



Determining redox properties of clay-rich sedimentary deposits in the context of performance assessment of radioactive waste repositories: Conceptual and practical aspects

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Radioactive substances and ionizing radiation are used in medicine, industry, agriculture, research, education and electricity production. This generates radioactive waste. In the Netherlands, this waste is collected, treated and stored by COVRA (Centrale Organisatie Voor Radioactief Afval). After interim storage for a period of at least 100 years radioactive waste is intended for disposal. There is a world-wide scientific and technical consensus that geological disposal represents the safest long-term option for radioactive waste.

Geological disposal is emplacement of radioactive waste in deep underground formations. The goal of geological disposal is long-term isolation of radioactive waste from our living environment in order to avoid exposure of future generations to ionising radiation from the waste. OPERA (OnderzoeksProgramma Eindberging Radioactief Afval) is the Dutch research programme on geological disposal of radioactive waste.

Within OPERA, researchers of different organisations in different areas of expertise will cooperate on the initial, conditional Safety Cases for the host rocks Boom Clay and Zechstein rock salt. As the radioactive waste disposal process in the Netherlands is at an early, conceptual phase and the previous research programme has ended more than a decade ago, in OPERA a first preliminary or initial safety case will be developed to structure the research necessary for the eventual development of a repository in the Netherlands. The safety case is conditional since only the long-term safety of a generic repository will be assessed. OPERA is financed by the Dutch Ministry of Economic Affairs and the public limited liability company Electriciteits-Produktiemaatschappij Zuid-Nederland (EPZ) and coordinated by COVRA. Further details on OPERA and its outcomes can be accessed at www.covra.nl.

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Summary

Redox reactions play a key factor controlling the mobility of redox sensitive radionuclides in clay-rich sediments which might serve as host formations for radioactive waste repositories. Assessing the redox speciation of radionuclides requires information about the redox conditions in the formation and the electron transfer kinetics between the redox active constituents in the sediment and the radionuclides.

Clay-rich sediments, like most natural systems, are usually not in redox-equilibrium when they received sufficient organic material during deposition to enforce anaerobic conditions during early diagenesis. Consequently, any derived redox potential (E_h) to characterize the conditions in the formation should include an evaluation about which half reactions were probed by the used technique or indicate for which half reaction(s) the value was calculated.

Conventional E_h measurements, performed with an inert electrode in the pore water retrieved from clay-rich sediments, are unlikely to provide meaningful values. This is due to the intrinsic limitations of this technique to probe the redox potential of environmentally relevant dissolved constituents and because many redox reactions in clay-rich sediments involve solids. Electrochemical techniques which probe the redox properties of solids in aqueous suspensions or in salt matrix are promising alternatives but their applicability in clay-rich sediments still has to be tested. When these techniques live up to the expectations, their application in combination with geochemical characterization and thermodynamic calculations might be the most reliable approach to constrain the E_h of redox active constituents in clay-rich sediments.

A large variety of redox active species of the elements H, O, N, C, Fe, Mn and S might be present in clay-rich sediments. A straightforward approach to obtain E_h values for various redox couples in the sediment is to use thermodynamic calculations in combination with a rigorous geochemical characterization of the sediment. However, not for all redox active species, which are of possible importance for controlling the redox states of radionuclides, reliable thermodynamic data are available. This is in particular the case for structurally bound Fe in clay minerals, organic matter, and secondary minerals formed during early diagenesis or after burial.

The role of many of these redox couples for redox transformations of radionuclides has been experimentally investigated under environmentally relevant conditions. Examples for different reactions are compiled in this report. In general, the reduction of oxidized species of U, Se, and Tc by reduced species of Fe, S, and C in the absence or presence of microbial mediation have been frequently studied. Studies on transuranium elements, other redox sensitive radionuclides, and the oxidation of radionuclides are more rare.

Information about the kinetics of redox reactions between radionuclides and the oxidized or reduced species of redox sensitive major elements in the formation should be used to interpret the E_h value(s) obtained for one or more redox couples in the formation. An E_h value obtained for a redox couple in the sediment is only of relevance for predicting the redox state of a radionuclide when the time scale of the redox reaction is shorter than the half-life of the radionuclide and the residence time of the radionuclide in the formation. Often, redox reactions between radionuclides and redox active constituents of the clay-rich sediment only proceed rapidly in one direction while the reaction in opposite direction is kinetically hindered. In this case, the E_h derived for a redox couple in the sediment should only be used as an upper or lower limit to constrain the redox speciation of the radionuclide of interest.

As a general conclusion, it can be stated that while clay-rich sediments in many cases are considered to be reducing, the exact redox potential, the *in situ* activity of the various redox couples, and their effect on redox sensitive radionuclides are less evident. This frequently results in pragmatic and stylised approaches when transferring phenomenological knowledge to safety assessment calculations.

Samenvatting

Ondergrondse kleilagen kunnen mogelijk dienen als gastgesteente voor eindberging van radioactief afval. In deze kleirijke sedimenten spelen redoxreacties een belangrijke rol bij de mobiliteit van redox-actieve radionucliden. Om de redoxspeciatie van de radionucliden te achterhalen, is er informatie nodig over de redoxcondities in de kleiformatie en over de kinetiek van de elektronenoverdracht tussen de redox-actieve bestanddelen in het sediment en de radionucliden.

Om de redoxcondities in een systeem te karakteriseren wordt vaak een redoxpotentiaal (E_h) aangegeven. Echter, kleirijke sedimenten zijn meestal niet in redox-evenwicht wanneer tijdens depositie voldoende organisch materiaal is afgezet om anaerobe omstandigheden voort te brengen tijdens de vroege diagenese. Daarom is het belangrijk dat bij een berekende of gemeten E_h ook aangegeven wordt welke halfreacties met de gebruikte techniek gemeten kunnen worden of voor welk halfreactie(s) de waarde was berekend.

E_h metingen, uitgevoerd met een conventionele inerte elektrode in poriewater onttrokken uit de kleirijke sedimenten, geven meestal weinig inzicht in de redoxcondities in het systeem. Dit komt door de intrinsieke beperking van deze techniek om het E_h van vele opgeloste bestanddelen te meten en omdat in kleirijke sedimenten veel redoxreacties vaste stoffen omvatten. Elektrochemische technieken die de redox eigenschappen van vaste stoffen in waterige suspensies of in een zoute matrix meten, zijn veelbelovende alternatieven. Hun toepasbaarheid in kleirijke sedimenten moet echter nog worden onderzocht. Wanneer deze technieken voldoen aan de verwachtingen, kan de toepassing ervan, in combinatie met de geochemische karakterisering en thermodynamische berekeningen, de meest betrouwbare aanpak zijn om de E_h van redoxactieve bestanddelen in klei-rijke sedimenten te bepalen.

Een grote verscheidenheid aan redoxactieve species van de elementen H, O, N, C, Fe, Mn en S kunnen aanwezig zijn in kleirijke sedimenten. Een directe benadering om E_h -waarden van verschillende redox koppels in het sediment te verkrijgen, is het gebruik van thermodynamische berekeningen in combinatie met een grondige geochemische karakterisatie van het sediment. Echter, niet voor alle redoxactieve complexen, die mogelijk van belang zijn voor het bepalen van de redoxtoestand van de radionucliden, zijn betrouwbare thermodynamische gegevens beschikbaar. Dit is met name het geval voor structureel gebonden Fe in kleimineralen, organisch materiaal, en secundaire mineralen gevormd tijdens de vroege diagenese of net na begraving.

De rol van veel van deze redoxkoppels voor de redoxtransformaties van radionucliden werd in experimenteel onder relevante omstandigheden aangetoond. Voorbeelden van verschillende onderzochte reacties tussen radionucliden en redoxactieve bestanddelen in kleirijke sedimenten zijn samengevat in dit rapport. De reductie van geoxideerde species van U, Se en Tc door gereduceerde species van Fe, S en C in de af- of aanwezigheid van microben is veelvuldig onderzocht. Onderzoek over transuraan elementen, andere redoxactieve radionucliden, en over de oxidatie van radionucliden zijn zeldzaam.

Kennis over de kinetiek van redoxreacties tussen radionucliden en de verschillende species van redoxactieve hoofdelementen in de formatie kan gebruikt worden om E_h waarde(n) van redoxkoppel(s) in the sediment te interpreteren. Een E_h waarde is alleen relevant voor het voorspellen van de redox toestand van een radionuclide wanneer de tijdschaal van de redoxreactie korter is dan de halfwaardetijd van de radionuclide en de verblijftijd van het radionuclide in de formatie. In veel gevallen is het zo dat bij redoxreacties tussen de radionuclide en de redoxactieve bestanddelen van een element in kleirijke sedimenten de reactie uitsluitend in één richting snel verloopt, terwijl de reactie in tegengestelde richting kinetisch wordt verhinderd. In dit geval moet de E_h die voor één redoxkoppel in het sediment is bepaald, alleen gebruikt worden als een boven- of ondergrens om zo de verschillende opties voor redoxspeciatie van radionucliden te beperken.

Als algemene conclusie kan gesteld worden dat, hoewel kleirijke sedimenten vaak worden geacht reducerend te zijn, de exacte E_h , de in-situ werking en activiteit van de verschillende redox koppels, en hun effect op redox gevoelige radionucliden minder duidelijk zijn. Dit resulteert vaak in een pragmatische en gestileerde aanpak bij het toepassen van fenomenologische kennis bij berekening in de context van een safety assessment.

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1. Introduction

The redox potential is integral part of the pore water chemistry in the host formation. Pore water chemistry is of central interest when evaluating the evolution of the engineered barriers and the retention of any escaping radionuclides. Pore water chemistry and mineralogy affect, among other things, the sorption and retardation potential of the host formation (NAGRA, 2010)

1.1. The importance of redox speciation for radionuclide mobility

This report reviews conceptual and analytical aspects of assessing the redox properties of clay-rich sedimentary deposits. Clay-rich sedimentary deposits are potential host formations for radioactive waste repositories. The redox properties of the formation, including redox potential (E_h), electron donating capacity (EDC) and electron accepting capacity (EAC), are relevant for predicting the speciation, and by this, the mobility of radionuclides possibly entering the host rock. Knowledge of the redox properties is also important to assess the capacity of the host formation to reduce or oxidize intruding redox active constituents, and, by this its capacity to retard the progression of redox fronts.

When the redox state of a radionuclide changes, the coordination chemistry of the element in aqueous solution can be influenced and its tendency to form solids or to interact with solid surfaces can be altered. For example, selenium (Se) can feature redox states ranging from VI to -II in natural environments (Fig. 1). Selenium, in the oxidation states VI and IV, occurs as selenate and selenite, respectively. These oxyanions are relatively mobile in clay-rich sediments due to the electrostatic repulsion between anions and clay minerals with structural negative charge. The most important retardation mechanism of Se(IV) and Se(VI) in argillaceous sediments is considered to be the formation of inner sphere complexes at the surface of silicates and metal oxides. In its elemental form, Se(0) has a low solubility and can form eigencolloids. When Se is reduced to Se(-I) or Se(-II), it can precipitate with ferrous iron (Fe(II)) as, for example, FeSe, FeSSe or FeSe₂.

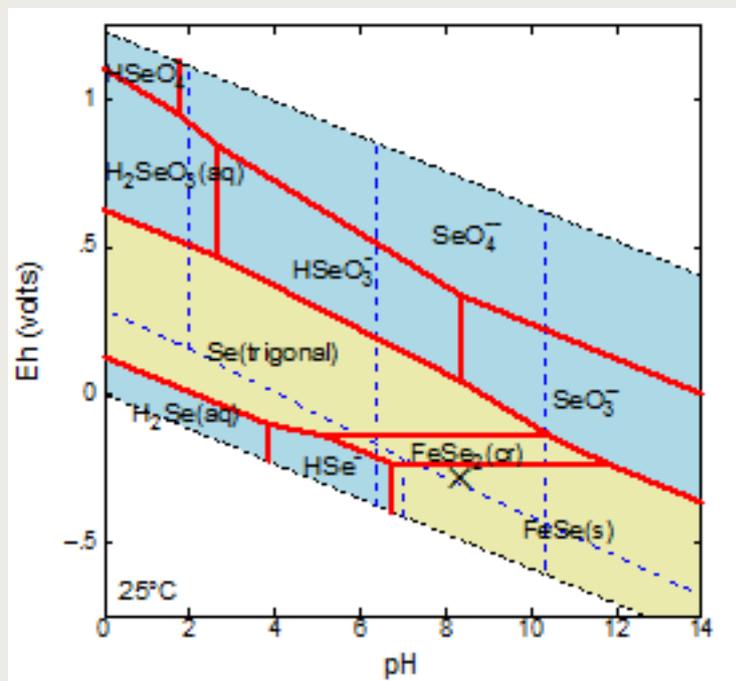


Figure 1: Eh-pH diagram of selenium (Se-C-S-O-H) for a reference Boom Clay pore water system (geochemical conditions reflect present-day Boom Clay in Mol area). Assumed activities of dissolved [Se] = 10^{-8} and [Fe] = 2.2×10^{-7} . MOLDATA TDB (Salah and Wang, 2014) , ER-198, Speciation and solubility calculations for waste relevant radionuclides in Boom Clay, 154 pp)

1.2. Assessing the redox speciation of radionuclides in the clay-rich host rock

Equilibrium thermodynamics provide a basis for predicting the chemical speciation of a radionuclide in the host formation surrounding the repository. When the physicochemical properties of the formation are known, the thermodynamically most stable species of the element of concern can be identified if the required thermodynamic constants are available. Stability or predominance diagrams indicate the most important chemical species at given pH and E_h when thermodynamic equilibrium is achieved. Figure 1 shows exemplarily a general stability diagram for Se.

The validity and applicability of this approach for predicting the redox speciation of radionuclides in clay-rich host rocks is challenged for several reasons. A prerequisite of performing thermodynamic calculations is the availability of a reliable and representative E_h . However, assessing a redox potential in clay rich sedimentary deposits can be problematic for three major reasons:

- The different redox active constituents of the formation are likely not in thermodynamic equilibrium with each other.
- Direct measurements might be biased when the probe is insufficiently sensitive towards the redox active constituents.
- Deducing the E_h from the chemical and mineralogical composition of the sediment could be limited due to the lack or uncertainty of thermodynamic properties.
- Measurements, however accurate and reliable, might suffer from oxidising perturbations on (samples of the) host formation which are very difficult to avoid, both *in situ* and under laboratory conditions.

The second source of difficulty is the potential kinetic hindrance of redox reactions between radionuclides and the host rock components. That is, even when the E_h of the redox active constituents of the clay-rich sediment can be determined, it is not certain whether the redox speciation of a radionuclide represents equilibrium at the given E_h value.

1.3. Outline of the report and objectives

First, the redox sensitivity of radionuclides in the anticipated waste will be evaluated. In the following, general aspects regarding redox equilibrium in clay-rich sediments and the kinetics of redox processes will be presented. In the third chapter, the relevance of the main redox couples for controlling the redox properties of clay-rich sediments and their interaction with radionuclides will be discussed. This chapter also provides an overview about studies on clay-rich formations which are investigated in the context of nuclear waste disposal. Finally, different approaches for assessing the E_h in clay-rich sedimentary deposits will be reviewed and evaluated in terms of the goal to predict the redox speciation of radionuclides.

The aim of the report is to provide an assessment of different approaches to determine redox conditions in subsurface environment regarding their strength and limitations in view of using the determined values to predict the redox speciation of radionuclides in clay-rich host rocks of nuclear waste repositories.

The issues related to determine redox conditions in geological formations has been frequently addressed in the context of the safety of nuclear waste repositories. The FP 7 EURATOM Collaborative Project “Redox Phenomena Controlling Systems” (RECOZY 2008-2012) was dedicated to the role of redox reactions in performance assessment. Within this collaboration, the determination of redox potentials, redox properties of the far field, and redox transformations of radionuclides were investigated. An overview of the documentation of the results can be found at <http://www.recosy.eu>.

The issue of characterizing redox conditions in subsurface systems is broached in many subfields of Earth Sciences including geochemistry, environmental sciences, hydrology, and sedimentology. The book *Redox: Fundamentals, Processes and Applications* (Schüring, et al, 2000) is devoted to determining redox conditions in natural environments with emphasis on subsurface systems. It is widely recognized that E_h values measured with standard redox electrodes in natural waters are only of very limited value for inferring the redox speciation of elements in the system and to derive

information about ongoing redox processes. Several complimentary or alternative approaches have been proposed and applied, particularly in the context of groundwater quality protection. A comprehensive review about characterizing redox properties in groundwater contaminant plumes, which applies for groundwater systems in general, has been given by Christensen et al. (2000). The challenges of evaluating the redox properties of aquifer systems and clay-rich sediments are comparable. However, the use of approaches which rely on the extraction of pore water or on active microbial communities (e.g. measurement of H₂, or characterization of microbial community, see section 3) is hampered in consolidated clay-rich sediments due to the difficulties of retrieving undisturbed pore water and the restricted microbial activity.

2. Redox sensitive radionuclides in anticipated waste based on the OPERA disposal concept

About half of the radionuclides expected in the radioactive waste in the Netherlands and listed in Table 1 has more than one dominant redox state within the stability field of water based on thermodynamic considerations. The upper and lower limits of the stability field of water in E_h / pH diagrams is usually defined by the redox potentials of water in equilibrium with O₂ and H₂ gas, respectively, with a pressure of 1 bar. However, it cannot be excluded that radionuclides could enter the host rock in an oxidation state which is thermodynamically only predominant at E_h / pH conditions outside the stability field of water. This could be the case when radionuclides occurred in the waste in this redox state, or when they are exposed to strong oxidants or reductants in the near-field. The latter could include reaction by peroxide formed during the radiolysis of water or elemental iron in steel containers.

Table 1 only provides an indication about the redox sensitivity of radionuclides in the anticipated waste considered for disposal in 2130 according to the OPERA concept. For detailed studies on the stability of redox sensitive elements as a function of pH, E_h, radionuclide concentration and solution composition, calculations with geochemical models are required. For a series of elements the NEA has published state-of-the-art reports on available thermodynamic data which are available online (<http://www.oecd-nea.org/dbtdb/info/publications/>). Evaluated thermodynamic data for also available via other sources, for example the PSI-NAGRA database (Thoenen et al. 2014). Table 1 only lists elements with radioactive isotopes characterized by a half-life of more than 10 years which are expected in the waste. The listed oxidation states were derived from E_h / pH diagrams calculated for aqueous solution at 298 K and 1 atm pressure in the absence of other ligands, potentially stabilizing the elements in one or other oxidation state, than those occurring in pure water (O²⁻, OH⁻, H₂O). The E_h / pH diagrams used for this purpose were obtained from two sources: *The Aqueous Chemistry of the Elements* (Schweitzer and Pesterfield, 2010) and the *Atlas of Eh-pH diagrams* (Takeno, 2005). For many redox sensitive elements, the appearance of the stability diagrams differs significantly depending on the way they were derived. Among other factors this is due to differences in the used thermodynamic data bases (Takeno, 2005). Whether or not a specific redox species of an element appears in the stability diagrams and what dimensions a predominance field has also depends on the total concentration of the element and the way how the calculation was performed (Kinniburgh and Cooper, 2004). Furthermore, the stability diagram only shows the predominant species at the given conditions. An element might naturally occur in other oxidation states than listed in Table 1. This oxidation state might only be thermodynamically metastable or only represent a minor fraction of the total concentration of the element when thermodynamic equilibrium is achieved.

Table 1. Redox sensitivity and dominant oxidation states of elements with radioactive isotopes expected in the waste according to the OPERA disposal concept. The table is based on table 6.1 in the OPERA report OPERA-PU-NRG1112A.

Element	Redox sensitive	Dominant oxidation state(s) within the stability field of water*
H	X	0, +I
Be		+II
C	X	-IV until +IV

Si		+IV
Cl		-I
Ar		0
K		+I
Ca		+II
Ti	(X)	+IV (+III)*
Ni	(X)	+II , (0, +III)
Se	X	-II, 0, +IV, +VI
Kr		0
Sr		+II
Zr		+IV
Nb		+V
Mo	X	+VI, +IV,(+III)
Tc	X	+VII, +IV, (+III, +II, +I) 0
Pd	X	+II, 0
Ag	X	+I, 0
Cd		+II
Sn	(X)	+IV, (+II)
I	X	+V, 0, -I
Cs		+I
Ba		+II
Sm		+III
Eu		+III
Ho		+III
Re	(X)	+VII, (+IV, +III, 0)
Pb	X	(+IV), +II, 0
Bi	X	+III, 0
Po	X	+IV, (+II), 0
Ra		+II
Ac		+III
Th		+IV
Pa		+V
U	X	+IV, +VI
Np	X	+III, +IV, +V
Pu	X	+VI, +V, +IV, +III
Am	X	+III, +IV
Cm	(X)	+III, (+IV)
Cf		+III

*Values in parenthesis indicate oxidation states which are not consistently found in the predominance diagrams or are only predominant at conditions at the limits of the stability field of water or at pH values below 2 or above 12.

When referring to “radionuclides” in the following, the term includes the radioactive isotopes of the elements listed in Tab. 1 with the exception of H and C. Carbon and hydrogen are redox sensitive major elements and are separately addressed in section 3 when discussing the redox speciation and reactivity of major redox sensitive constituents in clay-rich sediments. With the exception of the actinides, most elements listed in Table 1 are found in nature in the form of one of the stable, non-radioactive, isotopes. Our current knowledge of the fate of these trace elements in natural environments is based on field observations or experiments, which were predominately performed with the stable isotopes. Only exceptionally, radioactive isotopes are used in experiments for studying their interactions with sediments or soils. The biogeochemical behaviour of elements is practically the same for the different isotopes and the fractionation in natural processes is only very small. Hence, when discussing the relevance of redox transformations of radionuclides in the following, the assessment is based on the assumption that the radioactive isotopes of the trace elements listed in Table 1 behave identically to the corresponding stable isotopes

3. Thermodynamic equilibrium and kinetics of redox reactions in sedimentary systems

The redox potential is a numerical index of the intensity of oxidising or reducing conditions within a system. It is the potential, expressed as E_h in volt or millivolt, developed by a redox reaction involving transfer of electrons. The subscript “h” implies that the potential is relative to the standard potential of hydrogen (H_2/H^+) electrode (SHE). Another widely used concept equivalent to the redox potential is pE, defined as the negative logarithm of the electron activity:

$$pE = -\log\{e^-\}$$

The value of pE can be related to E_h at 25 °C and 1 atm pressure as:

$$pE = \frac{FE_h}{2.303 RT}$$

where F is the Faraday’s constant (96,485 C mol⁻¹), R the gas constant (8.314 J mol⁻¹ K⁻¹), and T the absolute temperature in kelvin.

3.1. Prevalence or absence of redox equilibrium in clay-rich sediments

The use of E_h as a master variable in natural systems is limited as biological activity can perturb redox equilibria and because electron transfer can be kinetically hindered. The energy metabolism of all known life forms on earth is based on redox reactions. This implies that redox disequilibrium is an inherent characteristic of the biosphere, which extends from the troposphere several thousand meters deep into the earth’s crust (Colwell and D’Hondt, 2013).

Via photosynthesis, light energy is converted and preserved as chemical energy in the form of creating a redox disequilibrium. That is, photosynthesis creates simultaneously highly reduced compounds (e.g. organic matter) and highly oxidized compounds (e.g. oxygen). During sedimentation, organic matter is buried together with dissolved oxygen in the pore water or other oxidized species which are formed in the presence of free oxygen. Biological activity in the sediments then leads to the oxidation of organic matter coupled to the consumption of oxidants which were produced as a result of photosynthesis. During early diagenesis, consumed oxidants, and to a lesser extent organic matter, can be replenished from the overlying water via diffusive and other mixing processes. This exchange with the overlying water column becomes more and more restricted when the sediment is buried into deeper layers. When a sedimentary deposit becomes isolated from its surrounding, spontaneous redox processes will advance the system towards equilibrium. As a consequence, the redox potentials of the different redox active constituents will converge towards an equilibrium value. However, after a sedimentary deposit has become isolated, thermodynamic equilibrium might not be reached within geological time scales and the biological signature in the form of redox disequilibria can be preserved for millions of years in sedimentary rocks. During early diagenesis, redox reactions can lead to relatively high electron fluxes but with

time redox reactions typically decelerate. One reason for the slowdown of the progression towards equilibrium is the decrease of reactivity of natural organic matter with progressing degradation (Middelburg, 1989). Another reason is that the potential energy gain of redox reactions decreases towards equilibrium. This limits the growth of a microbial community mediating the redox reactions eventually leading to lower numbers of metabolically active microorganisms.

Consolidated redox conditions in sediments can be perturbed due to input of photosynthesis products from the earth's surface (e.g. oxygen or organic matter) but also upon influx of compounds of geogenic origin, such as methane, and of anthropogenic origin, such as atmospheric oxygen introduced while constructing and operating galleries. Provision of geogenic compounds can fuel biological activity in the deep underground which is completely independent from photosynthesis and its products (Pedersen, 1997).

The distance from equilibrium and the required electron exchange to achieve equilibrium in freshly deposited sediments are a function of the fluxes of oxidants and reductants at the sediment boundary layer. Clay-rich sediments can be of lacustrine, riverine, estuarine, or marine origin. With the exception of deep sea sediments deposited in remote parts of the oceans, the flux of organic carbon is sufficiently high in comparison to the benthic fluxes of dissolved oxidants so that the buried organic matter does not become completely mineralized during early diagenesis. Hence, clay-rich sediments formed in sedimentary basins close to continental coasts, such as the Boom clay, are typically depleted in strong oxidants such as O_2 and NO_3^- and most of the reactive iron occurs in the form of Fe(II) when being buried. Microbial sulphate reduction can lead to complete sulphate depletion in sediment pore waters permitting methanogenesis to become the dominant organic matter degradation pathway in deeper parts of the sediment (Jorgensen and Parkes, 2010). The major elements O, N, Fe, Mn, and S are expected to occur in these sediments predominately in their reduced form. However, local redox inhomogeneities and post-burial alterations by intruding oxidants can cause the occurrence of oxidized forms of the listed elements in the clay-rich sedimentary formation.

In contrast to clay-rich sediments close to the continents, the organic matter flux into pelagic sediments can be so low that organic matter degradation does not lead to anaerobic conditions. When eolian input is the dominant mineral source this leads to the formation of 'red clays' or 'brown clays' (Glasby, 1991). The colour is indicative for the redox state of iron. Red and brown colours indicate the presence of Fe(III) while black, greyish, bluish colours denote the predominance of Fe(II). Red clays, which are poor in organic matter content and deposited under aerobic conditions, might not display pronounced redox disequilibria and one E_h value could be sufficient to characterize the redox state of the sediment constituents.

In contrast, the coexistence of redox couples in disequilibrium with each other might be the common situation in clay-rich sediments which received high organic matter deposition. As a consequence of displacement from thermodynamic equilibrium, different redox potentials can be derived even for only one element. For example, iron (hydr-)oxides with different thermodynamic stability are often found contiguously in natural environments. Consequently, the calculated E_h value of Fe(III)/Fe(II) redox couples is different depending on which iron (hydr-)oxide is used in the calculation to constrain the Fe^{3+} activity.

With prevailing redox disequilibrium, assigning one E_h to the whole system without constraints is not meaningful. In the context of safety assessment, it needs to be assessed to which redox couple(s) a reported E_h value applies. In the next step, relevant E_h values can be selected based on the interaction of the related redox couples with the radionuclides of interest. With this information, the likely redox state of the radionuclide in the far field can be evaluated.

It cannot be excluded that radionuclides can readily exchange electrons with different redox active constituents in the clay-rich sediment which are not in redox equilibrium with each other. This could be the case when the redox reaction among these constituents is kinetically hindered or is caused by spatial separation. In such a situation, the redox state of the radionuclide can change continuously and the radionuclide can serve as an electron shuttle. For example, the possible role of uranium as a redox shuttle between metal reducing bacteria and iron oxides has been proposed by Nevin and Lovely (2000). The redox cycling of the radionuclide will eventually come to rest when the other involved redox couples reach equilibrium. The latter usually requires depletion of one of

the reductants or oxidants in the system and their initial EDC and EAC can be used to assess the final state.

Redox properties determined for the clay-rich formation might not represent conditions in the vicinity of a nuclear waste repository. That is, the redox property of the clay-rich formation will change over time upon installation of a geological repository for radioactive waste, especially in the near field. In a first step, oxygen is introduced into the formation by the excavation and during the operation of disposal galleries. The introduced oxygen will oxidize phases such as pyrite, iron in clays and organic material. After closure, anaerobic conditions will again develop and a reducing environment is reinstalled. In these reducing conditions, anaerobic corrosion of steel canisters leads to the production of hydrogen gas. This gas can then enter the surrounding geological formation and act as a reductant.

3.2. Kinetic constraints on redox reactions between sediment constituents and radionuclides

When a clay-rich sediment is not in redox equilibrium, identifying the relevant redox potential for predicting the redox state of a radionuclide is a challenging task. With the knowledge of the redox potential of a system or, in the case of redox disequilibrium, of individual redox couples in the sediment these values can be compared with the redox potential of the radionuclide of interest. The direction of spontaneous redox transformations for one radionuclide in the sediment can then be determined. Whether the electron transfer between a radionuclide and an oxidant or reductant in the formation can reach equilibrium or not is depending on the kinetics of the process. The first step in a kinetic assessment, is to compare the time scale of the reaction with the half-life of the radionuclide and its residence time in the system. The time scale of a reversible reaction is defined by:

$$\tau = \frac{\xi_{\infty} - \xi_0}{\frac{d\xi}{dt}}$$

The reaction progress parameter, ξ , is the oxidized or reduced amount of radionuclide normalized to its stoichiometric factor. The extent of the reaction in thermodynamic equilibrium is given by ξ_{∞} and ξ_0 is the current extent of the reaction. The differential term in the denominator represents the rate of the redox reaction. A redox reaction between a radionuclide and one constituent in the sediment is only relevant when the corresponding time scale is shorter than the residence time of the species in the host rock and the half-life of the radioactive decay. As a consequence, only the E_h of those half-reactions are of interest which can be coupled to the redox transformation of radionuclides within the relevant time frame. Redox potentials of other constituents, which do not react with the radionuclide within the time period of interest, are insignificant.

Using one of these E_h values, in the next step, to calculate the equilibrium redox speciation of a radionuclide is only meaningful when two requirements are fulfilled: 1) the concentrations of the oxidized and reduced form of an investigated redox couple by far exceed that of the radionuclide of interest and 2) the forward and reverse electron transfer reaction is kinetically fast enough to reach equilibrium within the given time frame and are faster than any other, potentially competing redox reaction.

The reactivity of the oxidized and reduced forms of an element can vary considerably. As a consequence, the redox potential of the corresponding redox couple might only be useful to establish an upper or lower limit when comparing this element to a radionuclide. For example, dissolved sulphide S(-II) can reduce U(VI) in the timescale of hours or days while oxidation of U(IV) by sulphate is too slow to be relevant. In this case, the E_h of the $\text{SO}_4^{-2} / \text{HS}^-$ redox couple could be used to delineate the upper limit of the U(VI)/U(IV) redox couple in the system. That is, E_h of the U(VI)/U(IV) redox couple is not expected to be higher than that of the $\text{SO}_4^{-2} / \text{HS}^-$ redox couple but it could be lower as oxidation of U(IV) by SO_4^{-2} is unlikely.

The kinetics of many redox reactions between radionuclides with oxidants and reductants typically encountered in clay-rich sediments have been experimentally investigated under conditions relevant

for a repository far field. Due to practical constraints, experimental studies only last for relatively short periods and only exceptionally span periods of more than one year. The residence time of radionuclides in the host formation can be in the order of 10^4 or 10^5 years. Kinetics with time scales of these dimensions can only be inferred from natural analogues or by extrapolation of results obtained at conditions very different from those in the formation, in particular from experiments performed at high temperatures. Here, the discussion on the relevance of individual redox couples for redox transformations of radionuclides will be solely based on experimental studies performed under low pressure and temperature conditions. No attempt will be made to extrapolate results from kinetic studies at elevated temperatures. It is a task for future studies to constrain the kinetics of reactions which take too long to be experimentally determined under natural conditions but are possibly fast enough to be relevant in view of the time scale of performance assessment.

Microorganisms play a pivotal role in mediating redox reactions in natural environments. This includes redox transformations of radionuclides and microorganisms can enzymatically catalyse the oxidation or reduction of radionuclides (Behrends, et al, 2012). The presence of viable microorganisms in clay rich deposits, including Boom clay, has been demonstrated (Stroes-Gascoyne, et al, 2007; Wouters, et al, 2013; BoivinJahns, et al, 1996). However, the activity of these organisms is restricted by the spatial limitations of the pore space in clay-rich sediments and the transport limited replenishment of nutrients. In unperturbed, consolidated clay-rich sediments, the microorganisms are most likely in a dormant state but might become active when space becomes accessible and when they are provided with fresh nutrients. This could be, for example, the case, when fractures temporarily form in the formation. As a consequence, assessing the relevance of redox couples for radionuclide redox transformations should be made for two situations: a) including the activity of microorganisms and b) only including chemical reactions.

4. Redox speciation of major elements in sedimentary systems and their redox interaction with radionuclides

Calculating the redox potential of the diverse redox couples in clay-rich sediment is a straightforward approach to characterize the redox conditions in a sediment. The downside of this approach is that the sediment has to be thoroughly geochemically characterized. The application of this method is limited when the Gibbs energy of formation of one or more species of the redox couple are unknown or are afflicted with great uncertainty. The latter is particularly the case for redox reactions involving natural organic matter, adsorbed species, and, in general, for all heterogeneous redox reactions. This is because the thermodynamic stability of one type of mineral can vary considerably due to impurities, imperfections, and depends, for submicrometer particles, also on the particle size.

It is beyond the scope of this report to discuss the analytical requirements and procedures for a rigorous geochemical characterization of the pore water and the solids in a clay-rich sediment. However, analytical data only providing total elemental concentrations are not sufficient for this purpose. The mineralogy of the solids needs to be determined and as far as possible species-specific analytical methods should be used. In most cases analytical procedures have to be combined with thermodynamic calculations, for example, to account for ion-ion interactions in electrolyte solutions in order to determine the thermodynamic activity of a redox species. The activity of oxidized and reduced forms of an element are eventually used in the Nernst equation to calculate the E_h of the corresponding redox couple:

$$E_h = E_h^0 + 2.303 \frac{RT}{zF} \log \frac{\{Ox\}}{\{Red\}}$$

wherein E_h^0 is the redox potential of the halfreaction in relation to the H^+/H_2 redox couple under standard conditions, R is the ideal gas constant, T the temperature, F the Faraday constant, z the number of electrons transferred, and the terms in the curly braces are the activities of the oxidized and reduced form of the redox couple, respectively.

In view of their potential contribution to the Electron Accepting Capacity (EAC) and Electron Donating Capacity (EDC) in clay-rich sediments, following elements are of main interest: hydrogen (H), carbon (C), oxygen (O), nitrogen (N), sulphur (S), iron (Fe) and manganese (Mn) and the activity of the different species of these elements have to be determined for characterizing the redox properties of the sediment based on thermodynamic considerations. The redox chemistry of each of these elements in clay-rich sediments is shortly reviewed in the following section and the potential coupling to redox transformations of radionuclides is discussed.

4.1. Hydrogen

In biologically active, anaerobic systems, the H^+ / H_2 redox couple can be a valuable indicator for the redox conditions and ongoing redox processes of the system. In anaerobic sediments, concentrations of elemental hydrogen can reach detectable levels and its concentration can be used to identify the dominating respiratory pathway. Microorganisms can couple the oxidation of hydrogen to the reduction of oxidized species of the major redox sensitive elements including: nitrate, Fe(III) oxides, Mn(IV or III) oxides, sulfate, CO_2 etc.. Provided that the assumptions about the thermodynamic control of microbial processes are fulfilled (see below), the E_h of the H^+ / H_2 couple is close to that of the dominating respiratory pathway and constrains the upper limit of other redox couples linked to anaerobic respiration.

Hydrogen gas is a product of microbial fermentation and it can be used as an electron donor in anaerobic respiration. Microorganisms can couple the oxidation of hydrogen gas to the reduction of nitrate, manganese in the oxidation state IV and III, ferric iron (Fe(III)), sulphate, and eventually used by methanogens who gain energy from converting CO_2 into CH_4 . Microorganisms are only able to gain energy from these reactions when they can occur spontaneously. That is, the change of Gibbs energy has to have a negative value when the process occurs at constant pressure and temperature. The change in Gibbs energies of the different reactions depends on the hydrogen pressure and the speciation and concentration of the different electron acceptors. In general, the required hydrogen pressure for making the different reactions energetically feasible, increases in the above given sequence (methanogenesis > sulphate reduction > Fe and Mn reduction > nitrate reduction). For example, the hydrogen level in microbial cultures increases when the rates of sulphate reduction decline due to the depletion of sulphate and methanogenesis becomes dominant. Hence, the H_2 concentration can be used as an indicator for the dominant microbial respiration pathway in aquatic environments (Lovley and Goodwin, 1988). The turnover rate of hydrogen in microbially active subsurface systems is very high. Hence, the concentration of hydrogen gas responds quickly to changes in microbial activity, which depends, among other factors, on the availability of the different electron acceptors. Under the assumption that the respiratory rates in subsurface environments are limited by the activity of fermenting organisms, dissimilating organisms reduce the hydrogen concentration to the lowest possible value. That is, the E_h of the H^+ / H_2 couple is kept at a level which is just sufficiently low enough to allow reduction of the bioavailable electron donor with the highest E_h in the system. The change in Gibbs energy (ΔG) of a redox reaction is related to the difference in redox potential (ΔE_h):

$$\Delta G = F\Delta E_h$$

wherein F is the Faraday constant (96490 C mol^{-1}). The minimum change in Gibbs energy of a reaction which allows microorganisms to thrive is around -10 kJ mol^{-1} electron transferred (Hoehler, 2004). This value corresponds to a threshold difference in redox potential of about -0.1 V . In other words, the redox potential of the H^+ / H_2 has to be 0.1 V lower than that of the electron acceptor. Based on the above considerations, the H_2 concentration can be used to estimate the E_h of the redox couple including the dominant terminal electron acceptor (for example the E_h of the SO_4^{2-} / HS^- couple). Additionally, the E_h of other redox couples involving possible electron acceptors are expected not to exceed that of the H^+ / H_2 couple by more than 0.1 V . Field observations support this approach and H_2 concentrations follow the redox zonation in an aquifer with an corresponding offset of about 10 kJ mol^{-1} in terms of change in Gibbs energy (Jakobsen and Postma, 1999).

The E_h of the H^+ / H_2 couple is relevant for constraining the redox speciation of radionuclides for twofold reasons. When the E_h (H^+ / H_2) creates an upper limit for other major redox sensitive major elements, this limit also applies for redox sensitive radionuclides when electron exchange with the major elements is kinetically fast enough. Furthermore, microorganisms can not only reduce major elements but are also capable of directly reducing redox sensitive trace elements by enzymatic catalysis. This also include radionuclides such as U(VI), Np(V), Pu(VI), Se(VI), Tc(VII) (Behrends, et al, 2012; Brookshaw, et al, 2012). In view of these radionuclides, the same considerations apply as for other electron acceptors and H_2 concentrations can serve as a proxy for the feasibility of their microbial reduction.

There are only very few examples for microbially mediated oxidation of radionuclides relevant in the context of performance assessment. In particular, microbial generation of H_2 as a result of the oxidation of other electron donors than organic compounds has not been reported so far. Consequently, the E_h of the H^+ / H_2 couple is a useful indicator for predicting the highest possible, dominant redox state of radionuclides whose redox speciation is microbially controlled but its application as a lower limit for the E_h of radionuclides is questionable.

In clay-rich sediments, the microbial activity is restricted due to the transport limited replenishment of nutrients and the confinement of the interstitial space (Stroes-Gascoyne, et al, 2007) and fermentative generation of H_2 might not be feasible. It has been proposed that hydrogen gas could be produced upon adsorption of Fe(II) onto montmorillonite (Charlet, et al, 2007) but direct evidence for this reaction is still lacking. Corrosion of stainless steel containers is expected to create hydrogen gas ($H_2(g)$) which can also be formed by radiolysis processes. The produced $H_2(g)$ can enter the clay-rich host rock by diffusion and react with its redox active constituents. Under far field conditions the reduction of structural Fe(III) in clay minerals and the sulphur in pyrite might occur.

The extent of Fe(III) reduction by $H_2(g)$ depends on the temperature, the pressure and the reaction time. Didier *et al.* (2012) studied hydrogen gas adsorption on dry, synthetic montmorillonite-type clays and Callovo-Oxfordian clayrock (COx) at 90 and 120 °C for 30 to 45 days at a hydrogen pressure close to 0.45 bar. Up to about 0.10 wt% H_2 was adsorbed on the clays and the amount adsorbed showed no correlation with structural Fe(III) content. Less $H_2(g)$ was adsorbed at 120 °C compared to 90 °C. Probably, $H_2(g)$ adsorption processes are mainly dominated by physisorption, *i.e.* based on weak interactions on the surface such as van der Waals interactions. Spectrometric analysis showed that adsorption of $H_2(g)$ caused reduction of up to 6% of the structural Fe(III) which was initially present in the synthetic clays. However, no reduction was observed with the COx sample in the present experimental conditions. Thus, reduction of structural Fe(III) in COx is probably difficult to achieve at the (low) temperatures used in this study.

In a follow-up study, Didier *et al.* (2014) compared products of the reaction of $H_2(g)$ with synthetic montmorillonites at dry conditions (at 90 °C) with those obtained by the reduction with dithionite in aqueous suspension. Furthermore, the reduction by $H_2(g)$ (at 90 °C, partial pressure varying from 0.1 to 5.1 bar, 40 days reaction time) of a clay suspension (4.5 g/L) was compared to the reduction of dried clay samples by $H_2(g)$. It was found that with reduction of $H_2(g)$ under dry conditions, only incomplete reduction was achieved. Under wet conditions, reduction progressed further, possibly due to higher availability of structural Fe(III). An increase of availability can be attributed to an increase in interlayer distance because of swelling. In a suspension, reduction is also facilitated by proton hydration. The reduction of structural Fe(III) by hydrogen gas in solution can proceed by two reactions. Hydrogen gas can penetrate into the interlayer space before its oxidation and directly react with structural Fe(III). This reaction involves simultaneous transfer of two electrons, that is two Fe(III) are reduced at the same time. The authors concluded that the probability of having two neighbouring structural Fe(III) is low and that, therefore, the oxidation of $H_2(g)$ inside the clay mineral structure is less likely. The second reaction is started by the dissociation of H_2 into two hydrogen radicals. These radicals can then further react with structural Fe(III). This reaction is in analogy to the reduction of structural Fe(III) by dithionite.

Regarding the COx sample, 8-10% of Fe(III) became reduced by $H_2(g)$ at water saturated conditions. occurred during the experiment. Hydrogen gas reduced the clay stone to a same extent as sodium dithionite under the specified experimental conditions. However, no reduction occurred during the reaction with $H_2(g)$ under dry conditions. In this study, Didier and co-workers assumed that pyrite

does not react with $H_2(g)$ although reduction of pyrite to troilite (FeS) is thermodynamically feasible. Truche *et al.* (2010) observed reduction of pyrite (FeS_2) by hydrogen gas at temperatures higher than $90^\circ C$ and when the partial pressure of hydrogen gas was 8 bar. Simplified pyrite-calcite assemblages were reacted with fluid and with hydrogen partial pressure ranging from 0 to 18 bar at a temperature between 90 and $180^\circ C$ in hydrothermal vessels. Calcite was used to model the alkaline conditions prevailing in the Callovo-Oxfordian formation. In this study, the authors concluded that formation of methane by reaction of $H_2(g)$ with carbonates through Fischer-Tropsch type reactions are unlikely in view of the thermal constraints and the expected hydrogen generation in a nuclear waste repository. Also the reduction of sulphate by $H_2(g)$ can most likely not of significance. Truche *et al.* (2009) investigated the reaction of sulphate with $H_2(g)$ and extrapolation of the results obtained at $250-280^\circ C$ resulted in an estimated half-life of sulphate of 210,000 years at $90^\circ C$, the assumed thermal peak in the disposal site.

Hydrogen is not only a major element in clay-rich sediments, but it can also be a radionuclide and released as tritium from nuclear waste. The fate of tritium is depending on the chemical form in which it would be released from the waste. If entering the host rock, it would be effected by redox transformations in a similar way as hydrogen containing compounds in the sediment and the considerations about the redox activity of hydrogen in clay-rich sediments would also apply for tritium.

4.2. Oxygen

The presence of relevant concentrations of oxygen in the oxidized forms of O_2 (0) or H_2O_2 (-1) in undisturbed clay-rich sediments which turned anoxic during early diagenesis is unlikely. This is because sinks for elemental oxygen in layers above the formation of interest are expected to be effective enough to compensate the downward flux of atmospheric oxygen and internal sinks most likely are efficient enough to depleted dissolved oxygen. Atmospheric oxygen is produced by oxygenic photosynthesis and requires light. Hence there is no significant natural production of elemental oxygen in subsurface systems and the presence of oxygen in sediments can only be due to convective or diffusive transport from the atmosphere.

Building of an underground repository will most likely require ventilation so that at least during construction elemental oxygen will be present. Radiolysis processes can also lead to the formation of O_2 and H_2O_2 in the repository near-field (Buck, *et al.*, 2012). Both oxygen species are reactive oxidants and readily oxidize many redox sensitive radionuclides in their reduced form including: U (Singh, *et al.*, 2014), Se (Kumar and Riyazuddin, 2011), or Tc (Sheppard and Evenden, 1991) (Examples References). Consequently, when elemental oxygen is present in concentrations which can be detected with standard methods (ppb range and higher) the E_h of the O_2/H_2O redox couple might be of high relevance for predicting the redox state of radionuclides released from the waste. The progress of an oxidation front has been investigated in the Hades underground laboratory which is situated in Boom clay in a depth of 224m at Mol, Belgium. The retrieved pore water showed oxidation effects over a distance of about 1m away from the gallerie's wall. This distance was the same for different parts of the laboratory which were installed with a time difference of 20 years. Changes in Boom clay mineralogy were only detected up to 4.5 cm away from the concrete/clay interface (De Craen, *et al.*, 2011).

4.3. Nitrogen

Nitrogen can naturally occur in redox states between V to -III with the thermodynamically stable states +V (nitrate), +III (nitrite), 0 (N_2), and -III (NH_3 / NH_4^+ and most of biologically bound nitrogen). The redox cycling of nitrogen plays a pivotal role in biological systems because nitrogen is an essential nutrient and can be used as an electron donor or acceptor for aerobic and anaerobic respiration, respectively. There are examples for nitrate dependent microbial oxidation of uranium (Weber, *et al.*, 2011) implying that the redox potentials of nitrogen species and the radionuclide might be directly linked. In this case, the E_h of the NO_3^- / NO_2^- or NO_x^- / N_2 couples might constrain the lowest possible redox state of radionuclides, which are susceptible to microbial redox transformation. So far, the capability of microorganisms to oxidize ammonia with other electron

acceptors than O_2 or NO_3^- / NO_2^- (anammox process) has not been demonstrated so that there are no indications for the coupling of ammonia oxidation and radionuclide oxidation.

In the absence of enzymatic catalysis, most dissolved nitrogen species are chemically inert in dilute solutions at low temperatures. Nitric acid provides an oxidizing environment and metallic radionuclides undergo oxidation but in dilute solutions, nitrate, N_2 , and ammonium can coexist without showing synproportionation. Also chemical electron transfer of these nitrogen species with most radionuclides at environmental conditions is most likely kinetically hindered. An exception is, regarding its reactivity within the group of inorganic nitrogen species, nitrite (NO_2^-). Nitrite is reactive towards radionuclides and can act, for example, as an oxidant for U(IV) under environmental conditions (Senko, et al, 2002; Finneran, et al, 2002). Nitrite also reacts readily with Pu and Np. It oxidizes Pu(III) or reduces Pu(VI), Np(V), or Np(VI) in the time scale of minutes (Betti, et al, 2002). Hence, if nitrite is present, the E_h of the NO_2^- / N_2 and NO_3^- / NO_2^- couples might limit the lowest and highest redox states of radionuclides, respectively, which are reactive towards nitrite.

Nitrogen is only a trace compound of autochthonous and detrital minerals of sedimentary deposits and organic matter is the major carrier of solid-bound nitrogen in sediments. Functional groups containing nitrogen can undergo reversible redox transformations (Schwarzenbach, et al, 2002). The redox activity of organic matter is discussed in the section on carbon. When disregarding nitrogen in organic matter, only dissolved species have to be considered when evaluating the redox state of nitrogen as none of the inorganic nitrogen species tends to form salts with low solubility. Similar to oxygen, nitrate and nitrite are energetically favourable terminal electron acceptors in heterotrophic respiration. Hence, oxidized nitrogen is usually completely removed from solution during early diagenesis of clay-rich sediments with sufficient organic matter input. However, nitrate can occur in anoxic ground waters while the presence of nitrate can be attributed to intensive agricultural activity. That is, the convective transport of nitrate with infiltrating rainwater is efficient enough to exceed nitrate removal by denitrification on its passage towards the groundwater. Nitrate can be reduced by pyrite but the reaction requires microbial mediation (Zhang, et al, 2012; Jorgensen, et al, 2009; Zhang, et al, 2009). Hence, post-burial intrusion of oxidized nitrogen species into consolidated clay-rich sediments with restricted microbial activity cannot be excluded.

4.4. Carbon and organic matter

The mineralization of organic matter (OM) fuels biological activity in subsurface environments. Organisms can couple the oxidation of carbon in organic compounds to CO_2 to the reduction a various electron acceptors including O_2 , NO_3^- , Mn(IV or III), Fe(III), and SO_4^{2-} . Higher organisms (eukaryote) are only capable of using O_2 as a terminal electron acceptor (aerobic respiration) and exceptionally NO_3^- (Risgaard-Petersen, et al, 2006). In contrast, microorganisms of the domains bacteria and archaea are more versatile and include species which can use one or more of the other terminal electron acceptors listed above. Many of these organisms are also capable to reduce enzymatically redox sensitive radionuclides such as U(VI) (Wall and Krumholz, 2006), Se(IV) (Oger, et al, 2004), or Se(VI) (Yee, et al, 2007) and can preserve energy from coupling their reduction to the oxidation of organic compounds. Hence, when enzymatic catalysis is present, the redox potentials of CO_2 / OM reactions can be taken as a upper limit for the redox potentials of radionuclides which are susceptible to microbially mediated reduction. In reverse, the redox couples of terminal electron acceptors constrain the feasibility of the oxidation of biodegradable ^{14}C containing organic compounds and by this can impose a upper limit for the E_h the CO_2 / OM redox couple.

Applying the E_h of CO_2 / OM redox couples to evaluate the redox state of radionuclides in the system requires, besides microbial catalysis, thermodynamic data for the organic compound. For relative simple organic compounds such as short chain fatty acids, aminoacids, or carbohydrates the Gibbs energy of formation has been determined. These compounds have in common that they are also easily degradable and have a short lifetime in biological active subsurface environments. They are produced in the subsurface by enzymatic hydrolysis of macromolecules or as products of microbial fermentation. In the latter case, the significance of the corresponding redox CO_2 / OM redox

potentials is comparable to that of the H^+ / H_2 redox couple when the concentration of elemental hydrogen is controlled by fermenting organisms (see section 4.1). In consolidated, clay-rich sediments with low or absent microbial activity, the active production of easily degradable organic compounds is unexpected, and the enzymatic catalysis or radionuclide reduction coupled to OM oxidation is most likely not expressed.

When the organic matter in the sediment has been exposed to microbial degradation for long periods the refractory fraction might have become dominating. However, the low susceptibility for complete mineralization does not necessarily imply redox insensitivity. For example, humic substances can contain functional groups, in particular quinonic entities, which can undergo reversible redox transformations (Schwarzenbach, et al, 2002). Due to this ability, humic substances can act as electron shuttles and mediate electron transfer between different constituents of soils and sediments. The mediation is important when direct electron transfer between the different redox partners is hampered due to spatial separation or kinetic hindrance. The role of natural humic substances as electron transfer mediators has been extensively investigated in the context of microbial Fe(III) reduction. In this process, the humic substances facilitate the electron transfer between bacteria and iron (hydr-) oxides (Nevin and Lovley, 2000; Roden, et al, 2010).

The redox active moieties in humic substances can contribute to the electron donating and accepting capacities of soils and sediments (Aeschbacher, et al, 2011), implying that the refractory fraction of the organic matter might be an important reductant or oxidant in clay-rich sediments. The recent progress in characterizing electrochemically the redox properties of natural organic material (see section 5.2), also increased attention for its role in redox transformations in soils and sediments. Bruggeman et al. observed that Se(IV) became associated with dissolved humic substances from Boom clay and Gorleben but Se(VI) did not interact with the humic substances (Bruggeman, et al, 2007). Although direct evidence is missing, reduction of Se(IV) to Se(0) was likely the underlying mechanism for the formation of a colloidal Se fraction. The chemical reduction of metal ions by natural humic acids has been recently reported for Ag^+ (Akaighe, et al, 2011; Maurer, et al, 2012; Adegboyega, et al, 2013). The kinetics of the electron transfer between natural organic matter and radionuclides of concern still have to be explored further to delineate the relevance of this process in clay-rich host rock. However, the organic matter might be a carrier of reductive or oxidative capacity which has been accumulated during the diagenesis of the sediment and which can be readily used for redox transformations of radionuclides without the requirement of microbial catalysis.

Relating the E_h of redox active functional groups of organic compounds to those of radionuclides is difficult because the thermodynamic stability of the oxidized and reduced forms are influenced by other substituents and the structure of the molecule. Due to the structural complexity and diversity of natural organic macromolecules, natural organic matter might exhibit a broad range of E_h^0 values. For this reason, the redox properties of organic matter in the system need to be characterized before statements about their possible impact on the redox speciation of radionuclides can be made (see section 5.2). In contrast to the reversible, partial oxidation or reduction of functional groups, complete oxidation or reduction of organic carbon to CO_2 or CH_4 usually requires biological mediation in natural environments.

4.5. *Iron and Manganese*

Fe(III)/Fe(II) redox couples are of great relevance for determining the redox speciation of radionuclides in clay-rich sediments for two reasons: a) electron transfer kinetics between Fe(II) or Fe(III) species with several radionuclides can be relatively fast and b) reactive Fe(II) and Fe(III) phases are typically abundant in clay-rich sediments. Iron can contribute substantially to the EAC and EDC as sediments often contain solid-bound iron in both environmentally relevant oxidations states, Fe(II) and Fe(III). Iron is a constituent of many primary and secondary silicates as well as of various other secondary minerals. In its reduced form, Fe(II) can be found in sediments in the form of sulphides (FeS or FeS_2), carbonates ($FeCO_3$), phosphates and mixed redox state iron oxides such as magnetite. When oxidized, Fe(III) forms a variety of (oxyhydr-)oxides.

Oxidation of Fe(II) sulphides or carbonates to Fe(III) (oxy-)hydroxides and vice versa requires mineral dissolution and precipitation of a new phase. In contrast, oxidation and reduction of structural bound Fe in layer silicates can occur reversibly and without phase transition (Kostka, et al, 2002; Stucki, et al, 1988; Gorski, et al, 2012; Stucki, et al, 1987). These Fe containing clay minerals, in analogy to organic matter moieties capable of reversible redox cycling, are of specific interest as they can serve as reductants and oxidants with comparable reactivity. Consequently, their redox potential could be used for constituting the redox speciation of radionuclides in the sediment based on an equilibrium approach if the electron transfer kinetics are fast enough. Reversible Fe redox cycling in silicates is also of particular interest in clay-rich sediments, as clay minerals are a major component and highly abundant.

Regarding electron transfer reactions between radionuclides and Fe containing solids, reduction of radionuclides by solid bound Fe(II) has been extensively investigated (Table 2.). Examples for oxidation of radionuclides by Fe(III) (hydr-)oxides or other potentially reactive Fe(III) species are rare and the process has not received much attention. In the context of remediation of U contaminated sites, the possible oxidation of U(IV) in the form of uraninite (UO₂) by Fe(III) (hydr-)oxides has been postulated (Ginder-Vogel, et al, 2006) and experimentally verified (Ginder-Vogel, et al, 2010).

Table 2. Exemplarily compilation of studies demonstrating the reduction of radionuclides with various Fe(II) bearing solids

RN	Fe(II) sulphides (mackinawite, pyrite)	Adsorbed Fe(II)	Mixed redox state Fe oxides (magnetite, green rust)	Fe(II) carbonate or phosphate
U(VI)	Lee et al. 2013 Veeramani et al. 2011 Wersin et al., 1994	Liger et al., 1999 Chakraborty et al., 2010	Scott et al., 2005 O'Loughlin et al. 2003)	Veeramani et al. 2011
Se(VI)			Refait. et al, 2000	
Se(IV)	Charlet et al. 2012 Bruggeman et al. 2005	Charlet et al., 2007	Myneni et al. 1997)	Scheinost et al. 2008
Tc(VII)	Wharton et al. 2000	Yang, et al, 2012	Lloyd et al. 2000 Pepper et al. 2003	Cui and Eriksen, 1996

The redox potential of Fe redox couples is strongly depending on the coordination chemistry of Fe in the different redox states. This implies that knowing total Fe(II) and Fe(III) concentrations is insufficient to calculate a redox potential. The standard redox potential of Fe can range, depending on coordination environment, from -1.9 V to 1.1 V which spans over the whole stability field of water (Amonette, 2002). Consequently, the exact speciation of Fe in both oxidation states needs to be known in order to calculate the corresponding E_h . It is not uncommon in sedimentary systems, that the Fe speciation does not reflect thermodynamic equilibrium so that different E_h values can be derived depending on which Fe(II) and Fe(III) species is selected for the calculation. Another problem is that the thermodynamic data for natural Fe minerals can vary due to impurities, imperfections, or, when of colloidal dimensions, can depend on size. For some relevant phases thermodynamic data have not been experimentally determined so far. The latter is in particular the case for the change in thermodynamic properties of Fe-containing silicates upon Fe reduction or oxidation. Amonette (2002) calculated redox potentials of Fe(III)/Fe(II) couples in different minerals by accounting for the crystal field stabilization energy of Fe(II) depending on the Fe coordination in the minerals. However, other factors than crystal field stabilization energy can influence the redox properties of Fe which is structurally bound in these minerals and the experimental verification of these values is still required. In view of the challenges to calculate the E_h (Fe(III)/Fe(II)) of natural

samples containing a diverse suit of Fe minerals, electrochemical measurements which probe the Fe(III)/Fe(II) redox couple might be a suitable alternative (see section 5.2.).

Iron sulphides such as FeS (e.g. mackinawite), FeS₂ (e.g. pyrite) or Fe₃S₄ (e.g. greigite) contain two redox sensitive elements, iron and sulphide. Iron sulphides are ubiquitous in aquatic sediments which have been subjected to sulphate reduction and not experienced post-burial oxidation. Due to the high abundance of sulphate in seawater, pyrite formation is more pronounced under marine conditions than in fresh water sediments (Berner, 1984). In redox reactions, both or only either of the two elements can be involved in the electron transfer. The average oxidation state of S in FeS₂ and Fe₃S₄ is -1 so that reduction to S(-II) could be possible but the occurrence of this process in natural systems has not been reported so far. Environmentally more important is the oxidation of iron sulphides. At neutral pH and in the presence of oxygen, both constituents, Fe and S, are oxidized chemically and upon microbial mediation. However, at low pH and with weaker oxidants than elemental oxygen, preferentially S is being oxidized while Fe(II) can preserve its redox state and is released into solution or remains in the form of other Fe(II) containing solids such as siderite (FeCO₃). The reduction of radionuclides by iron sulphides has been reported in several experimental studies (see Tab 2.) and can be conceived as one of the most important reductive pathways for radionuclides in clay-rich host rocks .

Iron is about 50 times more abundant than Mn in the earth's crust and the contribution of Mn to the electron flux in subsurface environments is, in view of its abundance, often of subordinate importance. However, Mn can be of comparable importance as Fe for the electron fluxes in sediments despite its lower concentration (Thamdrup, et al, 1994). Furthermore, Mn can be selectively enriched in sediments and then be of pivotal importance for the elemental redox cycles in these sediments (Canfield, et al, 1993).

The biogeochemical behaviour of iron and manganese has many common aspects but there are also distinct differences. For example, Mn also occurs naturally in the oxidation state +IV and Mn forms, as a consequence, a larger diversity of oxide minerals (Tebo, et al, 2004). The affinity of Mn²⁺ for sulphide is lower compared to Fe²⁺ and the formation of pure Mn sulphides has only been reported in sediments with exceptionally high Mn content. When sediments are enriched in Mn(II) this is usually in the form of Mn(II) containing carbonates. When comparing the reactivity of the oxidized and reduced forms of Mn and Fe, Mn(II) tends to be less reactive than Fe(II), while Mn(IV) oxides can be more reactive compared to Fe(III) oxides. For example, the time scale of oxidation of dissolved Fe(II) is in the order of seconds at neutral pH while solutions of dissolved Mn(II) are stable for years under the same conditions. In contrast, As(III) is readily oxidized by Mn(IV) and Mn(III) oxides (Scott and Morgan, 1995; Tournassat, et al, 2002). Although As(III) oxidation by goethite (FeOOH) has been reported once (Sun and Doner, 1998), most studies find that arsenite (As(III)) forms inner sphere complexes on iron oxide surfaces without indications for oxidation when precautions are taken to prevent photoinduced oxidation (Ona-Nguema, et al, 2005). Likewise, Mn(III,IV) (hydr-)oxides oxidize effectively small organic acids such as oxalic acid (Wang and Stone, 2006) while the same reaction with Fe(III) oxides requires stimulation by UV light or Fe(II) addition to proceed quickly. It still needs to be investigated whether this trend of lower reactivity of Mn(II) and higher reactivity of Mn(IV) / Mn(III) compared to the comparable species of Fe(II) and Fe(III) can be extrapolated towards radionuclides or not. However, some observations support this trend. To our knowledge, reduction of Se(IV) by Mn(II) has not been reported so far while selenite is readily reduced by various Fe(II) species (see above). Although oxidation of U(IV) by Fe(III) oxides can occur, Mn(IV) oxides seem to be more efficient to reduce U(IV) in the form of uraninite (Wang, et al, 2013).

4.6. Sulphur

Sulphur takes oxidation states between +VI to -II in natural environments whereupon the oxidation states -II, 0, and VI can be dominant based on thermodynamic considerations. Sediments can contain solid-bound S in the form of sulphates (e.g. gypsum, barite), elemental sulphur, sulphides (e.g. pyrite), and as a constituent of natural organic matter. In sulphidic marine sediments, pyrite-bound sulphur often accounts for most of the total S content. In solution, sulphate and sulphide species usually represent the major part of dissolved sulphur but also sulphur species in

intermediate redox states, such as thiosulphate, can be detected during ongoing redox transformations of sulphur (Canfield, et al, 2012).

Sulphate is an inert molecule and at low pressure and temperature conditions microbial reduction is the only pathway for sulphate reduction. In contrast, dissolved sulphide (Hua, et al, 2006) and solid-bound sulphide (see table 2) are more reactive and have been shown to readily reduce radionuclides. Hence, the E_h of the S(0)/S(-II) and S(VI)/S(-II) redox couples might be used to define an upper limit for the E_h of radionuclides which are susceptible to chemical reduction by dissolved sulphide or sulphide minerals in clay-rich sediments.

5. Electrochemical measurements of redox potential

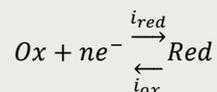
Electrochemical methods can be used for directly measuring redox potentials. The advantage of directly measuring redox potentials is that no extensive chemical characterization of the system is required and that the measurement directly targets the parameter of interest. All analytical methods for measuring E_h have in common that they are not equally sensitive towards all possible redox sensitive species in natural systems. As a consequence, the probe might not reach equilibrium with all of the redox active constituents. This is not a problem when the system is, in itself, in equilibrium because any of the probed redox couples reflects the equilibrium conditions. However, when the system is not in equilibrium, the interpretation of measured redox potential hinges on knowledge about the interaction of the probe with the different relevant redox couples in the system. This is particularly relevant, when the measured E_h is used to infer the oxidation state of radionuclides in the host rock.

5.1. *Potentiometric measurement of redox potentials of homogeneous solutions derived from sediment*

The standard electrochemical cell for measuring redox potentials consists of an inert electrode, usually made of platinum (Pt), glassy carbon, or gold, which is connected to a reference electrode. The difference in electrical potential between the indicator and reference electrodes is detected with a potentiometer. One possible approach to delineate redox conditions in clay-rich sediments, is to measure redox potentials with an inert electrode in the pore water retrieved from the clay-rich sediments. Pore water can be collected from clay-rich sediments by squeezing undisturbed samples or from piezometers installed in situ (De Craen, et al, 2004). Alternatively, an aqueous solution with a composition close to that expected in the formation can be equilibrated with the sediment in situ by using piezometers (Wersin, et al, 2011).

A possible shortcoming of this approach is that dissolved components only represent a part of the redox active constituents in clay-rich sediments (see section 4) and that the dissolved constituents are not in redox equilibrium with relevant redox active solids in the clay. Redox active solids, typically encountered in clay-rich sediments, include sulphides, organic matter, iron and manganese oxides or carbonates, and structural bound redox sensitive metals in silicates. Measurements of redox potentials in pore water might be biased if solubility equilibrium is not achieved between redox-active minerals (e.g. pyrite or metal oxides) and the solution. This is, in particular, the case for silicates with structurally bound Fe. The solubility of silicates is usually very low and dissolution kinetics are slow. The same restrictions apply for solid organic matter of which only a small fraction is readily dispersed or dissolved in water without mechanical treatment. The naturally present dissolved compounds are usually not capable to serve as effective electron transmitter between the indicator electrode and the solid phases. As a consequence, it is in most cases inappropriate to draw conclusions about the redox potential of heterogeneous reactions or solid phase reactions based on redox potential measurements in a separated aqueous pore water solution.

The meaningfulness of potentiometric measurements in sediment pore waters is further challenged by the inherent limitations of the technique. The problems of redox potential measurements in natural aqueous solutions have been frequently discussed for years but, nevertheless, are often ignored (Schüring, et al, 2000; Stumm and Morgan, 1996). Redox reaction at the electrode surface can be generally represented by the following equilibrium reaction:



Every oxidation and reduction reaction generates a current flowing in opposite directions (i_{red} and i_{ox}). Either of these currents has to be strong enough to polarize the electrode sluggish electrontransfer kinetics between many dissolved species and the electrode can hamper the equilibration between solution and the indicator electrode. Although a potentiometric measurement is, idealized, performed at zero current flow, reproducible polarization of an inert electrode requires sufficient high currents for the forward and reverse direction of electron transfer. The exchange current, which is the sum of reductive and oxidative current, and which is necessary to change the potential of the redox electrode depends on the instrument but is in the order of 10^{-7} A (Stumm and Morgan, 1996). Due to this constraint, perfect equilibrium between the electrode and the redox potential of one redox couple cannot be achieved and the discrepancy between the electrode potential and the redox potential of the probed half-reaction depends on the threshold exchange current and the slope of the current / potential curve. The dependency of the oxidative and reductive current on electrode potential can be described by the Butler-Volmer equation. At given electrode potential, the current linearly depends on electrode surface, concentration of the reagent, and the rate constant for the electron transfer between the electrode and the oxidant or reductant. The rate constants of at least one partner of many environmentally relevant redox couples are, in the absence of a catalyst, too low to allow reproducible redox potential measurements with an inert redox electrode. These redox couples include, for example, : DOM/ CO_2 , O_2/H_2O , NO_3^-/N_2 , NO_2^-/N_2 , NO_3^-/NH_4^+ , N_2/NH_4^+ , SO_4^{2-}/HS^- , CO_2/CH_4 . In the presence of oxygen, redox potential measurements with a platinum electrode are further complicated due the formation of platinum oxides. As a consequence, measured redox potentials with a Pt electrode in natural waters do not show any correlation with redox potentials calculated from the activities of the compounds of the above listed redox couples (Lindberg and Runnells, 1984).

Regarding its reactivity with an redox electrode, iron is an exception in the group of redox sensitive major elements. Many species of the oxidized and reduced form of the Fe^{3+}/Fe^{2+} couple can exchange electrons with inert electrodes with sufficient rates when present in environmentally relevant concentrations. Reliable redox potential measurements in solutions with dissolved Fe(II) and Fe(III) are possible when the concentrations of both redox forms are in the micromolar range. In natural systems, dissolved concentrations of Fe(II) and Fe(III) can exceed this threshold value under acidic conditions. At neutral pH and in the absence of complexing ligands, the concentration of dissolved Fe(III) is limited by the low solubility of ferric iron (hydr-)oxides. In this case, dissolved Fe(III) concentrations are too low to induce a sufficient reductive current and reliable redox potential measurements in the solution are not possible using inert electrodes. The same problem might arise when the dissolved Fe^{2+} concentration is controlled by sulfides (e.g. pyrite or FeS), carbonates (siderite) or mixed redox state iron oxides (magnetite). However, when electron transfer between the electrode and the Fe(III) or Fe(II) containing solids is possible and the related currents dominate the electron flux at the electrode surface, meaningful values for the Fe(III)/Fe(II) redox potential can be obtained (Stumm and Morgan, 1996).

Another issue of redox potential measurements in natural solutions is that solutions are often not in equilibrium and the measured value reflects a mixed potential. When several redox couples, which are in disequilibrium, induce comparable anodic or cathodic currents at the electrode, the measured value is a mixed redox potential. A mixed potential lies between the redox potentials of the different redox couples and is therefore difficult to interpret because it does not directly reflect any of the redox couples in the system directly (Peiffer, et al, 1992).

5.2. Potentiometric measurement of redox potentials of suspensions or of solids

Direct electron transfer between solids in suspensions and inert electrodes is possible and sufficient high currents can be realized for reliable potentiometric measurements. For example, measuring the E_h of suspensions containing dissolved Fe(II) and Fe(III) (hydr-)oxides was used to infer the solubility product of the ferric iron minerals (Bonneville, et al, 2004; Liger, et al, 1999; Silvester, et al, 2005). For the electron transfer, it is required that the electrode surface and the solids are in intimate contact and a sufficient large interface is created. This requirement can be fulfilled when

analysing colloids. However, for larger particles, the creation of a sufficient large contact area is, in general, sterically hindered. This implies that the electrode potential is not influenced by direct electron exchange with the solid. The redox potential of a heterogeneous half reaction, e.g. $\text{Fe(III)(s)} / \text{Fe(II)(aq)}$ can be nevertheless directly determined by potentiometric measurements when the solution is in solubility equilibrium with the solid, and the equilibrium concentration of the dissolved solid is high enough to exert a sufficient high exchange current with the electrode.

Another option is to facilitate the electron transfer between redox sensitive solids and an inert electrode by applying soluble mediators. Development, selection, and application of soluble electron shuttles for characterizing the redox properties has been successfully demonstrated for humic substances (Aeschbacher, et al, 2012; Aeschbacher, et al, 2012; Aeschbacher, et al, 2011; Aeschbacher, et al, 2010) and Fe containing clay minerals (Gorski, et al, 2011; Gorski, et al, 2013; Gorski, et al, 2012; Gorski, et al, 2012). The use of mediators allows to explore the redox potential of these, in principle, reversible redox transformations of solids which might be of interest for constraining the redox speciation of radionuclides in clay-rich sediments (see section 4). Furthermore, the redox potential of natural organic matter and Fe in clay minerals cannot be easily derived from thermodynamic calculations as the required thermodynamic data are missing or uncertain.

For determining the redox potential of a solid, a mediator is required with a standard redox potential E_h^0 close to the E_h value of the probed redox couple. Examples of successful applications of this approach solely include homogenous redox transformations of solids and the performance of this technique for measuring redox potentials of heterogeneous half reactions have to be assessed in the future. Furthermore, the applicability of mediators for E_h measurements in suspensions with different types of redox active components has to be tested. For the interpretation of a measured value in complex, natural samples it has to be investigated which electroactive components interact with the applied mediators. Despite the remaining open questions, redox potential measurements mediated by electron shuttles are a promising approach to derive E_h values for clay-rich sediments which are possibly of high relevance for constraining the redox speciation of radionuclides. This would be in particular the case when the reactivity of the redox active constituents of the sediments towards the mediators would be correlated to the kinetics of electrontransfer reactions between the redoxactive clay constituent and the radionuclides of interest.

5.3. Inferring redox potentials of clay-rich sediments from other electrochemical measurements

Electron shuttles have been used to determine electrochemically the EAC and EDC of humic substances (Aeschbacher, et al, 2010) and Fe-containing clay minerals (Gorski, et al, 2011) in aqueous suspensions. In this approach, a potential is applied to the working electrode and the resulting current is integrated over time to obtain the electron accepting or donating capacities. When using mediators with different standard redox potentials, it is possible to measure the EAC and EDC at different electrical potentials. When the applied potential is identical to the redox potential of the analysed material, in theory, the resulting EAC and EDC should be both zero. So far, no attempts have been reported to derive a redox potential for natural samples in this way. Redox profiles obtained for Fe-containing clays showed pronounced hysteresis between repeated oxidation and reduction cycles (Gorski, et al, 2012). Furthermore, part of the electron transformations turned out to be irreversible. These observations imply that it is not possible to assign an unequivocal redox potential to an Fe-containing clay solely based on the Fe(II)/Fe(III) ratio. That is, the corresponding redox potential depends on the history. Gorsky et al. found that the E_h values corresponding to identical EAC and EDC can vary by up to 0.56 V when measured during oxidation or reduction, respectively (Gorski, et al, 2012).

In an alternative approach, the redox properties of solids can be determined electrochemically in the absence of water. Perdicakis and Beretta obtained results indicating that voltammetric analysis of pyrite and clay minerals is possible by using “salt matrix voltammetry” (Perdicakis and Beretta, 2012). The technique has been directly applied to material from Callovo-Oxfordian argillite. The Callovo-Oxfordian clay is investigated in France as a model for an argillite host formation. The advantage of the salt matrix voltammetry is that it can be applied with minimum sample treatment

and by this reduce the risk of alteration prior to analysis. However, the applicability of these alternative electrochemical measurements to determine redox potentials or EAC/EDC of complex natural mixtures has to be investigated further. In view of the interpretation of the derived E_h , the same restriction applies as for the techniques discussed in section 5.2. In particular, it has to be possible to relate the obtained E_h to the corresponding redox couple(s) in order to evaluate the significance of the value for predicting radionuclide speciation.

6. Determining redox potentials by using indicators

Alternatively to electrochemical methods, indicators can be used to probe the redox potential of aqueous solutions and suspensions. Organic molecules with redoxactive moieties capable of reversible redox cycling, such as quinonic groups, are potentially suitable indicators. Similarly to organic mediators used within electrochemical methods, the indicator is assumed to reach redox equilibrium with the redoxactive components in the solution or suspension. In contrast to the electrochemical methods, other analytical techniques are used to determine the redox state of the indicator. For compounds, which change their optical properties upon oxidation or reduction, UV-visible spectrophotometry can be used to measure the concentrations of the reduced and oxidized form of the indicator. The use of indicators to monitor the redox state of bacterial suspensions is a standard microbial technique when working with oxygen sensitive organisms. Redox indicator dyes are also used to probe environmental oxidation and reduction processes (Tratnyek, et al, 2001). The application of molecular probes to characterize the redox properties of clay minerals has also been described (Yu and Bailey, 1996). The prerequisites of applying redox indicators is similar to those of using mediators in combination with electrochemical methods for determining the E_h of suspensions: the compound should readily react with the oxidant and reductant of the targeted redox couple, its application should not change significantly the redox state of the probed system, the compound should be soluble and not adsorb strongly in either redox state, its standard redox potential should be close to the E_h of the probed redox couple(s), and detection of the redox state of the indicator / mediator should be possible with the used analytical method.

In addition to organic compounds, also redox sensitive inorganic compounds can be used as redox indicators. In principle, the redox speciation of the naturally present major and trace elements can be conceived as an indicator of the redox state of the system. In view of the goal to assess the redox state of radionuclides in the sedimentary system, exposing redox sensitive radionuclides to the sedimentary material *in situ* or in laboratory experiments and monitoring their oxidation state is a straightforward approach to derive the desired information. These types of experiments have been frequently performed but not necessarily with the designated goal to constrain the redox conditions. Establishing a standard procedure in which a suit of radionuclides is exposed to the clay-rich sedimentary material to constrain the redox properties of the host rock formation could be considered. For the procedure, radionuclides should be selected with different standard redox potentials and which react sufficiently fast with the sedimentary material to monitor a change in redox state during the exposure time. It would be recommendable to expose the radionuclides in different redox states to the sediment material. When such a procedure could be developed, a transfer function would be required to extrapolate the kinetics and direction of the redox transformations of the probe radionuclides to other redox sensitive radionuclides. The conceptual idea of using probe radionuclides to assess the direction and rate of redox transformation of other radionuclides is in analogy to the approach taken by Elsner et al. (2004) to assess the reactivity of Fe(II) bearing minerals towards the reductive transformation of organic contaminants.

7. Characterization of redox properties of some argillaceous formations

In this section, we will discuss available knowledge on the redox properties of several argillaceous formations, currently considered as potential hosts for geological disposal facilities of radioactive waste or studied within this context.

7.1. Boom Clay (Mol, Belgium)

Due to the presence of pyrite and natural organic matter, the Boom Clay is reducing and therefore has negative redox potentials. The first reported value of the Boom Clay redox potential was -280 mV measured in a surface laboratory by Baeyens et al. (1985a) in a Boom Clay slurry. Many subsequent studies have focused on *in situ* measurement of E_h and a range of values between -250 to -400 mV has been reported (De Cannière et al., 1996). In the study of ARCHIMEDE-argile (Beaucaire et al., 2000; Griffault et al., 1996), although no distinct E_h values were reported, the interpretations on the water composition suggested a similar range of E_h between -240 to -400 mV.

Because of the very low buffering capacity of redox active species present in the pore water, the reliability of laboratory measurements, in view of rendering a representative *in situ* E_h value, is however doubtful. Therefore, it is estimated that most reliable measurements of E_h come from *in situ* measurements, although the implementation of redox electrode technology is also far from evident. However, the advantage of *in situ* measurements is that measurement conditions are close to the real conditions. This advantage makes it worthwhile to invest time and work in *in situ* measurements. High water pressure and long term electrode stability demand appropriate precautions and measures to obtain accurate and reliable *in situ* values of the redox tendency of Boom Clay pore water.

With this in mind, a dedicated flow-through cell set-up for pH electrodes and redox electrodes was designed and installed in the HADES underground research facility (Mol, Belgium). Specifically for redox measurements, the following precautions are foreseen: the anaerobic atmosphere prevents oxygen perturbation, the exclusive use of polymer or ceramic materials allows to circulate Boom Clay pore water that never has come in contact with redox active metal surfaces, and the use of different indicator electrode materials allows qualitative comparison of the redox measurements. To eliminate as much as possible errors linked to the redox measurement system, an electrode functionality and an electrode drift test is performed. These tests assure the good functioning of the used redox electrode(s) during the whole duration of the *in situ* measurement. These efforts resulted in a measured redox potential E_h of -310 ± 30 mV at the *in situ* hydraulic pressure (Moors et al., 2002).

Although the redox potential of Boom Clay has been proven difficult to measure and interpret, plausible processes controlling the measured E_h can be anticipated based on thermodynamic calculations in combination with the measured mineralogical and pore water compositions. For example, the E_h value of the S(-I)/S(VI) couple related to the equilibrium between pyrite and sulphate, when assuming that Fe^{2+} activity in the system is controlled by the solubility of siderite, is as follows:



$$E_h = 0.38 - 0.076\text{pH} + 0.0084 \log a[\text{SO}_4^{2-}] - 0.0042\log f[\text{CO}_2(\text{g})] \quad (3.2.2)$$

In equation (3.2.2.) $a[\text{SO}_4^{2-}]$ and $f[\text{CO}_2(\text{g})]$ refer to the activity sulphate and fugacity of carbon dioxide, respectively. Following the equation (3.2.2), under the reference Boom Clay condition, e.g., at pH of 8.2, $p\text{CO}_2$ of $10^{-2.4}$ atm, and taking a sulphate concentration as 0.1 mg/l ($\sim 1 \mu\text{M}$), the redox potential is -283 mV, which is the upper limit of the pyrite stability field.

The sulphate concentration of 0.1 mg/l is about the lowest measured in all piezometer waters. Since Boom Clay is a marine sediment, the threshold of the present-day sulphate concentration can be calculated from the seawater ratio between sulphate and chloride. According to the seawater composition given by Drever (1997), the ratio of chloride and sulphate in seawater is about 19.3. Taking the chloride concentration in Boom Clay pore water as 26 mg/l, the sulphate concentration is 3.6 mg/l and the redox potential calculated by equation (3.2.2) is -270 mV. This value might be taken as the maximum redox potential for a non-disturbed Boom Clay in Mol.

From the mineralogical composition of the Boom Clay, it can be seen that both pyrite and siderite are present in Boom Clay. So, the calculated E_h based on equation (3.2.2) should be a reasonable estimate assuming a chemical equilibrium. This model therefore suggests that the measured reducing E_h is controlled by pyrite-siderite equilibrium under the *in situ* partial pressure of CO_2 (g). If the Boom Clay pH is well buffered, the only factor influencing the system redox condition is then concentration of sulphate. This suggests that it might be practically interesting to use the sulphate concentration as an indicator to evaluate the degree of perturbation on water samples caused by oxidation. A significant higher concentration of sulphate than 3.6 mg/l should indicate severe oxidation of Boom Clay. A lower sulphate concentration, on the other hand, might originate from biochemical sulphate reduction processes.

The redox buffering capacity of Boom Clay pore water isolated from the solid phase is considered to be very low (De Cannière et al., 1996). Pirlet (2003) reported a measured value of 0.14 meq/l and interpreted it as being dominated by dissolved natural organic matter.

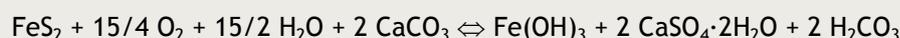
Both measurements and model interpretation support the conclusion that the reference redox potential (E_h) of the non-disturbed Boom Clay should be lower than -270 mV. This reference value is only indicative that Boom Clay is relatively reducing and implies that laboratory experiments should be performed in an anaerobic environment. However, because of the slow rate of redox reactions and the extremely low concentrations of redox species in Boom Clay pore waters, it is not recommended to use the reference E_h value to constrain the redox condition for laboratory experiments. Future work should focus on mechanisms controlling the redox potential and especially the redox equilibrium state of Boom Clay.

7.2. Opalinus Clay

The Opalinus Clay (OPA) was formed about 180 million years ago by deposition of fine mud particles. Between 40 and 80% of the OPA is made up of clay minerals. Around 10% of those minerals are capable of swelling and may increase in volume in the case of water influx. Other components include quartz (sand and silt), calcite, siderite, pyrite, feldspar and organic carbon (Tevissen *et al.*, 2004). The reducing nature and high redox-buffering capacity of the OPA is inferred from the presence of pyrite (1.1±1 wt%) and siderite (4±2.4 wt%), which show no signs of oxidation. From mineralogical observations, E_h measurements performed at Mont Terri and geochemical modelling, redox potentials of about -170 mV for the reference pore water and bounding values of about -140 to -240 mV were derived (NAGRA, 2002). The pH conditions are expected to be near-neutral but the uncertainties are rather large mainly because the partial pressure of CO_2 cannot be precisely constrained at present. Bounding pH values of 6.9 to 8.2 are proposed (NAGRA, 2002).

Pearson *et al.* (2003) describe the methods, results and interpretations of the WS ('water sampling') and GM ('geochemical modelling') experiments in the Mont Terri Rock Laboratory. These experiments were concerned with (a) developing and evaluating methodology for measuring compositions of pore waters, and (b) describing and modelling *in situ* compositions and processes that control the geochemical environment.

Monitoring results suggest that oxygen contamination has prevailed in most if not all redox measurements, with Pt-electrode potentials being consistent with the presence of dissolved oxygen. The redox buffer capacity of the Opalinus Clay depends principally on the SO_4^{2-} content of the system to buffer reducing tendencies and the reduced S, Fe(II) and reduced C contents to buffer oxidizing tendencies. Organic carbon and Fe^{2+} in siderite are the largest contributors to the total reduction capacity (TCR) of the formation. However, only the contribution from pyrite can be detected in studies of the oxidation of the formation under natural conditions. The generalised overall pyrite oxidation reaction may be described as follows:



The preferred redox-controlling reaction involves a fixed SO_4^{2-} concentration, and control of solution redox potential by the $FeS_2 \leftrightarrow SO_4^{2-}$ reaction. *In situ* dissolved Fe concentrations are thought to be controlled by siderite solubility.

The major redox-active elements present in the Opalinus Clay are C, Fe, Mn and S. The formation mineralogy is such that Fe(II) would be present in pyrite and carbonates, Mn(II) in carbonates, Fe(III) in silicates, principally chlorite, and S both in SO_4^{2-} and reduced sulphur minerals, principally celestite and pyrite.

Gases were also sampled but the sampling procedure was such that the gas composition data could not be interpreted quantitatively. Therefore, it was not possible to calculate redox potentials corresponding to the N_2/NH_4^+ , C^0/CH_4 or $\text{H}_2\text{O}/\text{H}_2$ couples even though all three gases were present, as well as higher hydrocarbons. The carbon isotopic composition of ethane and propane were consistent with the vitrinite reflectance of OPA, suggesting the origin of these gases is the formation itself. The carbon and hydrogen isotopic composition of methane, on the other hand, was not consistent with such an origin, suggesting that both acetate fermentation and oxidation to CO_2 may have affected methane in the boreholes.

With the aim of obtaining undisturbed pore water samples, Fernández *et al.* (2007) performed an *in situ* water sampling experiment from a dedicated borehole in the Mont Terri Rock Laboratory. Key water parameters, such as pH, E_h , Fe(II), S^{2-} and alkalinity were measured under controlled conditions inside an anoxic glove box. After an initial oxidizing perturbation, stable parameters were obtained. The waters are Na-Cl type, with ionic strengths ranging during the different water sampling campaigns from 0.43 M to 0.39 M. pH increased from 6.8 (during oxidizing perturbation) to 7.6, while E_h values (SHE) decreased from +83 to -24 mV. Fe(II) concentrations ranged between 1.0 and 3.1 mg/L. Total sulphide measurements were always below detection limit (< 0.1 mg/L) while sulphate stabilised at around 1600 mg/L after the initial oxidizing perturbation. The measured values for E_h are much higher than the expected value of the Opalinus Clay formation, which is around -200 mV (Pearson *et al.*, 2003; Wersin *et al.*, 2004). A model of the main water-rock interaction processes showed that the measured values corresponded to the $\text{Fe}^{2+} \leftrightarrow \text{Fe}(\text{OH})_{3(s)}$ redox couple. The redox value for undisturbed conditions was also modelled, and a value of -196 mV was obtained. In this system, the E_h is controlled by the sulphate/pyrite or pyrite/Fe(III) couples.

7.3. Callovo-Oxfordian formation

The Callovo-Oxfordian formation of the eastern Paris Basin is a 130 m thick clay rich sedimentary sequence. The Callovo-Oxfordian claystone (COx) was deposited during flooding events in the Callovian and Oxfordian. The claystones are mainly composed of clay minerals (40-60%, mainly illite, kaolinite and illite/smectite mixed layers), calcite (20-40%), quartz (15-35%) and pyrite (0-2%). Its water content is around 8 wt%, and its hydraulic conductivity is between 10^{-14} and 10^{-12} m/s (ANDRA, 2005).

Up to 2005, knowledge on the Callovo-Oxfordian pore water composition was mainly built on geochemical modelling. A geochemical model had been defined from physico-chemical and mineralogical characteristics obtained from bore cores drilled on the site of the Meuse/Haute Marne Underground Research Laboratory (URL) (Gaucher *et al.*, 2006). One of these characteristics is the EDC. The EDC of all reducing species was quantified roughly during oxidation of the sample by potassium dichromate (3 h - 150°C) after sulphuric acid attack (Gaucher *et al.*, 2004). The mean value for the formation is 4.7 ± 1.3 meq/g. These values are similar to those measured in the Opalinus Clay Formation, 4.8 ± 0.9 meq/g (Pearson *et al.*, 2003; borehole A6). The range of variation is narrow. With the exception of Mn, the concentration of species determining the reducing character of the rock (TOC, Fe and S), are well correlated with the general EDC value.

Three types of sulphide were identified: pyrite which is the most abundant sulphide; sphalerite (ZnS) was identified in a few samples, locally in combination with pyrite; chalcopyrite (CuFeS_2) was identified in only one sample. As a rule, pyrite is fairly abundant in the studied samples, occurring as isolated euhedral crystals, clusters without any particular form, and as pseudomorphs of bioclasts, but the most common are framboids. No trace of typical weathering minerals affecting the pyrites was identified. Also Fe-rich carbonates were identified, possibly siderite, mostly at the base of the formation.

Since 2005, water has been sampled *in situ* in several URL boreholes equipped with various setups. The experiments dedicated to pore water characterization were based on feedback from similar pore water studies in the Mont Terri rock Laboratory (Pearson et al., 2003). Two setups were used: water circulation experiments and gas circulation / water sampling experiments (Vinsot et al. 2008).

In the water circulation experiments, field pH measurements varied between 7.2 and 7.8. The lowest field E_h values were -200 and -65 mV in the first and the second experiment, respectively. These results are mainly based on immediate measurements, as the on-line measurements did not work properly. One month after the start of the first experiment, a smell of sulphide was detected; i.e., sulfate reduction set on, leading to a decrease of sulfate and an increase of sulfide concentrations at the end of the first run. The trend went on in the course of the second run during which sulfide concentrations of 2 mmol/L and above were measured. Concurrently, the carbon species changed. Organic carbon contamination occurred during the installation of the equipment which contained residues of alcohol used for disinfection. Alcohol slowly leaked out of the porous ceramic filter leading to peak organic carbon values of 0.8 mol C/L after 56 days. This carbon was transformed partly into acetic acid, as shown by isolated measurements: 3 mmol/L after 56 days, 18 mmol/L after 398 days and increased further to reach 32 mmol/L in the last measured sample (day 576). This caused the alkalinity to increase to a similar concentration (31.4 meq/L). Microbial analyses confirmed the presence of sulfate reducing bacteria. 6000 cells/mL were detected in the first run of the first experiment after 56 days. Despite the water replacement, sulphate reducing bacteria were thriving during the following run, but weaker, around 600 cells/mL in the most recent sample (day 621 of the 4th run).

In the second experiment, despite some precautions, such as equipment disinfection, addition of bactericide in the synthetic pore water, and the avoidance of organic carbon contamination, a slight sulfate reducing activity was detected by microbial analyses after 44 days with 2.5 cells/mL of sulfate-reducing bacteria. Thiosulfate reducing bacteria were still below the detection limit of 0.5 cells/mL. In the next samples the population of sulfate reducing bacteria increased and seemed to stabilize between 250 and 600 cells/mL. In this experiment, sulfide concentration was measurable in the first month of the experiment (days 9 and 33) and again after 287 days; in between it was below the detection limit of 0.5 mg/mL.

In the first gas circulation / water sampling experiment in which some alcohol remained after installation, the pH value ranged from 5.5 to 7.5 between the 150th and the 350th day of the experiment, then stabilized to 7.5 ± 0.2 between the 450th and the 650th day. In the case of the second experiment, the pH value remained stable at 7.2 ± 0.2 during more than 300 days. The representative values of the on-line E_h measurements (i.e. Pt electrode potentials) are mostly between -160 and -220 mV. They seem to converge to $-200 \text{ mV} \pm 20 \text{ mV}$ for both experiments. A geochemical model had been defined from physico-chemical and mineralogical characteristics obtained from bore cores drilled on the site of the Meuse/Haute Marne Underground Research Laboratory (URL).

8. Conclusions

The redox properties of natural clay-rich sediments can be complicated and its redox characteristics cannot be appropriately represented by only one master variable, E_h . Elaborated geochemical characterization in combination with thermodynamic calculations might provide the most reliable description of the redox state of the system. Recently developed electrochemical methods, which are capable of probing redox-active solids, might be suitable to provide complementary information about the redox state of constituents whose redox potential is difficult to determine based on chemical analysis and thermodynamic considerations. For predicting the redox speciation of radionuclides in the clay-rich sediments, it has to be known which redox couples in the system are represented by the reported E_h values. Depending on the reactivity of the corresponding species of these redox couples towards radionuclides the reported value might only constrain the upper or lower limit for the radionuclide's E_h .

9. Literature

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