]= 3.9 - 8.0 ppm, molecular weight distribution, [acetate]= 203μM, [formate]= 2μM, [lactate]=9 μM, [propionate]=27 μM
Elie and Mazurek (2008)	Opalinus Clay	Hot chloroform	Extraction with hot chloroform, separation of aliphatics and aromatics on silica microcolumn	GC-MS[11] (aliphatic fraction)	Terrestrial biomarkers
Merz (2008)	COx argillite clay rock	DI H_2O or 0.1M NaOH or synthetic porewater	S:L ratio of 500 g/L, 1000 g/L, 1500 g/L or 2000 g/L, shake for 1-10 days then centrifuge	LC-OCD, NEXAFS and FT-IR	Functional groups: acetate, sugars, alcohols, aldehydes, ketones and amino acids

[1] Deionized. [2] Solid to liquid. [3] Ultraviolet-visible spectroscopy. [4] Dissolved organic carbon. [5] Asymmetrical flow field-flow fractionation. [6] Near-edge x-ray absorption fine structure spectroscopy. [7] Total organic carbon. [8] Liquid chromatography-organic carbon detector. [9] High-performance liquid chromatography. [10] Fourier transform infrared spectroscopy. [11] Gas chromatography-mass spectrometry.

3.2 IMPLICATIONS FOR THE ENGINEERED BARRIER SYSTEM

Information about the relative amounts of humic and fulvic acid in the sample is not as important as the composition of either of these fractions. Determining the composition of the natural organic matter present in the clay will provide clues as to whether or not this material is being physically protected through interactions with the clay surface. Protected organic matter will be more difficult for microbes in the buffer vicinity to access. The concentration of dissolved organic carbon extracted from Opalinus Clay was found to be low by Lauber et al. (1998) and Courdouan et al. (2007) relative to the amount of organic carbon in the clay itself. This suggests that the natural organic matter is sorbed to the clay sufficiently strongly that it is not being removed using these water and NaOH extraction techniques. It is encouraging that only a small amount of organic carbon is easily extractable from the clay because this corresponds to the amount of NOM that will not be protected by sorption to the clay surface. However, information about the structure of this organic matter is also needed to further ascertain the potential of NOM to serve as a microbial substrate.

Studies which identified functional groups were able to provide some of the required structural information. Merz (2008) identified small molecules in COx argillite clay rock including acetate and sugars which may be substrates for microbes. The functional group findings from Vilks et al. (1996) do not clarify whether or not NOM found in bentonite clay will serve as a microbial substrate. The oxygen-containing functional groups identified are in agreement with the possibility of physical protection of organic matter by the clay as shown by the low amount of water extractable NOM. These findings may also provide insight into radionuclide transport since these sites have been recognized as preferential sorption sites for radionuclides on NOM (Pedersen, 1996). It can be concluded that these molecules and functional groups will interact with both the clay and radionuclides and may enhance or reduce mobility of radioelements in the repository.

Although some of the findings from previous studies are relevant for processes in the DGR environment, the lack of studies focusing specifically on bentonite clay makes it difficult to draw any conclusions relevant to this buffer material. A recent review of the SKB repository licence application suggested that the lack of knowledge about the composition of NOM in the bentonite clay that will be used as the buffer and backfill is one of the areas that should be improved upon before construction of the repository begins (OECD/NEA, 2012).

4. CHARACTERIZATION OF NATURAL ORGANIC MATTER IN GROUNDWATER

Once emplacement of used nuclear fuel in the DGR is complete and the DGR has been sealed, groundwater from the surrounding area will slowly resaturate the repository. Both shallow and deep groundwaters have been shown to contain some amount of dissolved NOM (Pedersen and Ekendahl, 1990; Sun et al., 1995). This may act as another potential source of NOM in the repository. The composition of NOM in groundwater is also largely unknown and thus it is difficult to determine how it may interact with microbes in the DGR. A summary of the studies done so far to characterize NOM in groundwater is provided, as well as implications for the DGR.

4.1 SUMMARY OF PREVIOUS WORK

NOM found in groundwater may be found in dissolved form, present as particulate matter or in colloidal form (Pedersen, 1996). A summary of NOM characterization in groundwater is given in Table 3. Although the Canadian DGR will be located at a depth of approximately 500 m, not all of the studies presented sampled deep groundwater. The shallow groundwater studies are included to provide a contrast between the characteristics of deep and shallow groundwaters. In general, higher concentrations of NOM were found in shallow groundwater compared to the concentrations found in deeper groundwater. Oxygen-containing functional groups were observed in dissolved NOM in groundwater, as in the case of NOM from clays, indicating potential reactivity between NOM and clay.

Table 3: Natural Organic Matter in Groundwater

Reference	Depth (m)	Location	Rock Type	Method	Findings
Pedersen and Ekendahl (1990)	129 to 860	Äspö, Sweden	Granite	TOC	[DOC] = 0.5 - 9.5 ppm
Sun et al. (1995)	316	Richland, Washington	Pleistocene outburst flood deposits	TOC	[DOC] = 2.1 ppm,
	1270				[DOC] = 0.4 ppm
Pedersen (1996)	6.4 to 105	Franceville, Gabon	Not reported	Isolation on a weak anion exchange resin, TOC, UV[1] and HPLC	Humic fraction, MW[2] distribution, [DOC] = 4 - 14 ppm
Buckau et al. (2000)	216 to 238	Gorleben, Germany	Salt dome	Isolation on XAD-8 resin, TOC	[DOC] = 0.5-184 ppm, [HA[3]] = 0.001-171 ppm, [FA[4]] = 0.13-22 ppm
Hendry et al. (2003)	0 to 43	Southern Saskatchewan	Clay-rich aquitard	FFF[5] with UV, TOC	[DOC] = 9-131 ppm, mostly fulvic acids
Courdouan et al. (2007)	33.9	Mont Terri, Switzerland	Opalinus Clay (porewater)	Isolation on DAX-8 resin, TOC, LC-OCD, HPLC, NEXAFS and FT-IR	[DOC] = 1.2-15.8 ppm, molecular weight distribution, [acetate], [formate], [lactate]
Mahara et al. (2007)	280	Toyama Prefecture, Japan	Sedimentary rock	TOC, isolation on XAD-8 resin, carbon isotope ratio analysis	MW distribution, OM originated from land plants
Mäkelä and Mannien (2008)	85	Onkalo, Finalnd	Granite	Isolation on DAX-8 resin, TOC, SEC-UV[6], HPLC-MS	[DOC] = 6.21-12.28 ppm, molecular size distribution, homologous series low MW humic acids
Caron et al. (2010)	108.3 to 649.7	Canadian Shield	Granite	Fluorescence/EEM[7] technique with PARAFAC[8] routine	Amounts of humic-, fulvic- and tyrosine-like components
Huclier-Markai et al. (2010)	445 to 490 (core)	Meuse Haute Marne, France	COx agrillite (porewater)	ESI-MS[9], APCI-MS[10]	Structual features: fatty acids, aldehydes, amino acids
Mladenov et al. (2010)	8 to 52	Araihazar, Bangladesh	Not reported	TOC, fluorescence/EEM technique with PARAFAC routine	[DOC] = 4.5-7.4. ppm, FI[11] and amino acid-like fluorophores
Szabo and Tuhkanen (2010)	0.8 to 133	Finland	Granite	TOC, HPLC-SEC with UV	[DOC] = 0-11.78 ppm, separation of high, intermediate and low molecular weight compounds
Borraro et al. (2012)	650	Canadian Shield	Granite	Fluorescence/EEM technique with PARAFAC routine	Amounts of humic-fulvic- and tyrosine-like components

[1] Ultraviolet spectroscopy. [2] Molecular weight. [3] Humic acid. [4] Fulvic acid. [5] Field-flow fractionation. [6] Size exclusion chromatography-ultraviolet spectroscopy. [7] Excitation emission matrix spectroscopy. [8] Parallel factor analysis. [9] Electrospray ionization-mass spectrometry. [10] Atmospheric-pressure chemical ionization mass spectrometry. [11] Fluorescence index.

4.2 COMPARISON OF SHALLOW AND DEEP GROUNDWATERS

Both Pedersen and Ekendahl (1990) and Sun et al. (1995) sampled groundwater over a large range of depths. Pedersen and Ekendahl (1990) found a lower concentration of dissolved organic carbon ([DOC]) in deeper groundwaters, as did Sun et al. (1995) who observed 2.1 ppm in a shallow groundwater sample (316 mbgs) and 0.4 ppm in a deeper groundwater sample (1271 mbgs). In the other studies listed in Table 3, groundwater samples were generally from shallower sites and there was considerable variation in the [DOC] even between samples taken from similar depths. In deeper groundwater, there will be a lower input of natural organic matter because the sources of this material are further away. The NOM that is observed at increased depths is also likely to be much older than surface NOM. Long-term diffusive transport of dissolved NOM is observed between shallow and deep groundwaters but this is not a rapid process (Hendry and Wassenaar, 2005).

4.3 IMPLICATIONS FOR THE ENGINEERED BARRIER SYSTEM

As with the characterization of NOM in clays, most of the methods used to study NOM in groundwater focus on concentration. While the DOC concentration allows for easy comparison of shallow and deep groundwaters, the only information it provides regarding the implications for a DGR is that there will likely not be high concentrations of NOM in the groundwater that enters into contact with the bentonite clay. This also means that there will not be much NOM available to form complexes with radionuclides or to be consumed by microbes. However, it is still unclear how NOM will interact with radionuclides and bentonite clay in the DGR due to the lack of NOM structural information. Similarly, amounts of humic and fulvic acid do not provide information on structure. The molecular weight distribution may provide some insight into the concentration of small molecular weight compounds but any conclusions drawn from this information would be purely speculative due to the lack of structural information.

As with the clays, some structural features have been elucidated (Hucklier-Markai et al., 2010) and concentrations of a few low molecular weight organic acids have been determined in groundwater samples (Courdouan et al., 2007). Once again, not much information is available regarding potential microbial usage but complex formation may occur between radionuclides and oxygen containing functional groups or organic acids. Considering that these organic acids are already dissolved in groundwater, the mobility of radionuclides in complexes with organic acids will likely be increased. In the study by Mäkelä and Mannien (2008), organic acids were found in groundwater from granite rock which could be analogous to groundwater from the Canadian Shield. However, this study focused on samples collected at a depth of 85 m and the results may not be comparable groundwater from a depth of 500 m, because lower concentrations are expected at greater depths, as stated above. Borraro et al. (2012), Caron et al. (2010) and Mladenov et al. (2010) used fluorescence/excitation emission matrix spectroscopy with parallel factor analysis to study natural organic matter in groundwater. The amino acid-like fluorophores observed by Mladenov et al. (2010) at depths of 40-52 m are indicative of material that may be bioavailable (Fellman et al., 2010) and could provide a microbial substrate in these shallow groundwaters. Caron et al. (2010) demonstrated a change in the composition of dissolved NOM in groundwater taken from the Canadian Shield with changing groundwater depth. Groundwater from depths of 620-650 m was found to have less humic- fulvic- and tyrosine-like components than shallower waters. However, the presence of tyrosine-like components at depth (Borraro et al., 2012; Caron et al., 2010) indicates that there is likely some bioavailable organic matter at depths relevant to a DGR which could potentially act as a substrate for microbes in a repository.

5. CONCLUSIONS AND RECOMMENDATIONS

The presence of NOM in the DGR may enhance or impede radionuclide mobility or may provide a substrate for microorganisms in the repository. The composition of NOM in bentonite clays and in Canadian groundwaters has not been fully elucidated. Low-resolution techniques such as UV/VIS and DOC measurements have been used so far to attempt to characterize organic matter. The information provided by these methods does not offer much insight into the fate of this organic matter and how it may alter processes in the repository.

High-resolution molecular-level techniques could be used to characterize NOM in bentonite clays under consideration for use in a DGR. Gas chromatography coupled with mass spectrometry and nuclear magnetic resonance spectroscopy are techniques capable of providing high-resolution information about the structure and composition of NOM (Feng and Simpson, 2011; Simpson et al. 2008). Information determined using these techniques will likely be useful for determining the fate of NOM in the DGR and its potential use as a microbial substrate. In addition, NOM characterization studies could provide information about the relationship between organic and clay components in bentonite. This could provide information that can compliment ongoing radionuclide sorption work (e.g. Vilks et al., 2011), by identifying if the organic matter contains functional sites conducive to radionuclide sorption.

Groundwater and/or porewater from the host rock will eventually saturate the bentonite clay barrier and the repository. Groundwater samples will be collected as part of detailed site characterization activities for a DGR, and analysis of the composition and concentration of NOM in these groundwaters would provide information about its lability and potential to serve as a microbial carbon source. However, dissolved organic carbon concentrations will likely be low in deep groundwater and may require concentration steps prior to analysis, and therefore, some method development will likely be required.

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