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Metallic corrosion processes reactivation sustained by iron-reducing bacteria: Implication on long-term stability of protective layers

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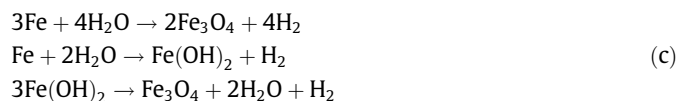
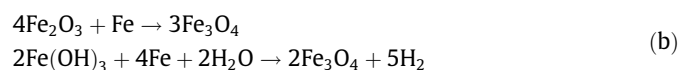
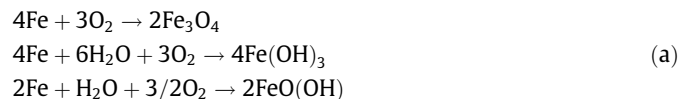
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In deep geological environments foreseen for the disposal of radioactive waste, metallic containers will undergo anaerobic corrosion. In this context, the formation of corrosion products such as magnetite may reduce the rate of corrosion processes through the formation of a protective layer. This study aims at determining the direct impact of iron-reducing bacteria (IRB) activity on the stability of corrosion protective layers. Batch experiments investigating iron corrosion processes including the formation of secondary magnetite and its subsequent alteration in the presence of IRB show the bacteria ability to use structural Fe(III) for respiration which leads to the sustainment of a high corrosion rate. With the bio-reduction of corrosion products such as magnetite, and H₂ as electron donor, IRB promote the reactivation of corrosion processes in corrosive environments by altering the protective layer. This phenomenon could have a major impact on the long-term stability of metallic compounds involved in multi-barrier system for high-level radioactive waste containment.

1. Introduction

The French concept for deep geological radioactive waste disposal is based on a multi-barrier system involving metallic containers placed in a thick clayey host rock in order to ensure radionuclide confinement. One of the most important criteria for the safety assessment of such geological facilities concerns the lifespan of the metal containers. In such deep geological environments (elevated pressure and temperature, low water content, presence of metallic components, and microbial activity), many factors may alter the expected containment properties of metal containers. In nuclear waste disposal conditions, many corrosion reaction processes are liable to occur: (a) aerobic aqueous corrosion during the operational phase, (b) transformation of minerals during the transition to anaerobic conditions and (c) anaerobic corrosion (Andra, 2005):



These classical aqueous corrosion processes form thermodynamically stable phases such as Fe-oxides (mainly magnetite Fe₃O₄) and produce significant quantities of H₂. Nevertheless, the stability of these oxide compounds, which protective role leads to low corrosion rates, may be affected by the action of biological agents sustaining the bio-catalysed mechanisms which are known to consume them (Kukkadapu et al., 2010). It is thus crucial to determine the quantitative impact of such bio-activated processes for the assessment of metal container evolution on the long term.

The activity of microorganisms has recently been evidenced in deep clayey environments: in Callovo-oxfordian argillite (Poulain, 2006), Opalinus clay (Mauclaire et al., 2007; Stroes-Gascoyne et al., 2007) and in bentonite swelling clay used as an engineered barrier (Pedersen and Motamedi, 2000). These observations raise the question of the impact of microorganisms on corrosion parameters due to processes such as "biologically induced corrosion" (Stroes-Gascoyne and West, 1997). As a first step, an inventory of the nutrients capable of supporting such bacterial activity was performed, taking into account energetic compounds and fluxes in the specific case of the French geological radioactive waste disposal concept (Esnault et al., 2009). Different sources of energetic compounds and nutrients were identified: organic matter and H₂ being among the most important. H₂ is known as one of the most

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efficient energetic substrates for deep terrestrial subsurface environments (Lin et al., 2005). Large amounts of H₂ gas are expected to be produced inside radioactive waste repositories, originating from the corrosion of metallic components in anoxic conditions and water radiolysis. Such conditions will consequently facilitate microbial activity in this specific environment (Libert et al., this issue; Galès et al., 2004). Fe(III) from minerals present in this environment could prove to be the main electron acceptor for microbial reduction. Corrosion products containing Fe(III), such as magnetite (Fe₃O₄), also sustain the development of iron-reducing bacteria (IRB) in these environments and could impact the geochemical conditions of deep geological environments. New research was carried out on the impact of iron-reducing bacteria (IRB) on metallic corrosion processes in order to determine the biological parameters necessary to assess geochemical variations and the sustainability of metallic components in geological disposal conditions. Biocorrosion processes triggered by IRB species have been less investigated compared to sulphate-reducing bacteria (Castaneda and Benetton, 2008; Rainha and Fonseca, 1997; Féron et al., 1997; Stott, 1993). However, it has already been seen that the reduction of insoluble ferric ion compounds into soluble ferrous ion compounds facilitates the removal of protective corrosion products formed on exposed iron alloy surfaces (Videla, 1996). It has also been reported that IRB are involved in the formation of biofilms which promote corrosion (Geeseey, 1991). Nevertheless, the role of IRB in biocorrosion is still under debate: while IRB is thought to enhance corrosion processes, other studies suggest that IRB may constitute a protection for carbon steel by the formation of a protective biofilm (Dubiel et al., 2002; Lee and Newman, 2003; Herrera and Videla, 2009).

The objective of this research is to determine the impact of IRB activity on corrosion processes under geochemical conditions representative for a deep geological repository. To support these investigations, physicochemical studies were performed in the presence of a model microbe species: the ferric-reducing bacterium "*Shewanella oneidensis strain MR-1*". This paper particularly investigates the capacity of this bacterium to reduce Fe(III) from magnetite using hydrogen according to the following reaction: $H_2 + Fe_{magnetite}^{3+} \rightarrow Fe_{solution}^{2+} + 2H^+$ in metallic corrosion processes.

2. Material and methods

2.1. Batch experiments

Two types of experiments – abiotic (without bacteria) and biotic (viable or no viable bacteria) – were performed in sterile anaerobic Teflon reactors (Table 1) containing 100 mL of a synthetic medium (Mclay) which has, as a base medium, the following composition: 9.0 mM (NH₄)₂SO₄, 0.33 mM K₂HPO₄, 0.33 mM KH₂PO₄, 2.0 mM NaHCO₃, 1.01 mM MgSO₄, 0.485 mM CaCl₂, 56.6 μM H₃BO₃, 10.0 μM NaCl, 1.0 μM FeSO₄, 5.0 μM CoSO₄, 5.0 μM Ni(NH₄)₂(SO₄)₂, 3.87 μM Na₂MoO₄, 1.5 μM Na₂SeO₄, 1.26 μM

MnSO₄, 1.04 μM ZnSO₄, 0.2 μM CuSO₄, 0.115 μM arginine, 0.118 μM glutamate, and 0.190 μM serine. This Mclay medium was prepared by making minor changes to the medium's composition according to Kostka et al. (1996) in order to resemble the chemical composition of natural argillite interstitial water as much as possible (Beaucaire et al., 2008). In a second step, 1 g of metallic iron powder (Merck, Ø 10 μm) or synthetic magnetite mineral powder (Aldrich 31,006–9, <5 μm), sterilised in an irradiator at the CEA/Cadarache Centre (Cobalt radioactive source (⁶⁰Co) delivering a total dose of 35 kGy to kill live bacteria), was added to the reactor. After introducing the bacteria samples (biotic experiments only), these batches were incubated at 40 °C in the dark under permanent stirring. Control experiments (abiotic experiments) were conducted in the same conditions with no viable bacteria obtained by heating at 120 °C for 1 h. Biotic experiments were performed at pH 7 (pH of Mclay medium) and abiotic experiments were conducted with 3 different pH levels (pH 6, pH 7 and pH 8) by adding the appropriate volume of HCl or NaOH (0,1 N). Three replicates for each abiotic or biotic experiment were performed. The results will be given as an average of those obtained for these three replicates. Anaerobic conditions were obtained during incubation by bubbling a gas mixture: 90% N₂, 10% CO₂ for metallic iron experiments and 60% H₂, 30% N₂, 10% CO₂ for magnetite experiments.

2.2. Bacteria

The facultative anaerobic bacterium *Shewanella oneidensis strain MR-1* was used as the iron-reducing bacteria (IRB). This bacterium is an obligate-respiratory bacterium, incapable of fermentation (Scott and Nealson, 1994). *Shewanella oneidensis MR-1* was grown in the Mclay culture medium with 50 mM of Fe(III) citrate as the electron acceptor prior to transfer to the experimental reactor. The initial cell density of all cultures was 2×10^6 mL⁻¹, as estimated by the relationship between optical density and direct cell counts (Francois et al., 2005). Optical density was measured at 600 nm using Cary 5G, UV–Vis–NIR spectrophotometer (Varian®). Measurements were corrected by a blank containing only pure Mclay medium. The viability of the *Shewanella oneidensis MR1* cells was checked using a combination staining of Syto® 9 green fluorescent nucleic acid (Molecular Probes, Eugene, OR, USA) and propidium iodide (Sigma–Aldrich, Steinheim, Germany). Cells with an intact cell membrane, considered as living, will stain green, while cells with a damaged cell membrane, which are here considered as dead, will stain red. The protocol is based on the LIVE/DEATH® BacLight™ Bacterial Viability Kits (Molecular Probes).

2.3. Geochemical analyses

2.3.1. Aqueous iron

A 4 mL reactor sample was taken to monitor any chemical changes in the trace element (i.e. iron) and filtered at 0.22 μm (Millipore® filter). The batch solution was monitored for total Fe

Table 1
Initial conditions for abiotic and biotic experiments.

Experimental conditions	Medium	Minerals	Initial pH	Gas mixture	Replicates
<i>Abiotic</i>					
No bacteria	Mclay	Fe	6	N ₂ (90%)CO ₂ (10%)	3
	Mclay	Fe	7	N ₂ (90%)CO ₂ (10%)	3
	Mclay	Fe	8	N ₂ (90%)CO ₂ (10%)	3
<i>Biotic</i>					
Dead bacteria	Mclay	Fe	7	N ₂ (90%)CO ₂ (10%)	3
	Mclay	Magnetite	7	H ₂ (60%) N ₂ (30%) CO ₂ (10%)	3
Live bacteria	Mclay	Fe	7	N ₂ (90%)CO ₂ (10%)	3
	Mclay	Magnetite	7	H ₂ (60%) N ₂ (30%) CO ₂ (10%)	3

(dissolved FeII + FeIII) using coupled plasma-atomic emission spectroscopy (ICP-AES Jobin Yvon® ultra-trace). The sample was acidified with Merck Suprapur nitric acid (4%, final volume).

The Fe(II)/Fe(III) ratio in solution was monitored using Ferrozine colorimetric methods adapted from Viollier et al. (2000), which utilises dissolved Fe(III) solutions and their reduced products after the addition of hydroxylamine hydrochloride as standards, and interpreted according to the updated procedure described by Washington et al. (2004).

2.3.2. H₂ produced

An optimised method of H₂ measurement at low pressure was carried out using gas chromatography (Varian® GC 4900) coupled with a sensitive pressure sensor (Baumer®; $0-2 \times 10^5 \text{ Pa} \pm 10^{-2} \text{ Pa}$). To perform gas analysis, thermostatic reactors were linked to gas chromatography by a sterile syringe. Gas was pumped and mixed with a vector gas (nitrogen) and analysed through a molecular sieve packed column in order to identify the H₂ proportion in each reactor by catharometric detection.

2.3.3. Corrosion products

Samples were characterised before and after biotic and abiotic alteration by X-ray Diffraction (Bruker®). At the end of each experiment, the sample was collected and washed carefully twice with 50 mL ultrapure water. Slurry of the final suspension was deposited on XRD-dedicated glass slides and air-dried to enable a favourable orientation of the particles for efficient diffraction. XRD scans were recorded between 2 and 40°2θ (counting time of 2 s per 0.02°2θ step size) with a Bruker D8 diffractometer (Cu radiation at 40 kV and 40 mA) equipped with a Göbel mirror and a Sol-X detector.

3. Results

3.1. Abiotic corrosion processes

H₂ is produced during the aqueous anaerobic corrosion experiments (Fig. 1); its concentration increases in a non-linear fashion with time (the corrosion kinetics increase during a first step from 0 to 300 h, before decreasing from 300 to 1200 h during a second step). In parallel, the iron concentration increased and peaked at 100 h, then decreased from 100 to 200 h, before finally stabilising after 200 h. This is interpreted as a decrease in the corrosion kinetics (H₂ production curve) while a significant proportion of the iron, initially released, precipitates in solid form in the system. This phenomenon is more obvious in the experiment with pH 6 than in the experiment with pH 8, as can be expected due to the well known dependency of corrosion processes on pH (decreasing corrosion

rate from pH 6 to pH 8). An increase in pH was observed at the end of the experiments (7.72 for the pH 6 experiments, 8.05 for the pH 7 experiments and 8.56 for the pH 8 experiments). The fact that the precipitation of iron minerals is followed by a decrease in the H₂ production suggests that a protective layer may have formed on the surface of the metallic iron (Papillon et al., 2003). XRD analysis does show the formation of magnetite in a large proportion and siderite in a smaller proportion for abiotic corrosion experiments (Fig. 3).

3.2. Biocorrosion processes (with or without viable bacteria)

These experiments (see Step One, Fig. 2) were started in the same conditions as the abiotic experiments for up to 400 h. Bacteria samples (dead for the control experiment and alive for the biotic experiment) were then added to the reactor with iron powder in the MClay solution media at pH 7. No significant differences were observed in the corrosion process between both biotic experiments – dead (grey line) or live bacteria (red line). The same corrosion profile was obtained for both the abiotic and biotic experiments (Fig. 1), i.e., increased H₂ production and iron concentration in solution (up to 100 h) followed by a decrease in both the dissolved iron concentration and the H₂ production kinetics (from 100 h to 300 h). Nevertheless, the corrosion rate is higher in the presence of organic biomass, live bacteria or dead bacteria (Fig. 2, Step One) in comparison with the abiotic experiment at pH 7 (Fig. 1). Metallic corrosion is therefore accelerated when the ionic strength of the solution is high: $1.0 \pm 0.05 \text{ mmol}$ of H₂ is produced in the abiotic experiment (Fig. 1 at 200 h) compared with $1.3 \pm 0.08 \text{ mmol}$ of H₂ in the biotic organic experiments (Fig. 2 at 200 h). Moreover, no bacteria are alive at 380 h, which can be explained by the lack of Fe(III) mineral at the beginning of the experiment which entails dead cells.

In the second step (Fig. 2, Step Two) at 400 h, bacteria samples (irradiated or alive) were once again added to both the control experiment (irradiated bacteria) and the live experiment. This was necessary so as to determine the influence of living bacterial activity on the corrosion process when corrosion products are present in the system. Irradiated bacteria were added in order to compare results at the same ionic strength for both biological experiments with pH 7. No difference was observed between the abiotic corrosion experiment with pH 7 (Fig. 1) and the experiment with additional irradiated bacteria (Fig. 2, grey curve) in terms of H₂ production and iron in solution (decrease in both parameters). This indicates that the change in the ionic strength does not affect the alteration of corrosion products in these experimental conditions (Fig. 3). In living bacteria experiment, bacteria are still alive at the end of experiment ($1 \times 10^7 \text{ mL}^{-1}$). Moreover, a significant increase in the iron concentration in solution and an increase in

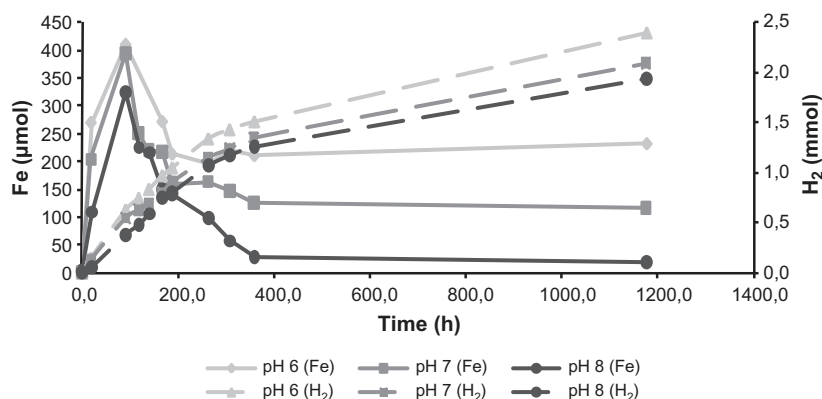


Fig. 1. Anaerobic aqueous corrosion of iron powder at different pH: variation in total dissolved iron (solid lines) and H₂ (dashed lines) concentration in batch reactor. (Dashed lines = H₂, solid lines = dissolved Fe).

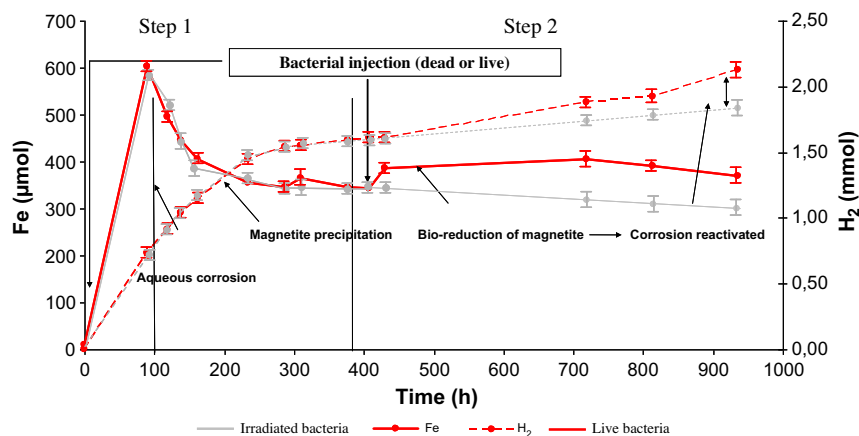


Fig. 2. Influence of IRB on metal corrosion: bioreduction of corrosion products (grey curve: experiment with dead bacteria; red curve: experiment with live bacteria; iron (solid lines) and H₂ (dashed lines) concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

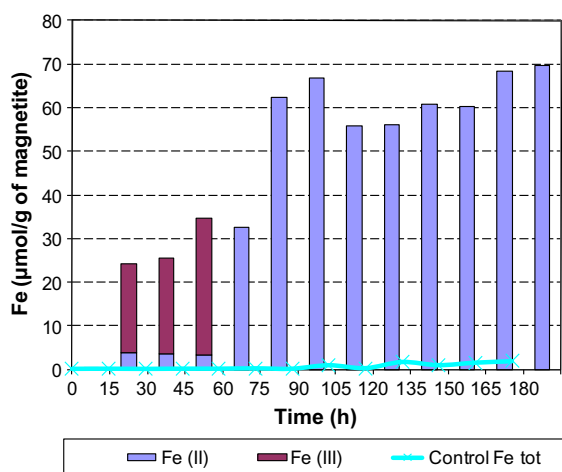


Fig. 3. X-ray diffraction analysis: Biotic impact on corrosion process: Magnetite disappears in presence of IRB and the siderite peak increases in intensity.

the H₂ production were observed in the presence of living bacteria (Fig. 2, red curve), i.e. the activity of living bacteria governs the reactivation corrosion processes. XRD analyses confirm this observation; they reveal the complete dissolution of magnetite in favour of siderite in the presence of bacterial activity, whereas magnetite is still present in the case of iron corrosion with irradiated bacteria (Fig. 3). The formation of Fe (II)-phosphate mineral such as vivianite was not observed due to the low concentration of phosphate in solution (simulating the composition of deep water). In the context of corrosion of radioactive waste containers, IRB development is sustained by the consumption (H₂) and the reduction of corrosion products (iron oxides such as magnetite). The IRB activity could therefore decrease the effect of the “protective” magnetite layer and consequently increase or reactivate the corrosion rate. The bacterial activity could therefore have an indirect influence on the corrosion processes.

3.3. Bio-reduction mechanisms of corrosion products in deep geological environments

In order to validate magnetite reduction by hydrogenotrophic metabolism, several new experiments containing pure magnetite were performed in the same conditions, but with an anaerobic atmosphere (H₂/N₂/CO₂ gas, 60%/30%/10% respectively). These

experiments showed an increase of Fe(III) and Fe(II) in solution in presence of IRB species compared with the same experiment in abiotic conditions (see the total Fe in the control experiment in Fig. 4). The microbial alteration of magnetite is only possible due to the bioavailability of structural Fe(III) and H₂ consumption (results not shown) in a process involving live metabolism. The biocorrosion hypothesis is therefore validated through the respiration of Fe(III) contained in magnetite, and supported by H₂ as single electron donor.

Previous experiments have shown that the presence of corrosion products such as magnetite may decrease the iron corrosion rate. It is thought that magnetite forms a protective layer on the metallic iron surface and that H⁺ from the water can not access the metal: this phenomenon is a well-known corrosion process which includes the formation of passivation layer which protects metal frames (Sanchez-Lopez, 1998). Nevertheless, IRB activity promotes the Fe(III) reduction of magnetite with a decrease in the redox potential (−200 to −350 mV) compared with the abiotic experiments (−100 to −250 mV), together with the alteration of the magnetite protective layer. Moreover, Fe(III) respiration results in H⁺ production which may significantly affect the stability of others minerals (carbonate and clay minerals), e.g. promoting the formation of siderite at the expense of calcite (Fig. 5). Therefore, chemical equilibrium tends to favour the formation of siderite in the disposal environment when carbonate is found in the interstitial water (around 10^{−2} mol L^{−1}, see Fig. 5).

4. Discussion and conclusion

The activity of iron-reducing bacteria has been investigated under conditions close to those expected in radioactive waste repositories in order to assess its impact on corrosion processes, which control the duration of the containment properties of metallic components on the long-term.

This study does not demonstrate the corrosive protective phenomenon of IRB in terms of metal behaviour as discussed in a previous study by Videla and Herrera (2009). These authors explain that corrosion inhibition is developed on biofilmed metal surfaces when the exopolysaccharide (EPS) impede the dissolution of Fe²⁺ corrosion products. EPS behaves as a barrier between the metal and the environment. However, this is still a matter of debate as previous studies (Myers and Nealson, 1998; Ottow and Munch, 1980) show that physical contact between bacteria and the iron oxide is necessary to achieve iron reduction. However, others experiments have shown that the iron reduction of Fe(III) hydroxides was possible at a distance through a biosynthesized electron shuttle (Lies et al.,

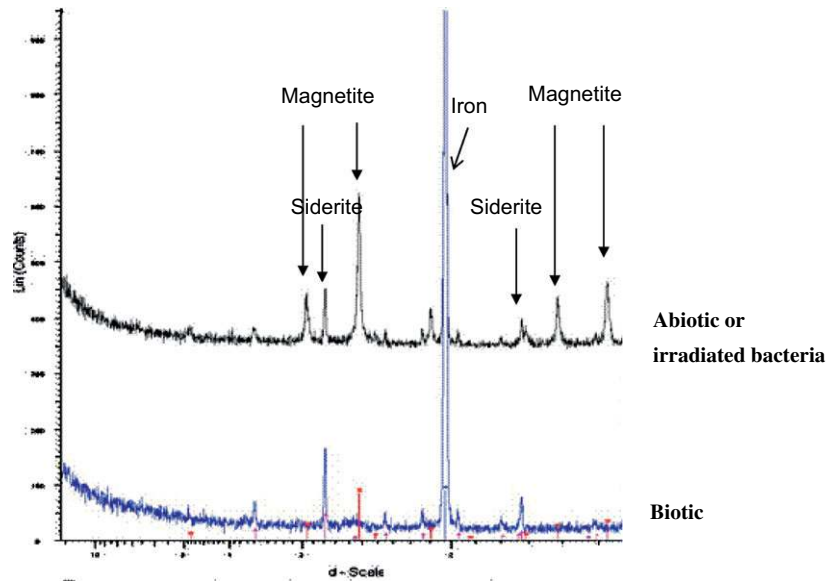


Fig. 4. Bio-alteration of magnetite by *Shewanella oneidensis* MR1 in the presence of H₂ as electron donor. Fe Speciation is plotted in the graph: purple bars (Fe³⁺) and blue bars (Fe²⁺), blue curve represents abiotic experiment).

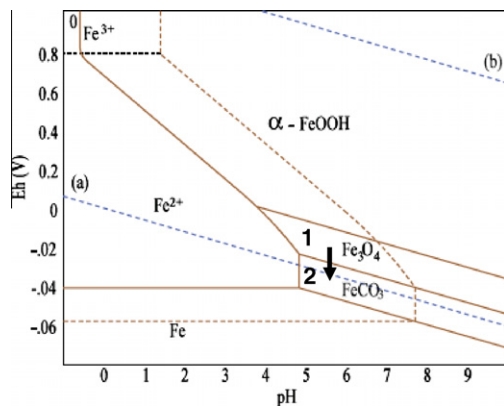


Fig. 5. Pourbaix diagram for Fe–H₂O–CO₂ (pCO₂ = 10⁻² atm and a(Fe²⁺) = 1). A level of 10⁻² atmosphere of carbon dioxide is used in this model. This partial pressure is representative in the groundwater environment. Influence of bacteria reduction on Fe(III) oxides to promote the formation of iron carbonate (FeCO₃); transition from stage 1 to stage 2 in the graph.

2005). In our study, the magnetite was destabilised and the production of H₂ increased significantly in the biotic experiments, while no reactivated corrosion was observed in the abiotic experiment. Even if a biofilm is formed, the H₂ production nevertheless increases significantly after bio-reduction, which indicates that the metal surface is not protected against the corrosive environment. Fe²⁺ corrosion products are released into the solution and may react with carbonates to promote the formation of siderite.

Potential impacts include the geochemical equilibrium in the interstitial water and its effect on the stability of the corrosion products. Previous studies stressed the role of IRB, which can surpass SRB and methanogenic bacteria in the use of H₂ as an energy source (Fredrickson and Gorby, 1996). In clayey sedimentary and diagenetic environments, the geochemical control of the iron cycle is the result of competition between reactions involving sulphur, carbonate and clay minerals. Experimental and modelling studies of iron–clay interactions (Lantenois et al., 2005; Jullien et al., 2005; Bildstein et al., 2006; De Combarieu et al., 2007) have shown

the presence of iron oxide (magnetite essentially) and Fe-rich silicate from the serpentine group as corrosion products. The formation of magnetite or other Fe(III)-bearing minerals and molecular H₂ may promote the selection of hydrogenotrophic IRB species for bacterial activity. This study demonstrates the possibility of using Fe(III) produced from magnetite (anaerobic corrosion of metallic iron) as an electron acceptor for bacterial development with the presence of H₂ in the context of active metallic corrosion. Consequences of this Fe(III) bacterial respiration include the alteration of the magnetite protective layer and the possible reactivation of iron corrosion (with further H₂ production), considering that the metal surface will be exposed to the corrosive solution. The IRB species therefore promote indirect corrosion by the respiration of Fe(III) contained in corrosion products.

In conclusion, the role of IRB activity could be a key parameter in the safety assessment of deep geological disposal. Corrosion products, the mixed valence of Fe oxides (e.g. magnetite) and H₂ gas will all favour the hydrogen-oxidising IRB development in the context of active corrosion of metallic radioactive waste containers. This bacterial activity may alter the corrosion products acting as a protective layer on the metal surface. In the geochemical conditions of a deep geological repository, IRB activity could be favoured in environments of active corrosion. This could support the reactivation of corrosion processes and consequently have an impact on the sustainability of metallic compounds involved in safety functions of underground disposal components.

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