

# **TECHNICAL REPORT 89-06**

**AN APPROACH TO  
MICROBIOLOGICAL MODELLING:**

**APPLICATION TO THE NEAR FIELD  
OF A SWISS LOW / INTERMEDIATE-  
LEVEL WASTE REPOSITORY**

JUNE 1990

H. A. GROGAN <sup>1)</sup>  
I. G. MCKINLEY <sup>2)</sup>



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## ABSTRACT

This report presents a general approach to modelling of microbiological activity in a geological system constrained by the availability of nutrients and energy sources. Application of this model to determine the possible consequences of such microbiological activity in a repository for low- and intermediate-level nuclear waste (L/ILW) is demonstrated both for the repository considered as a whole and for a more realistic sub-section containing a particular waste type (ion-exchange resins immobilised in cement). Possibilities for further development of the model to consider the spatial distribution of components within the near field are also discussed.

## ZUSAMMENFASSUNG

Dieser Bericht behandelt in allgemeiner Weise die Modellierung mikrobiologischer Aktivität im Rahmen eines geologischen Systems. Die Aktivität wird durch die Verfügbarkeit von Nährstoffen und Energiequellen eingeengt. Die Anwendung dieses Modells zur Bestimmung möglicher Folgen einer solchen mikrobiologischen Aktivität innerhalb eines Endlagers für schwach- und mittelaktive Abfälle wird sowohl bezüglich des Endlagers als Ganzes dargestellt als auch für eine realistischere Untereinheit, die eine bestimmte Art von Abfall enthält (Ionentauscherharz, das mit Zement verfestigt worden ist). Möglichkeiten zur Weiterentwicklung des Modells, um die räumliche Anordnung der verschiedenen Komponenten innerhalb des Nahfelds zu berücksichtigen, werden ebenfalls in Betracht gezogen.

## RESUME

Ce rapport présente une approche généralisée de la modélisation de l'activité microbiologique dans un système géologique qui est soumise à la disponibilité d'éléments nutritifs et de sources d'énergie. L'application de ce modèle pour déterminer les possibles conséquences d'une activité microbiologique dans un dépôt final pour déchets nucléaires de faible et moyenne activité est présentée d'une part pour le dépôt considéré dans son ensemble et d'autre part, ce qui est plus réaliste, pour l'une de ses parties renfermant un type particulier de déchets (résines échangeuses d'ions immobilisées dans du ciment). Le rapport discute également les possibilités de développement du modèle afin de considérer la distribution spatiale de composants dans le champ proche.



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## **1 INTRODUCTION**

### **1.1 Background**

Microorganisms are known to be important factors in many geochemical processes and their presence in the environment of a Swiss L/ILW repository can be assured. Some may naturally occur in the host formation whereas others will be present as contaminants in the waste or introduced during repository construction. Repository conditions are not sufficiently hostile to preclude their continued presence and growth. It is therefore necessary to assess the impact of microbial activity on repository performance.

Some of the most likely processes for the release of radionuclides from a repository into the biosphere involve transport via flowing groundwater. Microorganisms can influence this release in a number of ways:

- Changing the chemical conditions in and around the repository (e.g. Eh, pH, complexant production)
- Gas production (e.g. CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>S)
- Changing the physical properties of the natural and engineered barriers (e.g. enhanced concrete degradation due to acid production etc.)
- Uptake of radionuclides by mobile microorganisms.

For an active microbial population to develop, sources of carbon, nitrogen, phosphorus, sulphur and energy are essential, plus certain trace elements.

For this reason the modelling approach adopted focusses upon the availability of the key nutrients (C, N, P, S) and energy within the repository environment in order to determine maximum biomass production. In this report, the consequences of this are considered only in terms of organic complexant production (previously identified as the most important influence) and the resultant increase in the release rate of specific radionuclides. The significance of microbial gas production has been studied separately (Wiborgh et al., 1986) and is not considered further here.

It should be noted that this report provides an update to an earlier report (Grogan, 1987) in which a modelling approach for describing the influence of microbial activity on the release and transport of radionuclides from a L/ILW repository was proposed. In order to avoid unnecessary duplication of information, the reader is referred to both McKinley et al. (1985) which describes the earliest modelling efforts with reference to a HLW repository and Grogan (1987) which documents subsequent development allowing consideration of the more complex environment of a L/ILW repository. The relevant background literature is also summarised and referenced within both of these reports.

In this report the modelling approach is described in detail specifying the key assumptions allowing quantitative consideration of microbial effects within a particular environment. The near field of a Swiss L/ILW repository is taken throughout this report to illustrate the application of the model.

## 1.2 Modelling approach

The conceptual model of microbial activity in the near-field of a repository is summarised in Fig. 1-1. In the current model attention is focused upon the near-field whereby the near-field inventory (waste, matrix, barrier materials) defines to what extent nutrients and energy are available for microbial biomass production and activity. The far-field is only considered in a limited way, in that the flux of groundwater passing through the repository is a source term supplying a certain quantity of nutrients and energy to the system. Naturally, before commencing an evaluation of the consequences of microbial activity in a particular system, it is prudent to determine if, in fact, microbial life could occur in such an environment. This is represented as "environmental constraints" in Fig. 1-1.

For the Swiss L/ILW repository, the near field would be characterised by a high pH ( $\geq 12.0$ ), a pressure set by  $\approx 450$  m of overburden ( $\approx 4.5$  MPa hydrostatic,  $\approx 11$  MPa lithostatic), increased temperatures ( $\approx 50^\circ\text{C}$ ; Hopkirk & Wagner, 1986) and locally increased radiation fields ( $\approx 1$  Gy hour $^{-1}$  in some cases; Nagra, 1984). Reviews of the limits of growth of microorganisms (e.g. West et al., 1985) identify examples of great tolerance to extreme environments - e.g. temperature, pressure, salinity, nutrient concentration, etc. For example, although claims of microbial activity at temperatures  $\approx >250^\circ\text{C}$  are somewhat controversial, an upper limit for life as high as  $150^\circ\text{C}$  seems to be considered reasonable (Stetter et al., 1986). These temperatures are well in excess of the expected ambient repository temperature. If the geological system under consideration contains liquid water and is located at depths less than a few kilometers, it is likely that microbial life is possible. Recent examination of subsurface sediment samples collected aseptically at the Savannah River Plant, Aiken, South Carolina, at depths ranging between 38 m to 233 m has identified significant numbers of viable aerobic (and/or facultative anaerobic) chemoheterotrophic bacteria (Fliermans, 1988). Furthermore, these microorganisms were shown to grow rapidly and degrade organic compounds under the right conditions.

Of particular relevance to the L/ILW near-field, where high pH's are anticipated due to the massive quantities of concrete, are the results of microbial sampling of the hyperalkaline waters in Oman which showed extensive populations of "relevant" micro-organisms such as sulphate reducers (Bath et al., 1987).

Microorganisms have been observed in the primary cooling system of a nuclear reactor in Belgium which has a neutron flux of  $5 \times 10^{14}$  neutrons/cm<sup>2</sup>-sec (Margeay et al., 1984) and **micrococcus radiodurans** can survive a single radiation dose in excess of  $5 \times 10^5$  rad (Nasim & James, 1978). These levels of radiation are well in excess of those likely to occur in a L/ILW repository.

Consequently, it is unlikely that the repository provides a sufficiently hostile environment to rule out microorganisms. The impact of the calculated microbial biomass and activity, as a function of time, on key near-field processes is then determined. To date the emphasis has been on the changes in speciation, solubility and hence sorption and mobility of the radionuclides. However, as the modelling and its supporting data develops a comprehensive range of effects will be accounted for including feedback mechanisms.

### MICROBIAL EFFECTS

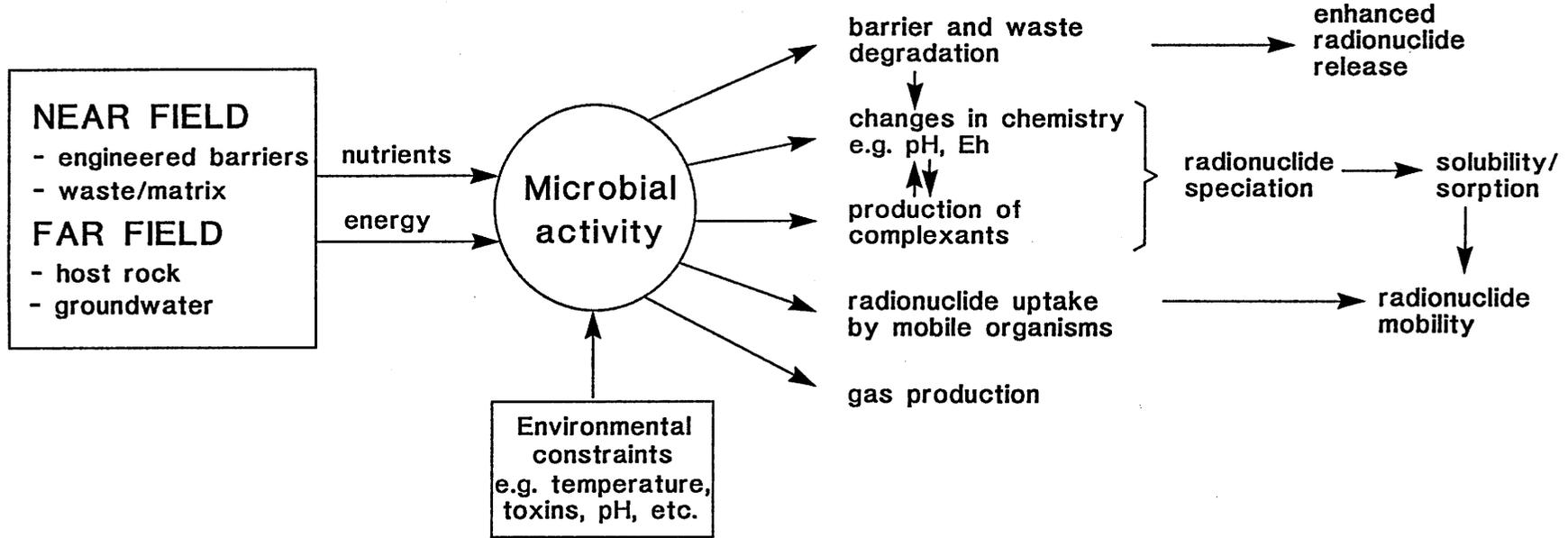


Fig. 1-1: Conceptual model of microbial activity in a L/ILW repository

**2 DESCRIPTION OF THE MODEL**

**2.1 Introduction**

In this section, a simple approach to quantifying the constraints on microbial activity is described. This involves a detailed description of the model used previously in Grogan (1987) with an expansion to examine kinetic effects not previously considered. The model output is maximum inventories of biomass or biomass production rates. The consequences of such activity are considered in section 3.3, after an example of application of the model to the near field of a repository for L/ILW.

**2.2 The box model**

In the simplest case, we can represent the system to be studied as a homogeneous region of volume  $V$  ( $m^3$ ) which will be referred to as a box containing solid and aqueous phases only (Fig. 2-1). The total porosity of this box is specified by  $\theta$  and all porosity is assumed to be connected and water filled. Transport of material into or out of the system is assumed to occur only by advection in the aqueous phase which is specified by a volumetric flow rate  $F$  ( $m^3 a^{-1}$ ).

Assuming conservation of water, the inventory of any component within the box,  $x$  say, at time  $t$  is given by

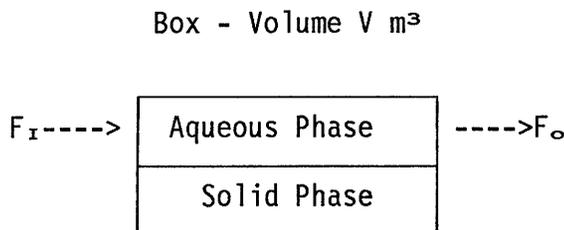
$$I_x(t) = V\theta[x]_A + V(1-\theta)[x]_S + Ft([x]_I - [x]_O) \tag{1}$$

where:

$I_x$  is the inventory of  $x$  within the box (kmol)  
 $[x]$  is the concentration of  $x$  (kmol  $m^{-3}$ )

and the subscripts:

A refers to the initial aqueous phase in the box  
 S refers to the initial solid phase in the box  
 I refers to the inflowing water  
 O refers to the outflowing water



**Fig. 2-1: Principles of the simple box model**

The maximum possible inventory of each of the key nutrient elements (C, N, P, S) as a function of time is calculated, using equation (1), taking  $[x]_0 = 0$ . It is always possible that other trace elements may be limiting, although given the very diverse chemical composition of the near field this would be difficult to guarantee. The current approach using the key nutrient elements assures conservative estimates.

The ratio of the inventories can then be compared with a typical formula for a micro-organism, e.g.  $C_{160}(H_{280}O_{80})N_{30}P_2S$  (Stanier et al., 1977) to indicate which element is limiting and the maximum possible biomass at a given time. Alternative microbial compositions can be found but they are not expected to significantly change the following conclusions.

In applying the approach described above it is simplistically assumed that all the nutrient elements can be used with 100 % efficiency by the microorganisms. In reality, efficiency of utilisation will be lower and, in particular, supply from the solid phase will be kinetically controlled. The rate of supply of a particular element (again here x) may thus be better represented by

$$R_x = F ([x]_I - [x]_0) + K_x V (1-\theta)[x]_s \quad (2)$$

where:

$R_x$  is the rate of supply of x within the box ( $\text{kmol a}^{-1}$ )

$K_x$  is the fractional release rate of x from the solid phase ( $\text{a}^{-1}$ )

This equation would hold directly only for cases where the initial aqueous phase inventory is low (or has been consumed) and the release rate from the solid phase is very low. Alternatively, the release term could be specified as a function of time - e.g. assuming an exponentially decreasing release:

$$R_x = F([x]_I - [x]_0) + V(1-\theta)[x]_s E_x \exp - (E_x t) \quad (3)$$

where:

$E_x$  is the decay constant for release of x from the solid phase ( $\text{a}^{-1}$ )

Element-specific supply rates can also be compared to identify the limiting nutrient and obtain a maximum biomass production rate.

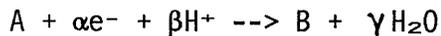
A closer approach to reality can be obtained by dividing the single box into a series of boxes representing specific components of the system. For the case of a one-dimensional advective flux, the equations above hold for each individual box but the analysis is complicated by the temporal variation of the composition of input fluxes due to the evolution of upstream boxes. In specific cases where diffusion is significant the transport calculation would be more complex.

### 2.3 Evaluation of energy sources

In the geosphere the energy needed for microbial growth is supplied chemically<sup>1</sup>. Simplistically, it can be considered that the micro-organisms couple thermodynamically favourable electron transfer (redox) reactions to the energetically unfavourable production of organic material. As the coupling is indirect, micro-organisms can utilise several reactions yielding relatively little chemical energy to drive a single, highly unfavourable reaction (Thauer and Morris, 1984). These principles are indicated schematically in Fig. 2-2. Nevertheless, the overall reaction must balance energetically, and the production of by-products is inherently limited by the total free energy supplied by the source reactions.

The reacting chemical species can, in principle, be treated exactly like the nutrients considered in the previous section and maximum inventories and supply rates can be calculated.

In order to calculate the available free energy within a system, it is convenient to consider the redox reactions involved in terms of separate half-reactions (e.g. McCarty, 1971). Tabulation of the standard free energy change normalised to the number of electrons transferred allows the most energetically favourable reactions to be identified. If all reactions are written in a standard form -

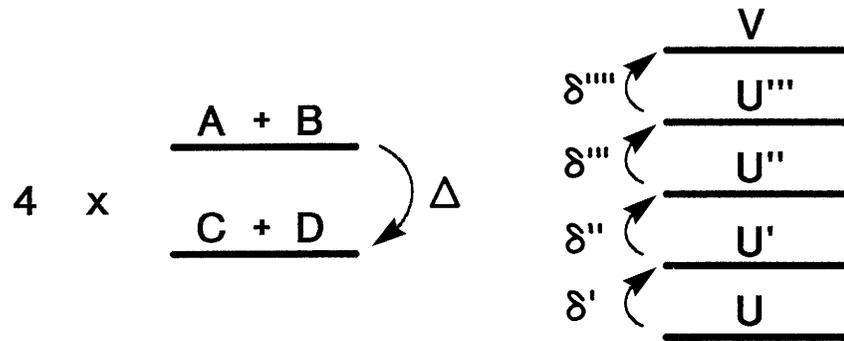


the half-reaction with the most negative normalised standard free energy change will be favoured to proceed as a reduction coupled to the most positive half-reaction running in reverse (as an oxidation). It should be noted that such a calculation is only valid for standard conditions and the free energy changes must be corrected for the concentrations of the reactants. As many reactions result in a net production or loss of protons, these will show a pH dependency. Appendix 1 provides a summary of these principles for the use of the thermodynamic data.

The inventories or supply rates of all reactants can thus be combined to evaluate the maximum available free energy (c.f. next chapter for an example of application). Very simplistically, such total free energy can also be expressed as biomass with the assumption that 64 MJ is required to synthesise and maintain 1 kg (dry) of cell mass (see discussion in Appendix 3). Alternatively, individual redox reactions may be discounted if the energy supply per kmol of electrons transferred is considered too small to be usable. There is currently some controversy about the limit of utilisation of energy, but a value of 15 MJ kmol<sup>-1</sup> might be considered reasonable (discussed in Thauer and Morris, 1984).

---

1) Phototrophic microbial activity during the operational phase is assumed to be negligible



$$|\Delta| > |\delta'|, |\delta''|, |\delta'''|, |\delta''''|$$

Each step in the  $U \rightarrow V$  chain is coupled to one " $A + B \rightarrow C + D$ " reaction

Fig. 2-2: Principles of the microbial energetics calculations

### 3 APPLICATION OF THE MODEL TO THE L/ILW NEAR FIELD

#### 3.1 Specification of the reference near field

In this report we consider the Type B repository for L/ILW as described in Project Gewähr 1985 (Nagra, 1985). Appendix 2 presents the inventories of waste and engineering materials in such a repository derived from a previous study (Grogan, 1987). The various components of the near-field can be considered to be homogeneously distributed for modelling purposes and the composition in an average volume can be specified (Table 3-1). Such an averaging process is, however, inherently unrealistic as it allows reaction between components which are spatially separated by large distances. A better approach is to consider only a limited part of the repository containing just one waste type. In this section, we will describe how the data required for modelling such a single region can be specified.

**Table 3-1: Components of an average 1 m<sup>3</sup>**

Component	Total Repository With All Waste Types			Tunnel Section With BA-Ib Waste		
	mass (kg)	% vol.	% mass	mass (kg)	% vol.	% mass
Organics	(w) 41	4.1	1.7	73	7.3	3.1
Steel	(s) 121	1.7	5.0	121	1.7	5.2
	(w) 110	1.4	4.5	0	0	0
Concrete/ cements	(s) 1813	77.2	74.1	1813	77.2	77.7
	(w) 325	13.8	13.3	325	13.8	14.0
Salt con- centrates	(w) 18	0.9	0.7	0	0	0
Other	(w) 18	0.9	0.7	0	0	0

w = waste/matrix

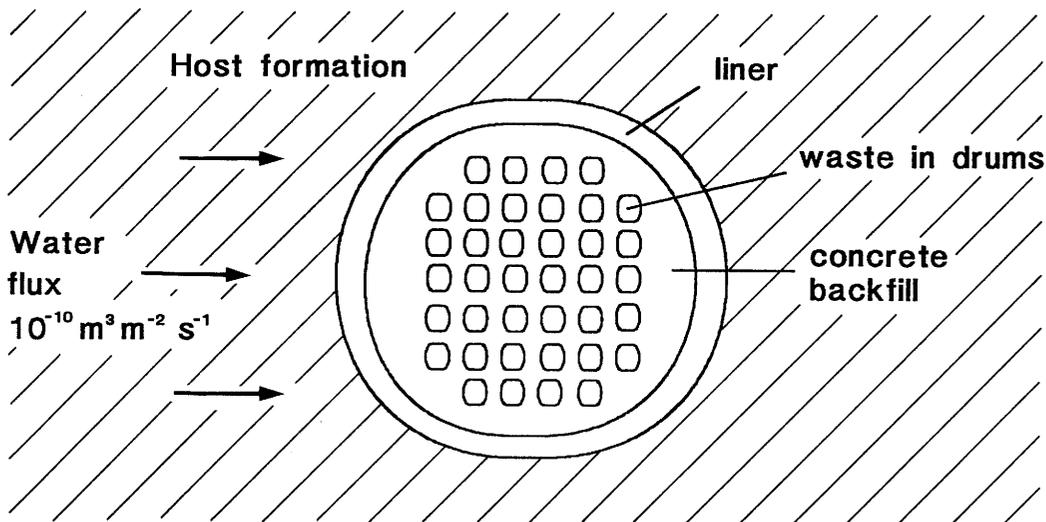
s = structural (canisters, backfill, lining)

As an example, we consider a section of emplacement tunnel containing a single waste type - BA-1b (ion exchangers immobilised in concrete - Fig. 3-1). This particular example is reasonable as such waste is currently being produced (i.e. well specified) and is a major component in terms of volume. Waste type BA-1b was chosen in preference to BA-1a because despite being 10 times less in volume its activity is more than 100 times greater. Table 3-1 shows the components of an average 1 m<sup>3</sup> of the total repository where all waste types are considered. In the equivalent 1 m<sup>3</sup> of tunnel section the only waste type present is organics and this is all

assumed to be ion exchangers immobilised in a concrete matrix. Therefore, in order to calculate the mass and volume of each component in this 1 m<sup>3</sup> tunnel section, the same structural components are present in the same quantities as in the 1 m<sup>3</sup> of total repository, however the total waste volume is divided between organics (ion exchangers) and concrete matrix alone. The resulting radionuclide inventory in the average 1 m<sup>3</sup> of tunnel section can then be derived from the data presented in Table 3-2, which is also compared to that of an average 1 m<sup>3</sup> of the entire repository.

Further information needed for the simple modelling approach is the flux and chemistry of the inflowing groundwater. In the reference case we consider the water flux through the repository to be 10<sup>-10</sup> m<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup> with the flow at right angles to the axis of the emplacement tunnels (c.f. Fig. 3-1). As the tunnels have a cross-sectional area of 154 m<sup>2</sup>, 1 m<sup>3</sup> would correspond to a tunnel length of 6.5x10<sup>-3</sup> m. As the tunnel diameter is 14 m, the equivalent cross section for flow is 0.091 m<sup>2</sup>. The flux through this region is thus 2.9x10<sup>-4</sup> m<sup>3</sup> a<sup>-1</sup>. The marl water chemistry assumed is listed in Table 3-3. Appendix 4 describes how this chemistry was obtained.

Finally, the average porosity of the near field needs to be specified. As concrete is the major component with expected porosities ranging from 15-40%, a value of 20% will be assumed for both the total repository and the tunnel section with BA-1b waste.



Diameter	= 14 m
Cross section	= 154 m <sup>2</sup>
"Equivalent length" for 1 m	= 6.5 mm

Fig. 3-1: Simplified sketch of the near field

**Table 3-2: Nuclide contents (mol) in an average 1 m<sup>3</sup>**

(at time of emplacement)

Radio-nuclide	t1/2 (a)	Total repository	Tunnel Section with BA-Ib waste *
Cl-36	3.0x10 <sup>5</sup>	4.4x10 <sup>-7</sup>	6.1x10 <sup>-6</sup>
Ni-59	7.5x10 <sup>4</sup>	1.6x10 <sup>-2</sup>	6.6x10 <sup>-3</sup>
Se-79	6.5x10 <sup>4</sup>	1.2x10 <sup>-7</sup>	no data
Tc-99	2.1x10 <sup>5</sup>	2.2x10 <sup>-5</sup>	4.2x10 <sup>-4</sup>
Pd-107	6.5x10 <sup>6</sup>	4.6x10 <sup>-5</sup>	2.2x10 <sup>-6</sup>
Sn-126	1.0x10 <sup>5</sup>	5.1x10 <sup>-6</sup>	1.7x10 <sup>-7</sup>
I-129	1.6x10 <sup>7</sup>	8.0x10 <sup>-6</sup>	1.6x10 <sup>-5</sup>
Cs-135	2.3x10 <sup>6</sup>	1.4x10 <sup>-5</sup>	2.4x10 <sup>-5</sup>
Ra-226	1.6x10 <sup>3</sup>	4.9x10 <sup>-7</sup>	3.1x10 <sup>-21</sup>
Th-229	7.3x10 <sup>3</sup>	5.0x10 <sup>-14</sup>	2.9x10 <sup>-18</sup>
Pa-231	3.3x10 <sup>4</sup>	4.1x10 <sup>-11</sup>	3.9x10 <sup>-16</sup>
Np-237	2.1x10 <sup>6</sup>	3.4x10 <sup>-5</sup>	4.1x10 <sup>-9</sup>

\* Table 6-15, NGB 85-02; Assumes 200 l of waste per container

**Table 3-3: Marl groundwater chemistry and elemental flux**

(c.f. Appendix 4)

Species*	Concentration (kmol/m <sup>3</sup> )	Flux* (kmol/a)
Na <sup>+</sup>	1.3x10 <sup>-1</sup>	3.7x10 <sup>-5</sup>
Mg <sup>2+</sup>	6.6x10 <sup>-4</sup>	1.9x10 <sup>-7</sup>
Ca <sup>2+</sup>	2.7x10 <sup>-3</sup>	7.8x10 <sup>-7</sup>
Sr <sup>2+</sup>	9.2x10 <sup>-5</sup>	2.7x10 <sup>-8</sup>
SO <sub>4</sub> <sup>2-</sup>	2.6x10 <sup>-2</sup>	7.5x10 <sup>-6</sup>
NO <sub>3</sub> <sup>-</sup>	1.7x10 <sup>-3</sup>	4.9x10 <sup>-7</sup>
NO <sub>2</sub> <sup>-</sup>	1.1x10 <sup>-4</sup>	3.2x10 <sup>-8</sup>
Cl <sup>-</sup>	7.6x10 <sup>-2</sup>	2.2x10 <sup>-5</sup>
C <sub>inorg.</sub>	5.7x10 <sup>-3</sup>	1.6x10 <sup>-6</sup>
P	1.6x10 <sup>-5</sup>	4.6x10 <sup>-9</sup>

\*) to reference cubic metre of BA-1b for 10<sup>-10</sup> m<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup> flow rate

### 3.2 Application of the model

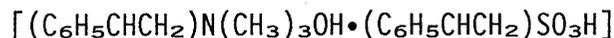
#### 3.2.1 Nutrients

As discussed in Section 2.2, the inventory of X (any nutrient) is given by

$$I_x(t) = V\theta[x]_A + V(1-\theta)[x]_s + Ft([x]_I - [x]_O)$$

For the averaged volumes described in 3.1 previously,  $V = 1\text{m}^3$ ,  $\theta = 0.2$  and  $F$  was calculated to be  $2.9 \times 10^{-4} \text{m}^3 \text{a}^{-1}$  for the groundwater flux of  $10^{-10} \text{m}^3 \text{m}^{-2} \text{s}^{-1}$  base case. The concentrations of nutrients in the inflowing water (and the product  $F[x]_I$ ) are given in Table 3-3.

In the first case, pore water and solid phase contributions are not distinguished, and the nutrient content of the unit volume derived from analysis of the components in Table 3-1 is simply assumed to be entirely available. The organics are entirely ion-exchangers and are assumed to be 50% polystyrene- $\text{N}+(\text{CH}_3)_3$  (anion exchanger) and 50% polystyrene  $\text{SO}_3^-$  (cation exchanger). A representative formula for the exchangers is therefore



(equivalent to  $\text{C}_{19}\text{H}_{27}\text{O}_4\text{NS}$  with a formula weight of 365 daltons). The 73 kg of exchangers in the  $1 \text{m}^3$  of tunnel with BA-1b thus contains 0.2 "kmol of exchanger" with 3.8 kmol of C, and 0.2 kmol of both N and S. The only nutrients with significant concentrations in steel are C and N. Averaging the concentration of these elements in two representative steels (cf. Appendix 2, Table 6) gives contents of 0.1% and 0.01% by weight for C and N, respectively. This is equivalent to  $1.0 \times 10^{-2}$  and  $8.6 \times 10^{-4}$  kmol of C and N, respectively.

A range of different cements and concretes are found in the reference near-field but, initially, we consider the average composition of the structural concrete to be that specified in Table 3a of Appendix 2. C and S are both present at concentrations of 0.13% by weight equivalent to  $2.0 \times 10^{-1}$  and  $7.4 \times 10^{-2}$  kmol, respectively. No information was found for either N or P.

The elemental content of the waste matrix concrete has been derived from chemical analysis of the concrete currently used to immobilise ion exchangers. Such commercial data are not openly available and hence the exact chemical composition cannot be provided. No information was found for P, but it has been calculated that there are  $1.8 \times 10^{-3}$  kmol of N,  $6.6 \times 10^{-2}$  kmol of C and  $4.1 \times 10^{-2}$  kmol of S, present in the waste matrix concrete.

These data are summarised in Table 3-4. The equivalent calculation for the averaged repository is described in Appendix 2.

Even without further calculation, it is clear that phosphorus is the limiting nutrient as no source can be quantified. Phosphorus will, however, be present in trace quantities - perhaps most importantly as an additive to concretes (cf. Table 5 in Appendix 2). Arbitrarily, we take the P content to be 0.005 % by weight, equivalent to  $3.4 \times 10^{-3} \text{ kmol m}^{-3}$  as a reference value. The value was chosen assuming a P containing additive is present in the concrete below the detection level suggested in Table 3 of Appendix 2.

**Table 3-4: Nutrients in 1 m<sup>3</sup> of tunnel section with BA-1b waste**

Component		Content (kmol m <sup>-3</sup> )			
		C	N	S	P
Ion exchangers	(w)	3.8	$2.0 \times 10^{-1}$	$2.0 \times 10^{-1}$	-
Steel	(s)	$1.0 \times 10^{-2}$	$8.6 \times 10^{-4}$	-	-
Concrete	(w)	$6.6 \times 10^{-2}$	$1.8 \times 10^{-3}$	$4.1 \times 10^{-2}$	*( $5.2 \times 10^{-4}$ )
	(s)	$2.0 \times 10^{-1}$	-	$7.4 \times 10^{-2}$	*( $2.9 \times 10^{-3}$ )
Total		4.1	$2.0 \times 10^{-1}$	$3.2 \times 10^{-1}$	* $3.4 \times 10^{-3}$

w = waste/matrix

s = structural (canisters, backfill, lining)

\* assumed value - see text

The original inventory at  $t = 0$  is thus limited by phosphorus and the maximum biomass which could be produced is 6.87 kg (dry weight) assuming the average chemical composition of a microbial cell (dry wt) is:  $C_{160} (H_{280} O_{80}) N_{30} P_2 S$  (c.f. section 2.2). The reference groundwater contains C, S, N and traces of P. Again P will be limiting and, assuming 100 % utilisation, this supply rate ( $4.5 \times 10^{-9} \text{ kmol P a}^{-1}$ ) could produce up to  $9.0 \times 10^{-6} \text{ kg dry wt a}^{-1}$  of microbial biomass.

The calculations above clearly indicate the inadequacy of the database for near-field inventories. Previous calculations (Grogan, 1987) for the averaged repository gave an order of magnitude lower initial P content as only sources from ash, and not from concrete, were considered. If the values for P assumed above are reasonable, the nutrient supply from groundwater is negligible relative to that from the engineered barriers. Uncertainty in the microbial com-

position probably only accounts for a factor of two uncertainty in the calculated biomass.

It is interesting to develop this modelling approach one step further as described in Section 2.2 to see the significance of leaching kinetics on the biomass production. In this case 100 % efficiency of utilisation of the available nutrient elements is still assumed but the kinetically controlled rate of supply of the elements from the solid phase is accounted for. As an initial simplification, it is assumed that the inventories in Table 3-4 correspond to the solid phases, and that pore-water contents are negligible. Kinetic data for degradation of the materials involved are very sparse, but values derived from the literature are used to give a first estimate of the importance of considering this factor.

Microbial degradation rates reported by Caldwell et al. (1987) for a range of organic materials result in  $\text{CO}_2$  production rates in the order of 5-10  $\mu\text{g CO}_2/\text{g waste/day}$ . Assuming such waste had a 50 % water content and that the dry matter contained 50% carbon by weight, this corresponds to a degradation rate of  $\approx 5-10 \times 10^{-6} \text{ day}^{-1}$ . For the following calculations a value of  $10^{-5} \text{ day}^{-1}$  is used  $\approx 3.7 \times 10^{-3} \text{ a}^{-1}$ .

Corrosion rates of steel components are expected to range from  $\approx 10^{-3} - 10^{-4} \text{ mm a}^{-1}$  under repository conditions (Grauer, 1988) and expected corrosion times range from  $\approx 3000 - 30\,000$  years (Nagra 1985, Vol. 7). A fractional degradation rate of  $3.3 \times 10^{-4} \text{ a}^{-1}$  will be assumed, based on the shorter corrosion time.

The release rate of individual elements from concrete is more difficult to specify as it contains many individual mineral components which evolve with time in a complex manner. In the absence of better data, the release of all elements is assumed to be constant over the 10 000 years required for cement degradation (Nagra 1985, Vol. 7) - i.e. a rate of  $10^{-4} \text{ a}^{-1}$ .

Equation (2) from Section 2.2 can now be applied. Taking  $[x]_I$  data from Table 3-3, assuming  $[x]_0 = 0$  and the degradation rates above, allows the supply of each element to be calculated (cf. Table 3-5). Because the degradation rates for each of the materials are similar, the dominance of the ion exchangers as a nutrient source and limitation by phosphorus is again evident. The rôle of groundwater, however, is increased - contributing  $\approx 1\%$  of the potential biomass production rate ( $7.0 \times 10^{-4} \text{ kg a}^{-1}$ ). The nutrient supply rate as a function of time and cumulative nutrient supply are illustrated on Figures 3-2 and 3-3, respectively.

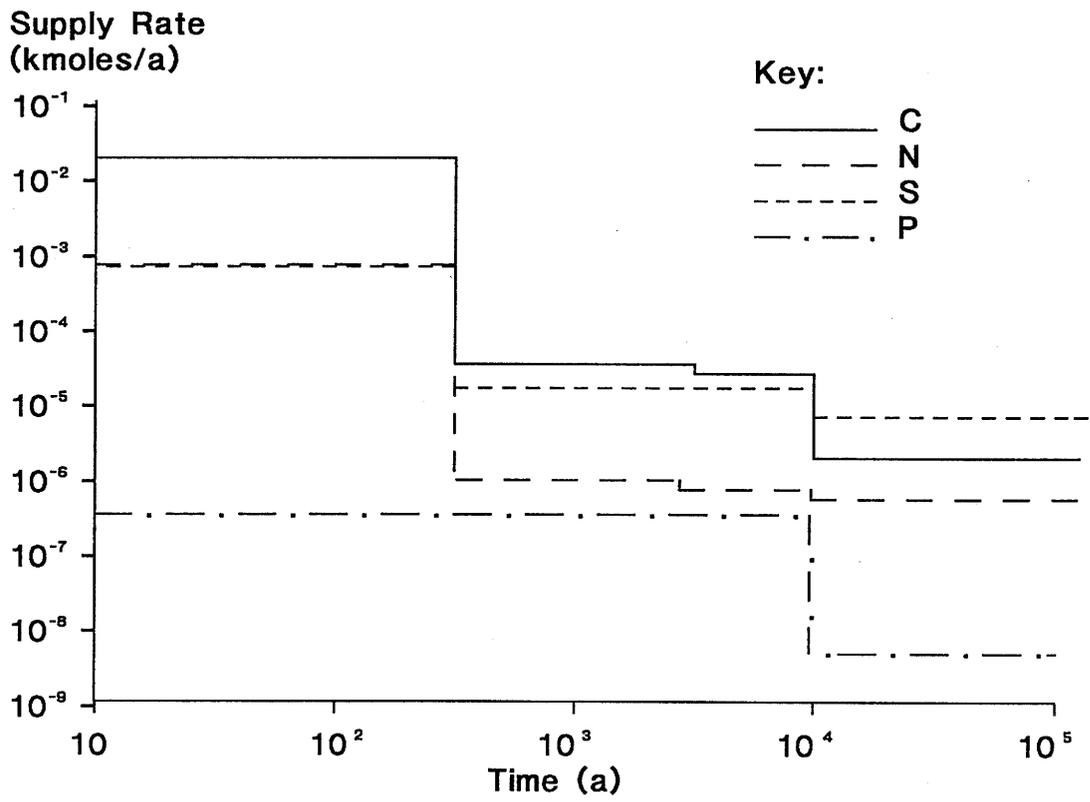


Figure 3-2: Nutrient supply rate (kmol a<sup>-1</sup>) in 1 m<sup>3</sup> of tunnel section

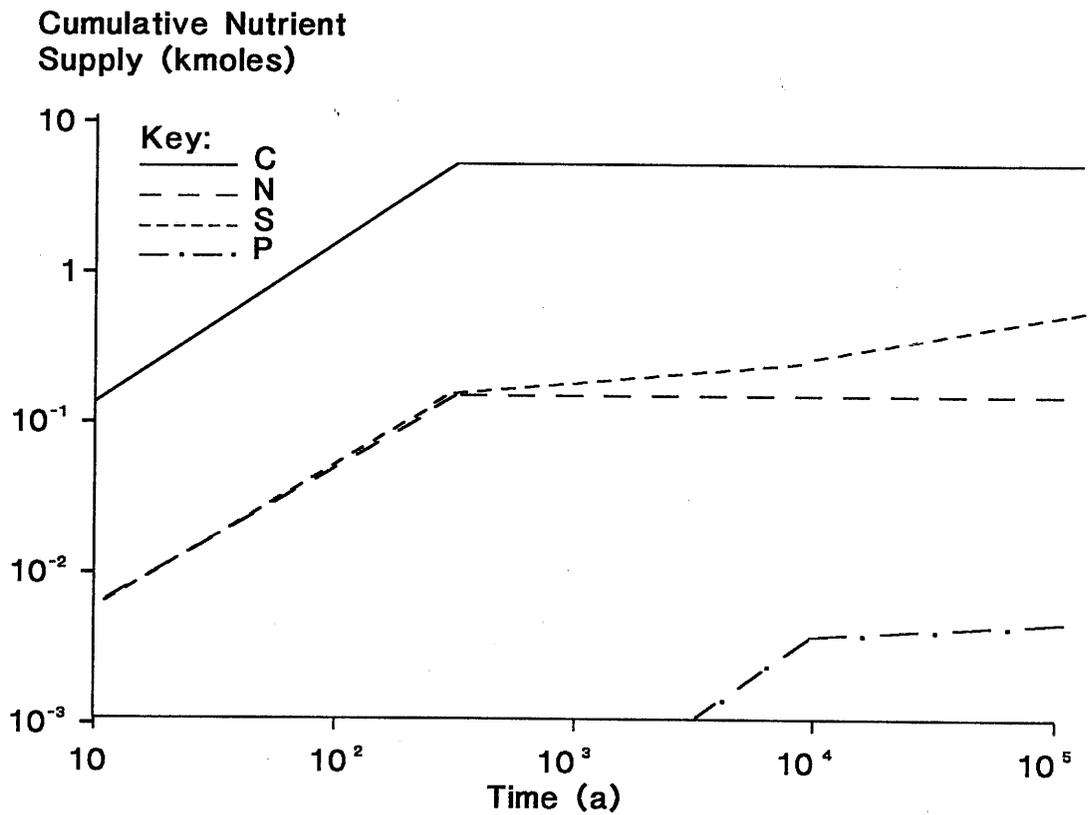


Figure 3-3: Cumulative nutrient supply (kmol) in 1 m<sup>3</sup> of tunnel section

**Table 3-5: Evaluation of the nutrient supply to the reference 1 m<sup>3</sup> tunnel section (c.f. eqn (2) in section 2.2)**

Source	Supply rate (kmol a <sup>-1</sup> )			
	C	N	S	P
Ion exchangers	1.4x10 <sup>-2</sup>	7.4x10 <sup>-4</sup>	7.4x10 <sup>-4</sup>	-
Steel	3.3x10 <sup>-6</sup>	2.9x10 <sup>-7</sup>	-	-
Concrete	2.7x10 <sup>-5</sup>	1.8x10 <sup>-7</sup>	1.2x10 <sup>-5</sup>	3.4x10 <sup>-7</sup>
$K \times V(1-\theta)[x]_s$	1.4x10 <sup>-2</sup>	7.4x10 <sup>-4</sup>	7.5x10 <sup>-4</sup>	3.4x10 <sup>-7</sup>
$F([x]_r - [x]_o)$	1.6x10 <sup>-6</sup>	5.2x10 <sup>-7</sup>	7.5x10 <sup>-6</sup>	4.6x10 <sup>-9</sup>
R	1.4x10 <sup>-2</sup>	7.4x10 <sup>-4</sup>	7.6x10 <sup>-4</sup>	3.5x10 <sup>-7</sup>

### 3.2.2 Energy

A list of redox half-reactions which could, potentially, be utilised by microorganisms as energy sources is presented in Table 3-6. The standard free energy change for these reactions is also given - evaluated for pH = 12 and normalised by the number of electrons involved in the reaction (c.f. Appendix 1). The data listed are thus in units of kJ mol<sup>-1</sup> of electrons - this formalism readily allows the most favourable reactions to be identified. The most negative reaction would be favoured as a reduction while the most positive would run backwards, as an oxidation. For example, the most favourable reductant in the list is H<sub>2</sub>O<sub>2</sub> which would preferentially react with Fe(OH)<sub>3</sub><sup>-</sup> to form H<sub>2</sub>O and magnetite (Fe<sub>3</sub>O<sub>4</sub>) with a free energy change of -236.4 kJ mol<sup>-1</sup> of electrons transferred. Formally, the actual energy change will depend on the concentration of the reactants but, in practice, it may be sufficient to evaluate pH effects only and otherwise consider the reaction to be irreversible (c.f. Morel, 1983, pp 326-329). Similarly, corrections for ambient temperature, pressure etc can generally be ignored.

Although the principles of the energy budget calculations are the same as those for the nutrients considered previously, in practice the calculations are somewhat more complex due to the number of competing reactions involved. It is convenient to separate the treatment of the early oxic phase from the later period when all oxygen in trapped air has been consumed.

Table 3-6:

Selected microbially catalysed redox half-reactions\*. The free energy change in these reactions (in kJ mol<sup>-1</sup>) is given for a pH = 12, normalised by the number of electrons involved (n)

		$\Delta G_r$ (pH=12) n
$H_2O_2 + 2e^- + 2H^+$	$\rightarrow 2H_2O$	-101.7
$NO_2^- + 3e^- + 4H^+$	$\rightarrow \frac{1}{2}N_2(g) + 2H_2O$	- 56.1
$O_2 + 4e^- + 4H^+$	$\rightarrow 2H_2O$	- 50.1
$NO_3^- + 5e^- + 6H^+$	$\rightarrow \frac{1}{2}N_2(g) + 3H_2O$	- 37.9
$NO_3^- + 2e^- + 2H^+$	$\rightarrow NO_2^- + H_2O$	- 10.6
$NO_3^- + 8e^- + 9H^+$	$\rightarrow NH_3 + 3H_2O$	- 1.4
$NO_2^- + 6e^- + 7H^+$	$\rightarrow NH_3 + 2H_2O$	1.8
$<HCHO> + 4e^- + 4H^+$	$\rightarrow CH_4(g) + H_2O$	29.1
$S(s) + 2e^- + H^+$	$\rightarrow HS^-$	40.2
$SO_3^{2-} + 6e^- + 7H^+$	$\rightarrow HS^- + 3H_2O$	44.5
$<HCHO> + 2e^- + 2H^+$	$\rightarrow <HCH_2OH>$	46.1
$SO_4^{2-} + 8e^- + 9H^+$	$\rightarrow HS^- + 4H_2O$	53.0
$CO_3^{2-} + 8e^- + 10H^+$	$\rightarrow CH_4(g) + 3H_2O$	56.3
$Fe(OH)_3^- + 2e^- + 3H^+$	$\rightarrow Fe(s) + 3H_2O$	57.1
$SO_4^{2-} + 6e^- + 8H^+$	$\rightarrow S(s) + 4H_2O$	57.3
$CO_3^{2-} + 6e^- + 8H^+$	$\rightarrow <CH_2> + 3H_2O$	59.3
$2SO_4^{2-} + 8e^- + 10H^+$	$\rightarrow S_2O_3^{2-} + 5H_2O$	59.4
$2CO_3^{2-} + 8e^- + 11H^+$	$\rightarrow CH_3COO^- + 4H_2O$	61.4
$CO_3^{2-} + 5e^- + 7H^+$	$\rightarrow <CH> + 3H_2O$	61.6
$3CO_3^{2-} + 14e^- + 19H^+$	$\rightarrow CH_3CH_2COO^- + 7H_2O$	61.7
$CO_3^{2-} + CH_3COO^- + 6e^- + 8H^+$	$\rightarrow CH_3CH_2COO^- + 3H_2O$	62.1
$H^+ + 1e^-$	$\rightarrow \frac{1}{2}H_2(g)$	68.5
$CO_3^{2-} + 6e^- + 8H^+$	$\rightarrow <HCH_2OH> + 2H_2O$	71.0
$Fe_3O_4(s) + 8e^- + 8H^+$	$\rightarrow 3Fe(s) + 4H_2O$	76.5
$CO_3^{2-} + 4e^- + 6H^+$	$\rightarrow <HCHO> + 2H_2O$	83.5
$CO_3^{2-} + 2e^- + 4H^+$	$\rightarrow <HCOO> + H_2O$	96.1
$\alpha FeO(OH)(s) + 1e^-$	$\rightarrow Fe(OH)_3^- - H_2O$	99.9
$\alpha Fe_3O_4(s) + 2e^- - H^+$	$\rightarrow 3Fe(OH)_3^- - 5H_2O$	134.7

\*) This list is limited by availability of thermodynamic data and the simple characterisation of the near-field

In the oxic period, it is initially assumed that the pore water is saturated with oxygen ( $P_{O_2} = 0.21 \text{ atm}$ ;  $O_2 = 2.6 \times 10^{-4} \text{ molar}$ ), which will react with the iron of the canisters. Also, 10 % of the repository volume is initially assumed to contain trapped air. The canisters are assumed to remain intact over this period and hence no interaction of oxygen with organic waste is assumed. Inside the canister, trapped air could react either with ion exchange resin or with the inner canister wall. Although reaction with carboxylate or aldehyde groups would be energetically more favourable, due to their absence from the reference organic formulation it is assumed that iron corrosion occurs. It can be calculated that these reactions could produce approx 502 kJ of usable energy in the reference volume (c.f. Table 3-7)

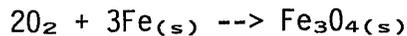
During this early period, radiolysis may also be important (c.f. Appendix 5). The radiolytic products can be assumed to be readily available for reaction, sulphate and sulphite acting as oxidants and trimethylamine and hydrogen as potential reductants. Reaction of sulphite and sulphate with hydrogen would yield free energies of 24.0 and 15.5 kJ mol<sup>-1</sup> of electrons transferred, respectively (c.f. Table 3-6). Such energies are rather low and, certainly for sulphate reaction, close to proposed limits for microbial utilisation. Reaction with iron would only be 8 kJ mol<sup>-1</sup> electrons more favourable (c.f. Table 3-7). As the system is inherently limited in oxidant, it is therefore assumed that the reaction occurs preferentially with iron and the other labile reductants are lost without reaction until the iron is totally consumed. The total potentially usable energy from this source is 190 kJ.

After this short initial period, a relatively steady state is established with supply of various reactants from the degradation of ion exchange resin, steel and concrete and advecting groundwater. The total inventories of potential reactants are listed in Table 3-8. Iron is the most powerful reductant in the system which would be capable of consuming all sulphate, sulphite and carbonate (consuming 1.41 kmol of the total 2.16 kmol present) yielding a total energy of 92 MJ.

As with the nutrients, a more realistic appraisal of the system involves an assessment of the kinetics involved. The rate of supply of reactants can be derived from the previously assumed degradation rates. In the first case, it is assumed that if redox active species are not utilised by microorganisms they either react chemically (without microbial catalysis) or are lost from the near field by advective transport. Table 3-8 illustrates this for the periods when initially the ion exchange resins and then the steel are consumed. When the rapidly degrading exchange resins provide a source of oxidant (sulphite), this dominates energy production which subsequently falls by a factor of 20 (from 149 to 7 kJ a<sup>-1</sup>). In the latter period, approximately 3 times more oxidant is leached from cement as is supplied from groundwater. After 3000 years there

**Table 3-7: Energetics during the early phase****1 Trapped air**

## a) Reaction



$$\Delta G_r \text{ pH} = 12 = -126.6 \text{ kJ}(\text{mol electrons})^{-1}$$

$$= -506.4 \text{ kJ}(\text{mol } O_2)^{-1}$$

## b) Pore water

$2.6 \times 10^{-4} \text{ mol } O_2 \text{ l}^{-1}$ ; 910 l  $\text{m}^{-3}$  concrete; 20 % porosity

--> 0.047 mol

## c) Trapped gas

100 l air; 0.21 mol fraction  $O_2$  in air; 0.045 mol  $\text{l}^{-1}$  gas

--> 0.945 mol

d) Total = 0.992 mol  $O_2$  --> 502.3 kJ

**2 Radiolytic products (c.f. Appendix 5)**

## a) Inventories

mol(ref  $\text{m}^3$ ) $^{-1}$

$N(CH_3)_3$

8.9

$H_2$

0.6

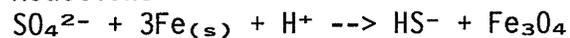
$SO_4^{2-}$

0.6

$SO_3^{2-}$

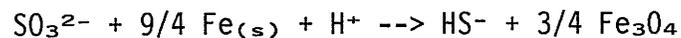
0.4

## b) Reactions



$$\Delta G_r \text{ pH} = 12 = -188 \text{ kJ}(\text{mol } SO_4^{2-})^{-1}$$

$$= -23.5 \text{ kJ}(\text{mol electrons})^{-1}$$



$$\Delta G_r \text{ pH} = 12 = -192 \text{ kJ}(\text{mol } SO_3^{2-})^{-1}$$

$$= -32 \text{ kJ}(\text{mol electrons})^{-1}$$

c) Total = 0.6 mol  $SO_4^{2-}$  + 0.4 mol  $SO_3^{2-}$  --> 189.6 kJ

**Table 3-8: Steady state energetics** (see text for details)

i)				
Source (mass in unit volume)	Reactant	Inventory (mol)	Supply rate (mol a <sup>-1</sup> )	Lifetime (a)
Steel (121 kg)	Fe <sub>(s)</sub>	2.2x10 <sup>3</sup>	7.2x10 <sup>-1</sup>	3x10 <sup>3</sup>
Concrete* (2138 kg)	SO <sub>4</sub> <sup>2-</sup>	87	8.7x10 <sup>-3</sup>	1x10 <sup>4</sup>
	CO <sub>3</sub> <sup>2-</sup>	232	2.3x10 <sup>-2</sup>	1x10 <sup>4</sup>
	Fe <sup>3+</sup>	328	3.3x10 <sup>-2</sup>	1x10 <sup>4</sup>
Organics (73 kg)	<C <sub>6</sub> H <sub>6</sub> >	400	1.48	270
	<CHCH <sub>2</sub> >	400	1.48	270
	<N(CH) <sub>3</sub> >	200	0.74	270
	<SO <sub>3</sub> >	200	0.74	270
Ground- water	SO <sub>4</sub> <sup>2-</sup>		7.5x10 <sup>-3</sup>	
	NO <sub>3</sub> <sup>-</sup>		4.9x10 <sup>-4</sup>	
	NO <sub>2</sub> <sup>-</sup>		3.2x10 <sup>-5</sup>	

\*) From Table 3a of Appendix 2

**ii)**  
Energy inventory from reaction with steel

	Total (MJ)
a) 87 mol SO <sub>4</sub> <sup>2-</sup> ; 3 moles of Fe per mole of oxidant; Free energy change 188.0 kJ (mol oxidant) <sup>-1</sup> :	16.4
b) 200 mol SO <sub>3</sub> <sup>2-</sup> ; 9/4 moles of Fe per mole of oxidant; Free energy change 192.0 kJ (mol oxidant) <sup>-1</sup> :	38.4
c) 232 mol CO <sub>3</sub> <sup>2-</sup> *; 3 moles of Fe per mole of oxidant; Free energy change 161.6 kJ (mol oxidant) <sup>-1</sup> :	<u>37.5</u>
Total Fe: 1.41x10 <sup>3</sup> mol	92.3

\*) CO<sub>3</sub><sup>2-</sup> --> CH<sub>4</sub> reaction - c.f. Table 3-6

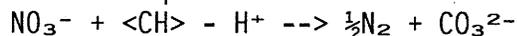
(Table 3-8 continued)

(iii) Energy production profile	Oxidant	Reductant	Energy (kJ a <sup>-1</sup> )
a) Time 0-270 years (ground-water NO <sub>2</sub> <sup>-</sup> ignored)	SO <sub>4</sub> <sup>2-</sup>	Fe <sub>(s)</sub>	3.0
	SO <sub>3</sub> <sup>2-</sup>	Fe <sub>(s)</sub>	142.2
	CO <sub>3</sub> <sup>2-</sup>	Fe <sub>(s)</sub>	4.0
	NO <sub>3</sub> <sup>-</sup>	Fe <sub>(s)</sub>	0.3
			<u>149.5</u>
b) 270 - 3x10 <sup>3</sup> years (ground-water NO <sub>2</sub> <sup>-</sup> ignored)	SO <sub>4</sub> <sup>2-</sup>	Fe <sub>(s)</sub>	3.0
	CO <sub>3</sub> <sup>2-</sup>	Fe <sub>(s)</sub>	4.0
	NO <sub>3</sub> <sup>-</sup>	Fe <sub>(s)</sub>	0.3
			<u>7.3</u>
c) 3x10 <sup>3</sup> - 1x10 <sup>4</sup> years	(SO <sub>4</sub> <sup>2-</sup>	<CH>	1.12*)
	NO <sub>3</sub> <sup>-</sup>	<CH>	0.24
	NO <sub>2</sub> <sup>-</sup>	<CH>	0.01
			<u>0.25</u>
d) Times >1x10 <sup>4</sup> years	(SO <sub>4</sub> <sup>2-</sup>	<CH>	0.52*)
	NO <sub>3</sub> <sup>-</sup>	<CH>	0.24
	NO <sub>2</sub> <sup>-</sup>	<CH>	0.01
			<u>0.25</u>

\*) n.b.: SO<sub>4</sub><sup>2-</sup> + <CH> gives only 8.6 kJ mol<sup>-1</sup> electrons and is therefore not included in the energy production calculations

**iv)**Resin degradation at times >3x10<sup>3</sup> years

## a) Assumed equations



$$\Delta \text{Gr pH}=12 = -99.5 \text{ kJ}(\text{mol electrons})^{-1}$$



$$\Delta \text{Gr pH}=12 = -59.8 \text{ kJ}(\text{mol electrons})^{-1}$$

(nb SO<sub>4</sub><sup>2-</sup> + <CH> gives only 8.6 kJ(mol electrons)<sup>-1</sup>)

## b) Supply rates

$$\text{NO}_3^-; 4.9 \times 10^{-4} \text{ mol a}^{-1}; 5e^- \text{ transferred}(\text{mol NO}_3^-)^{-1} \\ \rightarrow 0.24 \text{ kJ a}^{-1}$$

$$\text{NO}_2^-; 3.2 \times 10^{-5} \text{ mol a}^{-1}; 6e^- \text{ transferred}(\text{mol NO}_2^-)^{-1} \\ \rightarrow 0.01 \text{ kJ a}^{-1}$$

$$\text{Total} = 0.25 \text{ kJ a}^{-1}$$

is no obvious source of utilisable energy - although redox disequilibria exist in cement components and the groundwater - these would only be very slightly endoenergetic.

It is reasonable to assume that iron will corrode in this system even without microbial catalysis, but the situation with regard to degradation of the ion exchanger is less clear. The sulphite and trimethylamine groups may well be hydrolysed within 270 years as modelled, but the hydrocarbon framework would be considerably more refractory. If it is considered to persist beyond  $10^4$  years, this hydrocarbon source could be utilised by microbes as a reductant. The only oxidants in the system which would be sufficiently strong to produce usable energy from this source are nitrate and nitrite from groundwater; the calculations involved are summarised in Table 3-8.

To put the energetics data in context, energies are expressed in terms of equivalent biomass in Table 3-9. From these data, it appears that trapped air and radiolysis are not particularly important. After production of 2.3 g/year over the first 270 years, a steady rate of 0.11 g/year holds till 1000 years after repository closure. The subsequent rate of 3.9 mg/year would continue until all of the ion exchanger hydrocarbon was consumed - about 6 million years on the basis of a simple mass balance calculation.

**Table 3-9: Energy to biomass conversion**

	Energy	Biomass (dry wt)
1 Trapped air	502.3 kJ	7.8 g
2 Radiolysis	189.6 kJ	3.0 g
3 (Steel inventory)	92.3 MJ	$1.44 \times 10^3$ g
4 Profile		
0-270 a	149.5 kJ a <sup>-1</sup>	2.3 g a <sup>-1</sup>
270 - $3 \times 10^3$ a	7.3 kJ a <sup>-1</sup>	0.1 g a <sup>-1</sup>
$3 \times 10^3$ - $1 \times 10^4$ a	0.25 kJ a <sup>-1</sup>	$3.9 \times 10^{-3}$ g a <sup>-1</sup>
$>10^4$ a	0.25 kJ a <sup>-1</sup>	$3.9 \times 10^{-3}$ g a <sup>-1</sup>

### 3.3 Consequences of microbial activity

The possible roles of microbes in nuclear waste repositories have been extensively discussed elsewhere (e.g. McKinley et al., 1985, Grogan, 1987) and include gas production, corrosion and physical disruption of containers and barriers, direct uptake and transport of radionuclides etc. The most important potential influence of microbial activity was, however, identified as being the production of organic complexing agents which could increase the release rates of particular radionuclides. To illustrate the application of data produced by the model, this aspect alone will be examined.

Comparison of the nutrient supply rates in 1 m<sup>3</sup> of tunnel section (Table 3-5) with the energy production rates (Table 3-9) allows the constraints on accumulation of biomass to be established. The phosphorus supply from concrete would limit production to 0.7 g/year in 1 m<sup>3</sup> of tunnel section over the first 10<sup>4</sup> years which would drop 2 orders of magnitude when the supply from concrete is exhausted and the biomass is supported by groundwater supply alone. It would thus appear that P would be limiting during the early period of resin degradation but, thereafter, energy would be the limiting factor. At all times, the differences between these two constraints is not very large (a factor of 2-5) and is probably well within the range of uncertainty in such simple calculations.

In previous work (e.g. McKinley et al., 1985, Grogan 1987), the rate of production of organic byproducts was set equal to the rate of production of biomass - assuming that a steady state is established where the standing biomass remains constant and the rate of production equals the rate of loss. In such a case, assuming all products are potential complexants, 0.7 g/a in a water flux of 0.29 l/a would give rise to a concentration of 2.4 g/litre in 1 m<sup>3</sup> of tunnel section. This concentration is considerably higher than those reported in groundwater samples from the marl (Nagra, 1988) and hence could be of great significance.

The 2.4 g/l will correspond to a wide range of organic compounds of varying size and complexing ability. For first simple scoping calculations, however, we assume an average of 1 complexing group (e.g. carbonyl, amine) per 100 daltons to give a concentration of 24 mmol of complexing groups per litre. Such a concentration is high relative to the inventories of the nuclides in the waste (Table 3-2) and could be especially important for nuclides which may be solubility-limited (e.g. Ni-59, Tc-99, actinides) or, indeed, effectively insoluble in the near-field hyperalkaline, reducing conditions (e.g. Pd-107, Sn-126).

In order to assess the effect of such a concentration of organic complexants on specific elements, their complexation constants can be compared to those of the main inorganic ligand, OH<sup>-</sup>. In the absence of specific data on the range of organic byproducts present, several model complexants can be considered - e.g. oxalic

acid or ethylenediamine. Considering the simple system Radionuclide - OH<sup>-</sup> (pH=12) - complexant (10<sup>-2</sup>M), the relative concentrations of organic and hydroxo complexed species can be estimated using the theoretically extrapolated data of Brown and Wanner (1987). Some results of this simple calculation are shown in Table 3-10. In this table the predicted dominant hydroxo- and organocomplexes are shown and the calculated ratio of their concentrations at equilibrium. This simple calculation shows a range of behaviour for different nuclides; for Pu<sup>IV</sup> the hydroxo species are clearly more important, Np<sup>V</sup> represents a case where the ligands are equally important while, for Am and Pd, the ethylenediamine complexes more strongly than OH<sup>-</sup> which, in turn, is stronger than the oxalate complexation. It should be emphasised that alternatives for both the model complexants assumed and the database used could significantly change the results calculated, but the data in Table 3-10 provide a reasonable semi-quantitative indication of the possible consequences of microbial byproducts at the concentrations indicated. Note also that the results may be very dependant on the hydroxo- and organo-ligand concentrations - for the Am case in Table 3-10, an increase in pH of 1 unit would increase the ratio by 6 log units with a consequent change to hydroxo species domination for the ethylenediamine case.

Apart from increasing solubility, the organic-complexed nuclides may be more mobile than uncomplexed species, both in the near field and the far field. The calculations above indicate that microbial activity, for this particular waste sort, could easily produce sufficient complexant to bind with the entire nuclide inventory. A more realistic appraisal of this process required competing species (e.g. Ca<sup>2+</sup>) but lies outside the scope of the current report.

**Table 3-10: Relative importance of organic complexation (see text)**

Radionuclide	Hydroxocomplex	Organocomplex	Log ratio Hydroxo organo
Am <sup>III</sup>	Am(OH) <sub>6</sub> <sup>3-</sup>	Am(OX) <sub>3</sub> <sup>3-</sup>	- 4.6
	Am(OH) <sub>6</sub> <sup>3-</sup>	Am(EN) <sub>3</sub> <sup>3+</sup>	-20.2
Np <sup>V</sup>	NpO <sub>2</sub> (OH) <sub>3</sub> <sup>2-</sup>	NpO <sub>2</sub> (OX) <sup>-</sup>	0.1
	NpO <sub>2</sub> (OH) <sub>3</sub> <sup>2-</sup>	NpO <sub>2</sub> (EN) <sup>+</sup>	0.2
Pd <sup>II</sup>	Pd(OH) <sub>4</sub> <sup>2-</sup>	Pd(OX) <sub>2</sub> <sup>2-</sup>	30.3
	Pd(OH) <sub>4</sub> <sup>2-</sup>	Pd(EN) <sub>2</sub> <sup>2+</sup>	- 7.8
Pu <sup>IV</sup>	Pu(OH) <sub>6</sub> <sup>2-</sup>	Pu(OX) <sub>3</sub> <sup>2-</sup>	28.7
	Pu(OH) <sub>6</sub> <sup>2-</sup>	Pu(EN) <sub>3</sub> <sup>4+</sup>	8.4

OX = (C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup>      EN = (CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>

#### 4 OVERVIEW AND RECOMMENDATIONS FOR FUTURE WORK

The previous chapter illustrated application of the model to a reference 1 m<sup>3</sup> of repository tunnel containing a specific waste type and indicated how the results could be evaluated in the context of an overall safety analysis. The importance of P as a limiting nutrient in this system was noted - it is emphasised that the P inventory data are very poor and this is an obvious area where future improvements should be made.

The analysis in this report has been carried out for a single waste sort and the conclusions may not be generally applicable. The calculations involved are quite straightforward and could be repeated for other waste sorts. Ideally, the mathematical treatment could be handled by a computer programme which could be applied routinely during the certification of the acceptability of particular wastes. Iterative use of such a code would allow, in the first case, identification of key parameters which may need to be included in the waste specification. Sensitivity analysis would also allow definition of analysis limits, below which parameters could be considered insignificant.

More fundamentally, the model described did not examine the far field or the disturbed zone at the near-field/far-field interface. Although mainly aimed at HLW, these factors have been discussed in the supporting documents for the sediment study (Wittwer and McKinley, 1989 - far field; McKinley, 1989 - disturbed zone). The disturbed zone analysis may be particularly important if pyrite oxidation occurs to a significant extent (McKinley, 1989).

The consideration of the energetics of microbial activity could also be further improved. In the present analysis, a single pH was defined without consideration of variations in space (microenvironments) and time. Further, a cut-off for microbial utilisation of  $\approx 15$  kJ per mol of electrons transferred was assumed, which resulted in many organic reactions (e.g. with  $\text{SO}_4^{2-}$  - c.f. Table 3-8) and reactions utilising Fe(III) in the concrete as an oxidant being excluded. If a very much lower cut-off (e.g.  $5 \text{ kJ mol}^{-1}$ ) was adopted, the energy inventories and supply rates would be significantly increased. Considerable uncertainty is associated with the data for the limit of utilised energy in these processes (Morel, 1983). Both of these factors should be considered in more detail.

Finally, the analysis of the consequences of microbial activity should be expanded with the particular aim of defining levels at which effects could be considered negligible. The complexing ability of organic byproducts could be better defined while other effects (e.g. gas production, microbial mobility, pore clogging, etc.) need to be explicitly considered. The model, which predicts maximum possible effects, also needs to be checked against realistic simulation and experiments to check not only that it is indeed conservative but also that it is not unrealistically over-conservative.

## 5 ACKNOWLEDGEMENTS

This report was developed from discussions within the Nagra microbiology group which includes R. Bachofen, N. Christofi, K. Hanselmann, F. van Dorp and J.M. West. J.M. West participated in the conceptual development of the model described herein. Particular thanks to Drs. Russell Alexander, Hans Müller and Mike Thorne for constructive criticism during their detailed reviews of this report. The encouragement of J. Hadermann, C. McCombie and, especially, P. Zuidema is also gratefully acknowledged.

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**APPENDIX 1****THERMODYNAMIC DATA**

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Any redox half-reaction can be written in the general form:



for which a standard free energy of reaction ( $\Delta G_r^\circ$ ) can be specified. The  $\Delta G_r^\circ$  can be derived either from standard free energies of formation ( $\Delta G_f^\circ$ ):

$$\Delta G_r^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

or from an equilibrium constant (K):

$$\Delta G_r^\circ = -R T \ln K$$

where R is the gas constant and T the absolute temperature.

The equilibrium constant is defined as:

$$\log K = \sum x \log [\text{product}] - \sum x \log [\text{reactant}]$$

where x represents the appropriate stoichiometric coefficients and the values in square brackets represent activities.

The  $\Delta G_r^\circ$  values are defined for standard conditions which, for solutes, corresponds to unit activity. For the reference case pH = 12 (for a concrete-dominated near field), the activity correction is very important. At pH 12, the free energy of reaction for the general redox half-reaction is:

$$\begin{aligned} \Delta G_r^\circ &= \Delta G_r^\circ - b R T \ln [H] \\ &= \Delta G_r^\circ + (b \times 5.707 \times 12) \end{aligned}$$

where  $5.707 \text{ kJ mol}^{-1} = R T \ln 10$  at  $25^\circ\text{C}$ .

In the particular case of hyperalkaline reference conditions, it is important to ensure that the reactions considered take appropriate speciation into account. Thus, while  $\text{HCO}_3^-$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_4^+$  and  $\text{Fe}^{2+}$  may be appropriate for low or neutral pH, at pH 12 the relevant species are  $\text{CO}_3^{2-}$ ,  $\text{HS}^-$ ,  $\text{NH}_3$  and  $\text{Fe}(\text{OH})_3^-$ .

## APPENDIX 2

### **THE INVENTORY OF WASTE AND ENGINEERING MATERIALS FOR A L/ILW REPOSITORY USED TO DERIVE A REFERENCE UNIT CELL**

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#### **INTRODUCTION**

The specifications listed in this appendix have previously been published in Grogan (1987) and are calculated assuming a Swiss 240 Gwa nuclear energy scenario as defined in Project Gewähr (Nagra, 1985). This information was used to define a reference 1 m<sup>3</sup> unit cell of a repository which is made up of the appropriate volume of each of the major material categories. The unit cell thus provided a convenient description of the complex assembly of different wastes and materials in a repository on which microbiological modelling could be based. The sources of the data presented in the following tables have also been included for clarity.

#### **1 INVENTORIES**

The total quantities of materials in the waste and its solidification matrix are presented in Table A2-1 for a Swiss Type B repository (Nagra, 1984). Table A2-2 summarises the total contents of such a repository distinguishing between the waste and its solidification matrix and the canisters, backfill and lining. These quantities are calculated assuming a Swiss 240 Gwa nuclear energy scenario (Nagra, 1985).

##### **Concrete/Cement**

In a type B repository concrete is the dominant component of the entire material inventory (see Table A2-2). A typical concrete composition (elemental inventory) is given in Table A2-3 a). However, various special cements and concretes will also be used for different purposes. Barium will be used in some special concretes to provide extra shielding in some areas of the repository, but it is uncertain whether a non-calcareous cement will be used or whether barium sulphate aggregates will be employed in the concrete. If barytes were used then this would also provide a further source of sulphate. The elemental composition of such a barium concrete as currently produced is also given in Table A2-3 b).

**Table A2-1: Total quantities of materials in the waste and its solidification matrix in a Type B repository (taken from Wiborgh et al., 1986, Table 2)**

Material (Mg)	Operational Waste (BA)	Reprocessing Waste (WA)	Decommissioning Waste (SA)	Industry Medicine +Science (MIF)	Total
<u>Solidification Matrix</u>					
Cement	54 730	9 120	118 280	8 410	190 500
Bitumen	300	3 100	--	--	3 400
Polymers (polystyrene)	100	--	--	--	100
<u>Waste Material</u>					
Steel	2 800	23 600	39 700	--	66 100
Al/Zn	--	600	6	--	606
Salt concentrates	300	1 800	8 500	--	10 600
Ash	200	--	100	--	300
Glass	400	--	--	--	400
Ion exchange resin	12 200	100	--	--	12 300
Concrete	20	--	4 300	--	4 320
Cellulose	0	5 300	0	--	5 300
Polymers (coatings insulation, etc.)	5	600	3 000	--	3 605
Other organic material	0	1	--	--	1
Other solid material	3 000	--	2 400	3 300	8 700

(BA) Betriebsabfälle

(WA) Wiederaufarbeitungsabfälle

(SA) Stilllegungsabfälle

(MIF) Abfälle aus Medizin, Industrie und Forschung

**Table A2-2: Contents of a Type B repository**  
 (based on Tables 3 & 5 in Wiborgh et al., 1986)

a)	Waste/Matrix	mass (Mg)	density (Mg m <sup>-3</sup> )	volume (m <sup>3</sup> )
	organics	24 700	1.0	24 700
	steel	66 100	7.9	8 367
	concrete/cement	194 800	2.35	82 894
	salt concentrates	10 600	2.0	5 300
	other	10 000	1.77	5 650
				-----
				≈126 910
<hr/>				
b)	Canisters/Backfill/Lining			
	concrete/cement	1 086 000	2.35	462 130
	steel	77 500	7.9	9 810
				-----
				471 940
			Total	598 850

Table A2-3: (taken from B-2, Nagra, 1984)

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**a) Elemental inventory for a typical\* concrete,  
Density 2.35 Mg m<sup>-3</sup>**


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<u>Element</u>	<u>% by weight</u>
O	47.500
Si	25.324
Ca	19.300
Al	3.300
Mg	2.100
Fe	0.860
H	0.550
K	0.460
Na	0.330
C	0.130
S	0.130
Ba	0.016
	<hr/>
	100.000

---

**b) Elemental inventory for a barium concrete,  
Density 3.13 Mg m<sup>-3</sup>**


---

<u>Element</u>	<u>% by weight</u>
Ba	44.000
O	35.850
S	11.250
Ca	4.300
Si	3.500
H	0.450
Al	0.400
Fe	0.200
Cl	0.050
	<hr/>
	100.000

---

\*) The typical concrete as shown in Table A2-3 a) is made up from:

	<u>% by weight</u>
Portland cement	16.6
Gravel, sand	75.0
Water	8.4
	<hr/>
	100.0

The use of pozzolanic and similar cements is envisaged by Nagra as these have resistance to chemical attack, particularly from sulphates. The chemical compositions of Portland cement and two pozzolanas are given in Table A2-4. For a complete discussion of pozzolanas, see Lea (1970). The pH of these cements is lower than other forms of cement because of the lower lime content ( $\approx$ pH 10). This would have microbiological implications as the environment would not be so hostile. Alternative resistant cements include supersulphated types whose pH remains highly alkaline, the disadvantage of these varieties is the difficulty in obtaining good sets.

**Table A2-4: Chemical composition of Portland cement and possible pozzolanas**

Material	Chemical Content						
	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	Na <sub>2</sub> O SO <sub>3</sub>	K <sub>2</sub> O
Portland cement	64.1	5.5	3.0	22.0	1.4	2.1	--
Pozzolanas							
1. Burnt clay	3.3	18.4	9.3	58.2	3.9	1.1	3.9
2. Fly-ash (British)	2.1	27.5	10.3	47.4	2.0	1.3	5.7

Various additives are often incorporated into cements, but their exact compositions are usually trade secrets. Some of these are organic in nature which would be an additional nutrient source for microbial activity or could, in themselves, act as complexing agents. For example, plasticisers such as lignosulphonate or polymerised naphthalene sulphonate are frequently added ( $\approx$ 0.2% by weight of cement). Retarders and accelerators may be used and Table A2-5 lists some examples of four different types.

**Table A2-5: Classification of retarders/accelerators used in concretes (after Lea, 1970)**

#### Examples

CaSO<sub>4</sub>.2H<sub>2</sub>O, Ca(ClO<sub>3</sub>), CaI<sub>2</sub>  
 CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, CaBr<sub>2</sub>, CaSO<sub>4</sub>.½H<sub>2</sub>O  
 Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>  
 Na<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>B<sub>4</sub>SO<sub>7</sub>, Na<sub>3</sub>ASO<sub>4</sub>, Ca(CH<sub>3</sub>COO)<sub>2</sub>

It can be seen that although the list is incomplete most of the additives contain some component which could be utilised by microbes either as an energy or nutrient source. Thus it is essential that the amounts and compositions of additives are known if nutrient budgets, biodegradation rates, etc. are to be evaluated. The permeabilities of concretes vary in the range  $10^{-20}$  -  $3 \times 10^{-18}$   $\text{ms}^{-1}$  which corresponds to a hydraulic conductivity (k) of around  $10^{-13}$  -  $3 \times 10^{-11}$   $\text{ms}^{-1}$ . Porosities are assumed to lie in the range 15 - 40% (vol./vol.).

**Metals**

Metals comprise  $\approx 10\%$  (by weight) of the repository inventory, most of it being in several forms of steel. Two steel elemental compositions are given in Table A2-6.

Aluminium and zinc from reprocessing will be disposed of in the metal form. However, because of the high pH environment, corrosion products must be anticipated almost immediately.

**Table A2-6: Elemental inventory of two representative steels**  
(taken from B-6, B-7, Nagra, 1984)

<u>Type 1.6342 Density 7.86 Mg m<sup>-3</sup></u>		<u>Type 1.4550 Density 7.96 Mg m<sup>-3</sup></u>	
<u>Element</u>	<u>% by weight</u>	<u>Element</u>	<u>% by weight</u>
Fe	97.600	Fe	67.997
Ni	1.150	Cr	18.000
Si (max.)	0.350	Ni	11.000
Mo	0.350	Mn	2.000
Cr (max.)	0.300	Nb	0.800
Mn	0.130	Co	0.100
C	0.120	C (max.)	0.080
		N	0.020
		B	0.003
	100.000		100.000

**Ash/Glass**

Ash is currently produced from the incineration of operational low-level waste and its composition, like that of glass, is uncertain. Negligible amounts of carbon will be found in the ash but the possible presence of phosphate must be ascertained.

### Organics

Bitumen consists of a complex mixture of organic substances, particularly hydrocarbons, and will be used as an organic solidifying matrix.

Polymers (resins, plastics) will be present in both the waste and waste matrix. The precise nature of these varies depending on the material in question.

Cellulose will result from the reprocessing waste and it is not clear whether or not it will be incinerated.

## 2 UNIT CELL

In order to simplify calculations, the complex assembly of different waste types and materials present in a type B repository are mathematically "averaged" to give a reference 1 m<sup>3</sup> unit cell of repository.

The total repository inventory, as listed in Table A2-1, is used to calculate the percentage volume of each of the major material categories. The mass of each material type per m<sup>3</sup> is then calculated from the density (Table A2-7). It is assumed that on emplacement, 0.1 m<sup>3</sup> of air is trapped within each unit cell.

**Table A2-7: Reference 1 m<sup>3</sup> unit cell of type B repository**

Material Category	Percentage Volume	Mass (kg)	Percentage Mass
organics	4.1	41	1.7
steel	3.0	237	9.7
cement/concrete	91.0	2138	87.2
salt concentrates	0.9	18	0.7
other solid materials (ash, glass, etc.)	1.0	18	0.7

The radionuclide contents in the unit cell are shown in Table A2-8 and are taken from the Project Gewähr safety analysis (Nagra, 1985).

**Table A2-8: Radionuclide content (mol) in the unit cell  
(taken from Project Gewähr\* (Nagra, 1985))**

<u>Radionuclide</u>	<u>Mol</u>
Cl-36	$4.37 \times 10^{-7}$
Ni-59	$1.61 \times 10^{-2}$
Se-79	$1.23 \times 10^{-7}$
Sn-126	$5.13 \times 10^{-6}$
I-129	$8.01 \times 10^{-6}$
Cs-135	$1.42 \times 10^{-5}$
Ra-226	$4.89 \times 10^{-7}$
Th-229	$5.02 \times 10^{-14}$
Pa-231	$4.13 \times 10^{-11}$
Np-237	$3.41 \times 10^{-5}$

\*) inventories from Table 3-4, Nagra, 1985, Vol. 7, converted from Ci to mol and averaged over the total repository volume

The organics in the unit cell are sub-classified as shown in Table A2-9 and, for each class, a representative formula is chosen to allow an equivalent molar concentration to be calculated. It is appreciated that this is a great simplification, bearing in mind the heterogeneity in composition in each of these classes. Similarly, although many different types of concretes/cements will be used, a reference composition is assumed (Table A2-3 a)) from which the unit cell concentration of Fe, C and S are calculated (Table A2-10).

For further calculations, each of these elements is assumed to be completely oxidised (as  $\text{Fe}(\text{OH})_3$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , respectively). This approach is intended to be sufficiently conservative to compensate for particular compositions with larger contents of potential oxidants (e.g.  $\text{SO}_4^{2-}$  additives in grouts - Wakeley et al., 1985).

**Table A2-9: Subclassification of organics**

Class	Representative formula	Unit cell concentration	
		(kg m <sup>-3</sup> )	(mol m <sup>-3</sup> )
Bitumen	$[(CH)_6(CH_2)_4S_3/20N_1/20O_1/20]$	5.64	40
Polymer (PVC, polyethylene)	$[CH_2CHCl]$	6.14	98
Ion-exchange resin	$[(C_6H_5CHCH_2)_2(N(CH_3)_3OH \cdot SO_3H)]$	20.42	56
Cellulose	$[C_6H_{10}O_5]$	8.80	54

**Table A2-10: Unit cell concentration of specific elements in concrete**

Element	Weight (kg m <sup>-3</sup> )	Molar content (mol m <sup>-3</sup> )
Fe	18.4	328
C	2.8	233
S	2.8	88

**APPENDIX 3****DERIVATION OF BIOMASS PRODUCTION FROM AVAILABLE FREE ENERGY**

As a first step to linking biomass production and available free energy, a set of background data for average anaerobic chemotrophic bacteria are taken from the review of Thauer et al. (1977):

- a) 0.1 mol of ATP (adenosine triphosphate) is required to synthesis 1 g (dry) of bacterial cells (catabolism)
- b) The maintenance energy for such cells for movement, osmosis etc. is 0.1 mol ATP/1 g (dry) of cells (anabolism)
- c) The energy required for the production of the ATP within the cell (i.e.  $\text{ADP} + \text{P} \rightarrow \text{ATP}$ ) is  $32 \text{ kJ mol}^{-1}$
- d) The microbial efficiency of chemical energy utilisation for the production of ATP is 10 % (the balance of the energy being lost as heat).

Combining this information gives an external chemical energy requirement of 64 kJ/g (dry) of bacteria cells.

Such an approach can be used to predict biomass for short-timescale, energy-limited systems but its direct applicability to extremely oligotrophic systems is more speculative. In particular, in a system where the rate of energy supply is very low, it is not clear if the maintenance energy in (b) would be applicable to very low metabolic rates. In the model, described in the text, annual energy production rates are converted into biomass production. This biomass is actually a measure of microbial activity and cannot distinguish between a large standing biomass which is metabolising very slowly and a smaller standing biomass with a higher metabolic rate. In the steady state case (where production rate = loss), the standing biomass is not important and will, in any case, be nutrient limited. Nevertheless, it may be worth investigating the energetics of the metabolism of extreme oligotroph in order to improve on the data from average bacteria.

APPENDIX 4MARL GROUNDWATER CHEMISTRY

The groundwater chemistry assumed for a reference repository in Marl is based on a memo from Dr. B. Baeyens of PSI (02.09.88). From a regression on extrapolated values for major anions and cations reported by Scholtis (pers. com.) the following were defined:

Na	2802.00 mg l <sup>-1</sup>
Mg	16.10 mg l <sup>-1</sup>
Sr	8.03 mg l <sup>-1</sup>
SO <sub>4</sub>	2536.00 mg l <sup>-1</sup>
Cl	2700.00 mg l <sup>-1</sup>

With the further assumptions of calcite saturation,  $P_{\text{CO}_2} = 10^{-2}$ , Temperature = 25°C and  $p_e = 0$  the following water chemistry was derived using the PHREEQE geochemical code (Pearson database, Pearson et al., 1989):

Element	Molality
Na	$1.28 \times 10^{-1}$
Mg	$6.62 \times 10^{-4}$
Ca	$2.71 \times 10^{-3}$
Sr	$9.16 \times 10^{-5}$
SO <sub>4</sub>	$2.64 \times 10^{-2}$
Cl	$7.62 \times 10^{-2}$
Total inorganic C	$5.72 \times 10^{-3}$

Additional values for P and N were taken from Scholtis (pers. com.):

NO <sub>3</sub>	107.00 mg l <sup>-1</sup> = $1.73 \times 10^{-3}$ mol l <sup>-1</sup>
NO <sub>2</sub>	4.94 mg l <sup>-1</sup> = $1.07 \times 10^{-4}$ mol l <sup>-1</sup>
P	0.49 mg l <sup>-1</sup> = $1.58 \times 10^{-5}$ mol l <sup>-1</sup>

To produce Table 3-3 in the main text of this report, the data above were rounded to 2 significant figures and expressed as molarities (assuming unit density of groundwater).

APPENDIX 5ESTIMATION OF RADIOLYSIS IN THE REFERENCE VOLUME

From Wiborgh et al., 1986, the major radiolytic components formed from operational waste are  $(\text{CH}_3)_3\text{N}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{SO}_2$  ( $\approx 130$ , 24, 9 and 6 kmol, respectively over a period of 500 years). With the exception of  $\text{H}_2$ , these components result from radiolysis of ion exchange resins: from Tables 26 and 27 of Wiborgh et al., 1986, it can be concluded that 9 kmol of the  $\text{H}_2$  can be attributed to the ion exchange resins and the rest to radiolysis of bitumen or concrete. The reference waste sort (BA-1b) includes the most radioactive exchange resins (Nagra, 1985, Vol. 2) and hence all radiolysis can reasonably be attributed to this source. This is further assumed to be evenly distributed over the total waste volume of 3095 m<sup>3</sup>.

Almost 90 % of the radiolysis occurs within the first 50 years. Within this period, the production within the reference 0.211 m<sup>3</sup> would be:

	mol
$(\text{CH}_3)_3\text{N}$	8.9
$\text{H}_2$	0.6
$\text{H}_2\text{SO}_4$	0.6
$\text{SO}_2$	0.4

For the calculations in Table 3-7,  $\text{H}_2\text{SO}_4$  is assumed to be completely deprotonated and  $\text{SO}_2$  to be dissolved and deprotonated to yield  $\text{SO}_3^{2-}$ .