MEDIUM ACTIVITY LONG-LIVED NUCLEAR WASTE; MICROBIAL PARADISE OR HADEAN ENVIRONMENT – EVALUATION OF BIOMASS AND IMPACT ON REDOX CONDITIONS

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The evaluation of the impact of possible microbial activity in nuclear waste cells has been a subject for more than a quarter of a century (cf. NEA work-shop Paris 1985). Some of the items of interest in relation to microbial impact on near field biogeochemistry indicated in Table 1 had already been known as pertinent.

Table 1: Possible impact of microbes and microbial metabolism on near field biogeochemistry

Enhancement of redox reaction kinetics (particularly involving nitrates, sulphate, selenate, pertechnetate, organic matter and H_2), thus a faster move towards reducing conditions, important to guarantee the low mobility of critical RN
Increased retardation of mobile RN in biofilms (i.e. adsorption on microbial cell surfaces and products of possible bio-mineralization); complexation by embedded extracellular polymeric substances
Secretion of organic substances (i.e siderophores) known to complex RN and to enhance their mobility
Biodegradation of dissolved organic substances, such as those released form the waste (organic acids) or generated by microbes
Production of CO_2 or other gases that may affect cement integrity
Production of sulphides or thiosulphates that may enhance corrosion

Recently, it became clear that a distinction needed to be made between high-level, vitrified waste and organic matter containing intermediate-level waste, of which the bituminised waste is used as an example here. For high-level waste the canister walls play an important safety role and the most probable limiting aspects, next to space and water, are the low concentrations in organic matter as a carbon source and phosphorous and nitrogen as essential elements. In this particular case, microbially induced corrosion is of primary concern (cf. Stroes-Gascoyne *et al.*, this meeting).

In the case of the French intermediate bituminised waste, primary interest is on the impact of microbial activity on redox reactions, with the high pH environment, as a consequence of the concrete engineered barrier, as the most probable limiting condition. The canister wall has no explicit long-term safety role and all components for microbial activity will become readily available. The presence of nitrates, sulphates and Fe(III) as electron acceptors and organic matter, hydrogen gas and zero-valent metals (i.e. Fe) as electron donors allows the system to supply energy for bacterial activity and to move through the entire redox sequence from O_2 (present only shortly after waste-cell closure) to nitrate, Fe(III), sulphate and organic matter reduction (Figure 1, see also Small *et al.*, this meeting).

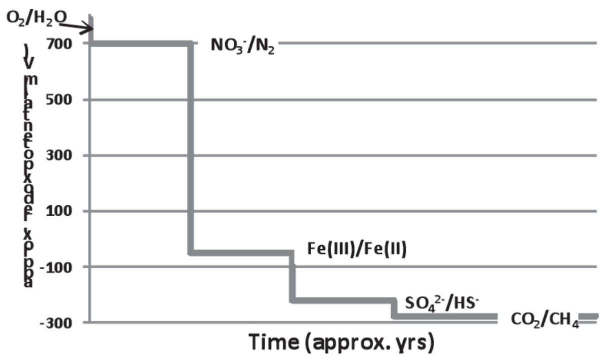

Figure 1: Evolution of the redox potential as a function of disap-pearance of electron acceptors.

Prevailing uncertainties do not allow specification of timing for the redox-changes shown on Figure 1. These uncertainties are essentially related to the lack of knowledge regarding microbial catalysis. As no natural or anthropogenic analogues are available, parameters need to be obtained from experiments (currently ongoing, cf. Pauwels *et al.* this meeting).

Two approaches will be presented that allow estimation of the near-field biogeochemistry without detailed knowledge of kinetic parameters:

The **first approach** is a mass balance which considers the masses of both the oxidizing and the reducing agents in a single waste cell. In the simplest case only nitrates, sulphates and Fe(0) are considered; nitrates are reduced to N_2, sulphates to S^{2-}, and all Fe is oxidised to Fe_3O_4, the latter generating hydrogen gas. Of the produced H_2, 25% serves to reduce nitrates and 55% to reduce sulphates. Further mass balance calculations are underway that consider the direct reaction of nitrates with Fe(0), a reaction for which very little relevant information is available. It is know that nitrate solutions may inhibit corrosion (Gaidis, 2004), but they are also known to react with iron (Yang & Lee 2005). Furthermore, Fe(III), initially present in the engineered barrier or in the host rock and produced as a consequence of Fe(II) oxidation by O_2 during waste cell opening, will also be considered.

The **second approach** combines the previous one with a quantification of free energies, which in turn can be used to form microbial biomass according to the simple relationship 1 g per 64 kJ (Thauer and Morris, 1984). With balanced stoichiometric reactions and thermodynamic data at pH 12 first estimates indicate a production of 0.7 kg of biomass per waste container. This is significantly higher than what has been estimated for high-level waste cells, where bacterial activity was modelled to be essentially limited to the first 100 years, when the system is partially characterised by the presence of O_2 (McKinley *et al.*, 1997). However, these preliminary calculations assume that all nutrients are simultaneously bioavailable and that the energy requirement for microbial biomass production at low pH can be used as a first estimate for higher pH setting. Ongoing work will be presented that considers parameter uncertainties using a Monte Carlo approach, results which allow assessing the upper and lower limits of bacterial production. These values can then be used to quantify the different types of bacterial impact given in Table 1.

Compared to a low food, low space, low water, "Hadean" environment of high-level waste cells, at least the bituminous waste cells may turn out to become a microbial "Paradise". But the bacterial action may well have a positive impact on the safety assessment, by catalysing the reduction of nitrate and sulphate and the oxidation of hydrogen gas; thus significantly reducing their concentrations and helping the system to move again toward the reducing conditions characterised by the sulphate/sulphide system initially controlling the host rock redox situation. But uncertainties remain regarding microbial development in the high pH concrete environment. The intermediate-level waste cells may thus just as well turn out to be a "Hadean" environment, unsuited for significant microbial development.

References:

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