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Main organic materials in a repository for high level radioactive waste

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Contents

1 Introduction

Within the interim report for SKB's assessment of the long-term safety for a KBS-3 repository /SKB 2004ab/ several issues dealing with geochemical aspects of the near field of the repository are described that need to be analysed. According to the KBS-3 concept, copper canisters with a cast iron insert containing spent nuclear fuel are surrounded by bentonite clay and deposited at approximately 500 m depth in saturated granitic rock. The chemical evolution of the buffer, backfill and rock is ultimately governed by the composition and flow of groundwater. During the excavation and the relatively long operational period, groundwater will suffer substantial changes in composition around the repository. The effects of several disturbances introduced to the system due to the works of the repository implementation are of relevance. In this regard, it is important to understand the chemical status of the repository system at closure in order to describe its immediate geochemical evolution after closure.

One of the disturbances identified in a high-level nuclear waste (HLW) repository is the presence of organic material. Although this effect is known to influence the system, no clear indications exist on the extent of the disturbance introduced. Organic materials may be decomposed through microbiologically mediated reactions, thus adding reducing capacity to the near-field of the repository. However, these materials might also be detrimental in enhancing the potential for radionuclide transport in groundwater. In SR-Can the possible effects of these materials will be reviewed from a chemical and microbiological standpoint /SKB 2003/.

Organic compounds can play an important role in the transport of radionuclides through the near- and far-fields of a radioactive waste repository because of their ability to form labile complexes, participate in redox reactions, and sorb onto solid surfaces. A good understanding of radionuclide behaviour is dependent upon accurate predictions of radionuclide speciation which must, therefore, include complexes with organic material.

In a HLW repository different categories of organic material may be leftover. There will be organic material produced by living organisms in the rock and tunnel environments. There will also be material brought into the repository by constructors. Finally, the mere presence of different human activities will generate organic material that remains in the repository, unless removed or prohibited. The main groups of possible residual organics in repository systems include;

- Different types of micro-organisms and small plants in the tunnels.
- Organic material entering with the ventilation air.
- Organic material in construction, buffer and sealing materials.
- Organic material in fuels and from vehicle emissions.
- Detergents and lubricants.
- Organic material from human activities.
- Organic remnants from blasting and/or rock-drilling operations.

This report is focused on identification of organic material that may be present in repository systems at the time of closure (unless removed), the chemical composition, structure and main organic degradation products of the identified material, as well as microbial processes that will have an effect on the material. Finally, a summary with recommended actions for the different types of organic material is supplied.

2 Microbial processes that may affect the organic material in the repository

2.1 Aerobic degradation of organic material

Biodegradation is a redox process through which organic material is oxidized. In complete oxidation, all organic carbon is converted into carbon dioxide. In aerobic degradation the organic molecules are oxidized by oxygen and converted into carbon dioxide and water:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad \text{equation 1}$$

Polymeric molecules will be split into monomers by the action of exo-enzymes produced by microorganisms. Molecules that contain nitrogen, sulphur and phosphate, for example proteins and nucleic acids, are degraded as shown in Figure 2-1. Some of the nitrogen, sulphur and phosphate groups are separated and expelled from the cell. However, the majority will immediately be assimilated by the degrading microorganism and used in biosynthesis. Consequently they will not be released to the environment.

2.2 Anaerobic degradation of organic material

There are two types of anaerobic degradations: fermentations and anaerobic respirations. A general picture of microbial degradation is shown in Figure 2-2. The figure shows the order in which the different microbial processes occur in an anaerobic environment. All biodegradation starts with hydrolysis of polymers to oligo- and monomers. The different monomers are then oxidized to other compounds or optimally to carbon dioxide by the different groups of microorganisms, depending on the available electron acceptors in the environment.

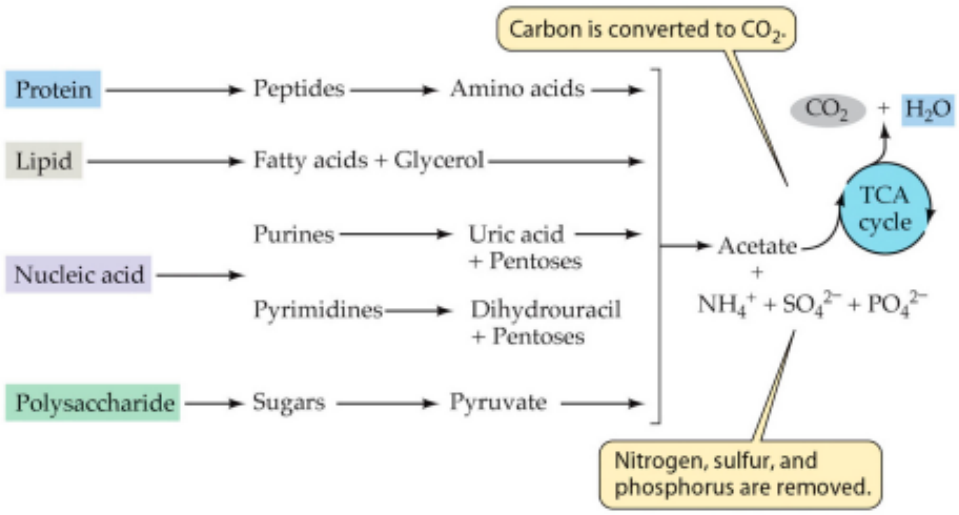


Figure 2-1. *Aerobic degradation of major cell components. The tri carboxylic acid (TCA) cycle, is one of the most central pathways in many degradation systems.*

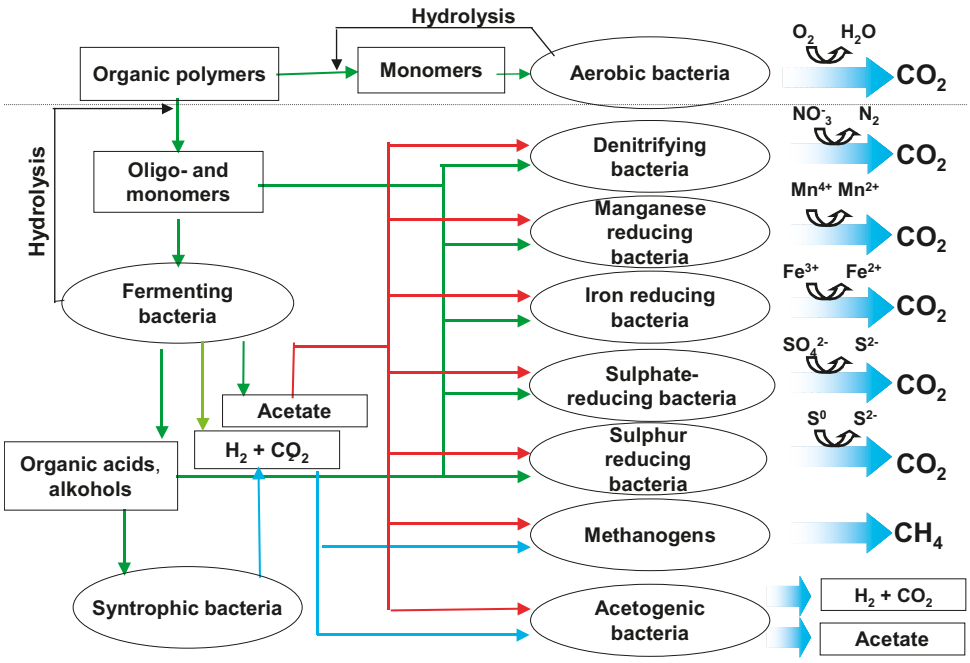


Figure 2-2. *Microbial degradation and the different microbial groups that are involved.*

2.2.1 Fermentation

In anaerobic systems with high amounts of organic material, fermenting microorganisms will thrive. Fermentations are degradation pathways that do not require external electron acceptors. Instead, electrons are shuffled around within the degraded molecule that has been split into two or more compounds. The degradation products consist of both more reduced and oxidized organic molecules such as organic acids, ketones and alcohols. Fermentation of sugar commonly gives carbon dioxide and ethanol.

Two fermenting bacteria common in the environment are *Bacillus* and *Clostridium*. They are often found in soil. Both are spore-formers but *Clostridium* is obligate anaerobic, whereas in the *Bacillus* genus obligate aerobes, facultative anaerobes and fermenting species are found /Madigan et al. 2003/. An example of the fermentation pathway of *B. licheniformis* follows (equation 2).

3 glucose $\rightarrow$ 2 glycerol + 2,3-butanediol + 4 CO_2 equation 2

From glucose, the fermenting organism produces glycerol, 2,3-butanediol and carbon dioxide.

Some of the *Clostridium*-species ferment sugars and occasionally starch and pectin to butyric acid, acetic acid, CO_2 and H_2 as the principal end products. As the acids in these fermentations accumulate, so-called butyric acid bacteria begin to produce more neutral compounds, including acetone and butanol from the acids. There are several other fermentation pathways in other species of fermenting organisms, but giving those details is slightly out of the scope of this report /Madigan et al. 2003/.

2.2.2 Anaerobic respiration

In natural environments anaerobic respiratory organisms follow a certain progression (see Figure 2-2). The first anaerobic respiration metabolisms that are activated when oxygen is depleted are those connected with the nitrate-, iron- and manganese-reducing bacteria. These organisms degrade short organic acids such as lactic acid and acetic acid but rarely larger organic molecules such as six-carbon sugars. The next metabolic type is represented by the sulphate-reducing bacteria. They use sulphur in sulphate as electron acceptor and produce hydrogen sulphide. Carbon and energy sources for sulphate reducers are short organic acids.

In a system with large amounts of organic material, like a compost, there should theoretically be a high production rate of hydrogen from various fermentation processes that could be utilised by methanogens and/or acetogens. In a deep ground water system on the other hand, the amounts of hydrogen coming from the degradation of organic material from surface or, as in the case discussed in this report, leftovers in the repository is probably quite small. Therefore the last part of the degradation chain in Figure 2-2 would be insignificant. This process, based on hydrogen from degradation of organic materials, must be distinguished from methanogenesis and acetate production that frequently occurs in deep ground water with hydrogen coming from thermo-catalytic processes in very deep environments inside Earth /Pedersen 2001/.

3 The chemical composition of microorganisms

The chemical composition of bacterial cells can vary but most of them have a similar constitution. An average bacterial cell has a total weight of $9.5 \cdot 10^{-13}$ g and a dry weight of $2.8 \cdot 10^{-13}$ g /Niedhardt et al. 1990/. In Table 3-1 the weights of the different macromolecules of an average *Escherichia coli* cell are listed.

There will be different types of microorganisms growing on the tunnel walls and in ditches in a repository during the construction and operational phases. Microorganisms growing on surfaces produce a film consisting of cells and a gel matrix, a so-called biofilm. The matrix is extra-cellular material, often polysaccharides /Christensen and Characklis 1990/. Most of the biological growth in a repository environment will occur in various types of biofilms, wherever there is liquid water.

3.1 The amount of organic material in biofilms – the microbial cells

The number of microorganisms that are present in a biofilm depends on the environment i.e. what nutrients are available, water flow, oxygen concentration, surface structure, temperature. Differences in these variables will be reflected both in the number of bacteria per surface area and the thickness of the biofilm. To estimate the amount of organic material in cells in a biofilm, different cell densities are evaluated here. The first biofilm density was reported by /Pedersen and Ekendahl 1990/. It was measured on glass slides placed in water flowing from 680 m depth in borehole KLX01 in Laxemar. This biofilm had about 10^9 microorganisms per m^2 and is regarded as a low-density biofilm. The other biofilm density evaluated was published by /Pedersen et al. 1986/ was established with a pure culture of a *Pseudomonas* sp. In both these studies the glass slides were incubated a short time, days or weeks, and only one layer of microorganisms developed. This biofilm had 10^{12} microorganisms per m^2 and is referred to as a high-density biofilm. In older biofilms, several layers of microorganisms can develop. In Table 3-2, calculations of the number of microorganisms per m^2, the corresponding biofilm thickness and the amount of organic material in microorganisms in hypothetical biofilms are presented. These calculations demonstrate that the contribution of the cells to the amount of organic material in a biofilm can vary from 10 μg m^{-2} to 3.0 g m^{-2}. The contribution of microorganisms in biofilms produced on tunnel walls and in ditches is more likely to be in the range 0.1 to 1,000 mg m^{-2} organic material because of low organic material content in the inflowing groundwater.

Table 3-1. Overall macromolecule composition of an average *E. coli* cell /Niedhardt et al. 1990/.

Cell constituent	Weight per cell (10^{-15} g)
Protein	155
RNA	59
DNA	9
Lipid	26
Lipopolysaccaride	10
Murein	7
Glycogen	7
Total macromolecules	273
Soluble pool	8
Total dry weight	284
Total weight	950

Table 3-2. Amount of organic material in microorganisms of a biofilm depending on cell density and number of cell layers. The calculations are based on data from Table 3-1.

Cell density per layer (m^{-2})	Number of cell layers	Organic material ($g\ m^{-2}$)
Low density:		
$3.5 \cdot 10^{9}$	1	$1 \cdot 10^{-5}$
$3.5 \cdot 10^{9}$	10	$10 \cdot 10^{-5}$
$3.5 \cdot 10^{9}$	100	$100 \cdot 10^{-5}$
High density:		
$1 \cdot 10^{12}$	1	0.03
$1 \cdot 10^{12}$	10	0.3
$1 \cdot 10^{12}$	100	3

3.2 The amount and composition of organic material in biofilms consisting of cells and exudates

3.2.1 Organotrophic biofilms

Organotrophic microorganisms, the group that degrades organic carbon in a respiratory metabolism, often produce an amorphous, extra-cellular matrix without microscopically recognisable structures. This matrix is commonly almost exclusively made of **E**xtra-cellular **P**oly**S**accharides (EPS). This gel-like material is formed when the organic macromolecules are partly hydrated and partly cross-linked /Christensen and Characklis 1990/. The monomer building blocks in bacterial EPS can be the following mono-saccharides, uronic acids and aminosugars: rhamnose, fucose, arabiose, xylose, mannose, glucose, glucuronic acid, galacturonic acid, mannuronic acid, N-acetylglucoseamin and KDO (2-keto-3-deoxy-octulosonic acid). Some bacteria produce EPS that consists of homo-polysaccharides. For example several *Acetobacter*-species produce extra-cellular cellulose that is chemically similar to cellulose in higher plants, i.e. β-1,4-linked un-branched glucans.

The biofilm thickness and density vary among different biofilms. Heterotrophic, EPS producing biofilms from different environments were reported to have thicknesses from 10 to 1,300 µm /Christensen and Characklis 1990/. The density in these biofilms varied from 5 to 105 kg m^{-3}. Calculations of the amount of organic material in biofilms per m^2 are presented in Table 3-3. Three different densities were chosen arbitrary: 10, 25 and 75 kg m^{-3}. These calculations show that the amount of organic material in a biofilm can vary between 0.1 and 75 g m^{-2} depending on thickness and density. Based on the calculations of organic material from microorganisms it can be concluded that between 0.1 and 1% of the organic material in a biofilm constitute microorganisms. The remainder is EPS.

Table 3-3. Amount of organic material in a biofilm depending on thickness and density.

Biofilm thickness (mm)	Estimated biofilm density ($kg\ m^{-3}$)	Amount organic material ($g\ m^{-2}$)
0.01	10	0.1
0.1	10	1
1	10	10
0.01	25	0.25
0.1	25	2.5
1	25	25
0.01	75	0.75
0.1	75	7.5
1	75	75

3.2.2 Biofilms of iron- and manganese oxidising bacteria

The most striking biofilm growth on tunnel walls and in ditches is that produced by the iron- and manganese oxidising bacteria. Several species in this group of bacteria produce extra-cellular material that has a distinct and recognizable shape.

Among the iron-oxidisers, the species *Gallionella ferruginea* and *Leptothrix ochracea* are predominant. Both were discovered by microscopy and described in the literature /Ehrenberg 1836, Kützing 1843/ in the first part of the 19th century.

Gallionella ferruginea

In the Äspö Hard Rock Laboratory (HRL) tunnel, the main biofilm forming bacterium is the iron-oxidiser *Gallionella ferruginea*. This bacterium produces large quantities of organic material, in the shape of a helical stalk, and oxidised iron on the tunnel walls and ditches at all positions in the tunnel where reduced ferrous iron containing groundwater intrudes and flows. /Anderson and Pedersen 2003/ measured the biofilm formation of *Gallionella* and its influence on iron oxide precipitation and the partitioning of lanthanides and actinides. Most of this study was done with a so-called BRIC, "**B**acteriogenic iron oxide **R**eactor, **i**n situ, **C**ontinuous flow" apparatus. The sampled material was produced inside growth tubes in the BRIC and simulates a biofilm in a ditch very well. In this study the *Gallionella* organisms produced stalks up to about 50 µm long per cell. The cell density was from 10^5 up to 10^6 per millilitre in the growth tubes. The BRIC system contains bacteria other than *G. ferruginea,* but the cell counting method used did not distinguish between different species.

The in situ BRIC experiments in the Äspö HRL corresponded very well with in vitro experiments in the laboratory when *G. ferruginea* was grown in pure cultures. In the growth tubes the highest measured number of *Gallionella* cells was $2.5 \cdot 10^6$ per ml and the average stalk length was 34 µm per cell and the maximum 60 µm per cell /Hallbeck and Pedersen 1990/.

/Hallbeck and Pedersen 1995/ reported that a *Gallionella*-biofilm produced in ground water used for heat exchange purpose, had a **T**otal **O**rganic **C**arbon (TOC) value of 0.147 µmol cm^{-2} and 0.330 µmol cm^{-2} Fe. This study also showed that the carbon/nitrogen ratio, (C/N), for cells was 4.3 but for cells and stalk material it was 6.8. The C/N ratio for *E. coli* cells is reported to be 3.4 /Niedhardt et al. 1990/. If the C/N ratio for cells in an iron oxidising biofilm is assumed to be 4 based on the data presented above, the factor between carbon in cells and biofilms will be 1.7 i.e. there will be 1.7 times more carbon in the *Gallionella* biofilms compared to if there were only cells. Iron oxidizing biofilms will, consequently, have a higher carbon content, 85%, compared to biofilms without stalks, e.g. 50% as used for the *E. coli* cells in Table 3-1. Calculating organic material content in biofilms cannot, therefore, be based on cell numbers only.

Using the TOC numbers for the biofilm formation in /Hallbeck and Pedersen 1995/ the 0.147 µmol carbon cm^{-2} correspond to 17.6 mg carbon per m^2 which in turn corresponds to 20.8 mg of organic material per m^2 if 85% of this is carbon.

The biofilm on the glass slides described above was estimated to be 30 µm thick and represented a thin biofilm of iron-oxidisers. If extrapolated, the amount of organic material will then be 690 g per m^3. On tunnel walls biofilms up to 10–15 cm can be formed, which then corresponds to about 70–100 g organic carbon per m^2 overgrown tunnel wall – a significant amount of organic material that should be accounted for.

Composition of the stalks and sheaths of iron- and manganese-oxidisers

The chemical composition of the stalks of *Gallionella* is still unknown. Titration studies of *Gallionella* cells and stalks have been published /Martinez et al. 2003/. It was shown that functional groups with acidic, basic and neutral pK_a values were present. Some of these groups are important for the sorption of iron oxides to the surfaces. The sheath composition of the

sheath forming and manganese oxidising bacterium *Leptothrix discophora* has been analysed /Emerson and Ghiorse 1993ab/. The analyses showed that dry sheaths consisted of 38% C, 6.9% N, 6% H and 2.1% S. The mass of the sheaths was distributed into the following groups of compounds; 34–35% were carbohydrates (polysaccharides), 23–25% were proteins, 8% were lipids and 4% were inorganic ash. The polysaccharides consisted of a 1:1 mixture of different uronic acids (glucuronic acid, galacturonic acid and mannuronic acid and at least one unidentified uronic acid) and one amino-sugar, galactose amine. Nine percent of the dry weight was 2,3-deoxyoctanoic acid. The surface of the sheaths probably has several hydroxyl-groups with binding properties for cations.

Biofilms with sulphur-oxidising bacteria

At some places in the Äspö HRL sulphur-oxidising bacteria can be found. There are both uni-cellular and filamentous organisms in this group of bacteria. The filamentous group is represented by species of *Thiothrix*, a sheath-forming bacterium that stores elemental sulphur inside the cells. This bacterium oxidises hydrogen sulphide with oxygen. It is thought to use organic carbon as a source of carbon and reduced electrons. Many other sulphur bacteria are autotrophic and use carbon dioxide as carbon source /Madigan et al. 2003/.

The composition of the sheaths of *Thiothrix* and other filamentous sulphur-oxidisers is not well explored. One reference suggests that the extra-cellular material is composed of cellulose because of its neutral sugar composition, methylation analysis and the identification of free oligosaccharides /Ogawa and Maki 2003/.

Literature is also lacking about biofilms made by sulphur-bacteria. A sulphur oxidising biofilm most probably consists of about the same amount of organic material as an iron-oxidising biofilm. This suggestion is based on the observation that sulphur oxidizing bacteria occur commonly in the Äspö HRL inter-mixed with iron oxidizers.

3.3 Fungi

Fungi belong to the Eukaryotes, which are organisms with a true nucleus and other cellular organelles. The cell wall of fungi is mostly built of chitin, although cellulose is present in some organisms /Madigan et al. 2003/. Chitin is a polymer of the glucose derivative N-acetylglucoseamine (Figure 3-1). It is laid down in micro-fibrillar bundles just like cellulose. Fungal cell walls are generally composed of 80–90% polysaccharide, with protein, lipids, polyphosphates and inorganic ions making up the wall-cementing matrix. In some organisms other glucans such as mannans, galactosans and chitosans replace chitin in the fungal cell wall. Fungi are often spread by spores, which are very resistant to heat and desiccation.

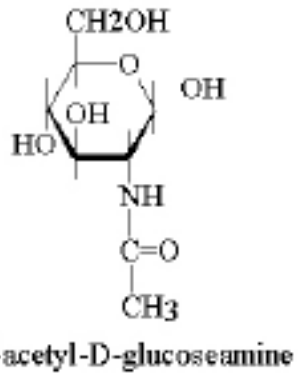


Figure 3-1. *N-acetyl-glucose amine molecule. Component of the fungal cell wall.*

3.3.1 Moulds

Moulds are filamentous, non-differentiated, multi-cellular fungi that are widely spread in nature. The moulds grow with hyphae that produce asexual spores called conidia. The conidia give mould its dusty appearance. Filamentous fungi are responsible for decomposition of wood, paper and cloth for example. Both cellulose and lignin are decomposed by fungi. Decomposition of lignin occurs almost exclusively by wood-rotting fungi. Lignin decomposing fungi is called white rot and cellulose decomposing is called brown rot since lignin is left unchanged. White rot fungi also decompose cellulose /Madigan et al. 2003/.

3.3.2 Yeasts

Yeasts are unicellular fungi. The most well studied yeast is *Saccaromyces cerevisiea*, also called Baker's yeast or Brewer's yeast. Ekendahl with co-workers /Ekendahl et al. 2003/ reported the existence of yeasts in deep granitic ground water. It is therefore plausible that yeasts will grow in biofilms on rock surfaces in a repository. The yeasts isolated from Äsö HRL groundwater were closely affiliated with *Rhodotorula minuta* and *Cryptococcus* sp. Many yeast species can live both with and without oxygen. In anoxic systems they use a fermentative metabolism and for example *S. cerevisiea* produce ethanol anaerobically /Madigan et al. 2003/.

3.4 Photosynthetic organisms

During the repository construction and waste deposition phases there will be electric light sources along the tunnels in the repository. Where the light intensity is high enough and water is present, growth of light harvesting, photosynthetic organisms such as cyanobacteria and green algae will occur. In the Äspö HRL tunnel cyanobacteria are common where the illumination is strong. At some places mats of mosses are growing on the tunnel floor, e.g. at tunnel length 1,320 to 1,335 m.

3.4.1 Cyanobacteria

The cyanobacteria belong to the domain *Bacteria* and are thus organisms without cell nucleus. Many species live as unicellular entities, but filamentous and colony forming types of cyanobacteria are also common. Some cyanobacteria have a cell wall that is similar to that of Gram-negative bacteria and their walls contain peptidoglycan. Others have cell walls made up of cellulose /Nobles et al. 2001/. Many cyanobacteria produce extra-cellular material that resembles envelopes or sheaths that bind groups of cells or filaments together in jelly-like masses.

Since cyanobacteria are photosynthetic they have photosynthetic pigments such as chlorophyll a and phycobilins. These pigments are found in large amounts in membrane structures inside the cells /Madigan et al. 2003/.

Many of the cyanobacteria have nitrogen fixation ability. In some species this unique process takes place in specialised cells called heterocysts. The cell wall of the heterocysts contains large amounts of glycolipids. In nitrogen fixating cyanobacteria up to 10% of the cell mass can be a nitrogen co-polymer of aspartic acid and arginine, a so-called cyanophycin.

The chemical composition of the biomass of two cyanobacteria, *Phormidium* sp. and *Spirulina maxima* showed that the distribution of the main components in cell differed (Table 3-4).

Table 3-4. The percentage chemical composition of *Phormidium* sp. and *Spirulina maxima* biomasses grown on synthetic media (% dry weight) /Cañizares-Villanueva et al. 1995/.

Component	*Phormidium* sp	*Spirulina maxima*
Protein	53.4	45.5
Lipids	9.4	2.5
Carbohydrates	27.5	42.5
Ash	9.7	9.5

Extra-cellular polymeric substances of cyanobacteria

Extra-cellular polymeric substances, EPS, of cyanobacteria vary between different species. The sugar components in EPS of a pure culture of *Phormidium* 94a were galactose, mannose, galacturonic acid, arabinose and ribose /Vicente-Garcia et al. 2004/. Another study of four filamentous cyanobacteria and one coccoid single cell green algae showed that the EPS contained 7.5–50.3% protein, 16.2–40.5% carbohydrates /Hu et al. 2003/. Among the mono-saccharides were found mannose, glucose, galactose, arabinose and rhamnose.

3.4.2 Unicellular green algae

Green algae should not be mixed up with cyanobacteria since they belong to a completely different domain of organisms. Green algae are eukaryotic organisms and thus they have a cell nucleus and other cell organelles. The photosynthesis takes place in organelles called chloroplasts. The cell walls of green algae are made of cellulose and their main carbon reserve materials are starch and sucrose /Perry et al. 2002, Madigan et al. 2003/. The cells themselves contain all components included in the bacterial cells (see Table 3-1).

The unicellular green algae are often found in environments inhabited by cyanobacteria and can therefore probably be found in green biofilms feed by artificial light sources in a repository.

3.4.3 Mosses

Mosses are plants without a clear differentiation in stems and leaves. They have a cell nucleus and other cell organelles such as chloroplasts and mitochondria. The cell wall is composed of cellulose and their carbon reserve material is starch.

The mosses thrive in environments with relative low light intensity and are favoured by high humidity. They are not a common contribution to the biota in tunnels and caves but have been observed in the Äspö HLW tunnel as mentioned above.

3.5 Biodegradation of organic material produced by microorganisms, fungi and photosynthetic organisms

The organic material produced by microorganisms will be degraded by other microorganisms both during the construction and the deposition periods. During the construction period most of the degradation will be aerobic, with oxygen. The first part of the deposition period in the closed repository will still be aerobic but in a relative short time the oxygen will be consumed by the degradation of organic material and anaerobic processes will increase.

Since the organic material discussed above is produced by living organisms, most of it is again degradable by microorganisms, given enough time and if water is available. This conclusion is based on the prominent role microorganisms have in perpetuating life and can be summed up in two adages termed Van Niel's postulate /Perry et al. 2002/:

"There are microorganisms present in the biosphere that can utilise every constituent part or product of living cells as sources of carbon and/or energy.

Microbes with this capacity are present in every environmental niche on Earth."

Even if the degradation processes of one organism are not running all the way to carbon dioxide, the organic waste products by this organism will be further degraded by other microorganisms. Fermentation products are good examples. Acids, alcohols, and ketones produced during fermentation can act as complexing agents, but they will probably be consumed by other microorganisms present in groundwater in the repository far before any radionuclides possibly escape a canister.

4 Organic material in the ventilation air

In the air coming from ground surface with the ventilation system to the repository tunnels there will be organic material. This material comprises seeds, pollen grains, spores and dust.

4.1 Seeds

Seeds from plants carry all nutrients necessary for the new plants development until a functional root and the first leaves have grown out. The chemical composition therefore differs compared to vegetative cells in the plant.

Seeds from caneberries, *Rubus* spp. such as red raspberry, blackberry and cloudberry had 6–7% protein and 11–18% oil /Bushman et al. 2004/. The seed of *Xylopia aethiopica* 63.65 g carbohydrates, 12.45 g protein and 9.58 g lipids per 100 g seed (wet weight) /Barminas et al. 1999/. The carbohydrate is starch that hydrolyses to sugar in a germinating seed.

4.2 Pollen

Pollen grains contain the male gametophyte produced by angiosperms, gymnosperms and seed plants. They are the vegetative and generative cells formed after mitosis (i.e. reduction division) of the microspore structure. They are usually between 10 and 100 µm in diameter and are encapsulated in a complex, sculptured cell wall.

Pollen grains contain cellulose and polymers made of cartinoids and cartinoid esters. They also have lipids as an energy resource and phytate as phosphorous source and contain enzymes and RNA and DNA /Rowley et al. 1981, Brooks and Shaw 1968/.

4.3 Spores

Spores can be both asexual reproduction bodies of filamentous fungi and the reproduction structures of cryptogams. The structure and composition of these spores are similar to seeds and pollen grains.

4.4 Organic dust

This kind of dust comes from living organisms and consists of a wide array of different bio-molecules.

4.5 Biodegradation of organic material from the ventilation

The seeds, pollen grains and spores coming with the ventilation air into the repository are products of living organisms and are generally biodegradable. The seeds and spores can germinate in the repository, like the moss in the Äspö tunnel. Plant material will be degraded by microorganisms when the tunnels are closed and backfilled, if not removed. One special property of seeds and spores is that the outer part is very resistant. If they do not germinate or are not biodegraded nothing else will affect them and they will probably be buried in the repository. Organic dust can also be degraded by microorganisms.

The amounts of seeds, pollen grains, spores and dust vary during the year with peaks in spring, summer and early autumn.

5 Organic material in construction material

5.1 Concrete

Concrete is a cement paste with different filling materials. All of this is inorganic material. To enhance different properties of concrete several additives can be added to the paste. The degradation of these agents will, with time, generate low molecular organics and, eventually, carbon dioxide. These additives can be divided into accelerating, retarding, water reducers, super plasticizers, and air entraining agents /Lindvall 2001/.

Accelators are inorganic salts. The most commonly used is $CaCl_2$.

Retarders are classified as any reactive chemical which will extend the pumping time and/or thickening time for cement slurry. Among others, powder, low temperature organic retarders appear to be relatively common, as lignosulfonates (solid) or organosulfonates (liquid). These compounds are adsorbed to or precipitated on the surface of the cement particles. Cellulose derivatives such as carboxymethyl hydroxyethyl cellulose (CMHEC) have been also used for many years as cement retarders.

Anti-foamers or defoamers are added to decrease foaming during mixing operations. These are commonly organophosphates.

Water-reducing additives. These compounds reduce the water content in the cement paste up to 15%. Most commonly used are lignosulfonates and sulfonated naphthalene (Figure 5-1) or formaldehyde. They disperse the cement particles because of their dipolar charging properties. The amount of this additive in concrete is 0–0.1% (weight).

Super plasticizers are the same as the water reducing additives but with stronger effects. They are used to lower the mix water requirement of concrete and they are added in amounts up to 0.4% of the weight. Within this type of additives, superplasticizers are broadly classified in four groups:

1. sulphonated melamine-formaldehyde condensates (SMF),
2. sulphonated naphthalene-formaldehyde condensates (SNF),
3. modified lignosulphonates (MLS), and
4. others including sulphonic acid esters, carbohydrate esters, etc.

Most available data, however, pertain to SMF- and SNF-based admixtures. They are supplied either as solids or as aqueous solutions. One of the most common superplasticizers is sodium-sulphonated naphthalene formaldehyde condensate (Na-SNFC). Other known superplasticizers are polymers of sulphonated melamine formaldehyde, sodium lignosulphate and gluconic acid /Gascoyne 2002/.

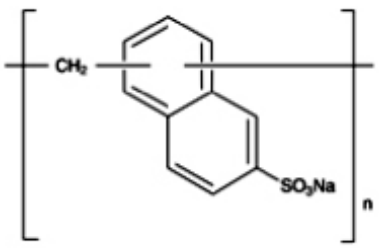


Figure 5-1. *Chemical structure of naphthalene sulphonate.*

Air entraining agents – AEA are used to enhance the resistance against freeze-thaw actions by increasing the air content in the concrete. The most commonly used compounds are acryl sulfonate, alkyl sulfonates and phenol ethoxylates. They are added in amounts up to 0.01% (weight).

5.2 Asphalt

Asphalt is composed of a bituminous binding agent and a stone material. The binding agent can be in the form of bitumen, soft bitumen or emulsion of bitumen. Bitumen is a distillation product of crude oil. It has thermoplastic properties. Road oil and bitumen lacquer are other products used in asphalt. Also bitumen emulsion is used. This is an emulsion of bitumen and water together with an emulsifier /Swedish National Encyclopedia 1990ab/.

The composition of bitumen is very much dependent of the source of the crude oil and the distillation procedure, but the main fraction is heavy hydrocarbons of different kinds. The bitumen is often what is left after the refining procedure has made gasoline, diesel and other fuels. This fraction includes very heavy organic molecules that often have oxygen, sulphur and nitrogen atoms in their structures /Tissot and Welte 1984/. The chemical composition and physical properties is still not fully understood.

5.3 Bentonite clay

Bentonite is an inorganic clay which is currently mined in many different places around the world. The chemical name is hydrated sodium calcium aluminium silicate and the weight-% of the different elements is 9.98% Al, 20.78% Si, 4.10% H and 65.12% O. The exact composition depends on the origin of the clay.

Data on chemical analyses of the organic material in bentonite are very sparse. /Sjöblom 1998/ made the assumption that bentonite will be contaminated by organic material in the environment it was deposited in and by the mining and transportation operations. The organic material is suggested to be humus and the calculated amounts were < 0.1 g/kg bentonite from the environment and < 0.1 g/kg bentonite from the mining operation. There will also be some contamination of lubrication from the compaction of bentonite into blocks, 0.5 g/kg bentonite.

Humus is a collective name for the organic material in soil and water that is composed of large organic molecules that are not easily degraded. It has three different fractions, one insoluble fraction named humin, and two soluble fractions, named humic and fulvic acids. Humic acids can be isolated by decreasing the pH. At pH 2 the humic acids start to coagulate and the formed precipitate can be separated by filtration. The humic acids are melanin-like polymeric aromatic phenols and carboxylic acids. Fulvic acids are left in the filtrate. These are small aromatic and aliphatic compounds that are soluble at every pH. They have a molecular weight between 1,000 and 10,000 and have many carboxyl- and hydroxyl-groups that make them chemically active /Stevenson 1994/.

Three different types of bentonite clays are suggested to be investigated for potential use in the repository: Friedland Na^+, Milos Ca^{2+} and Wyoming Na^+ bentonites /SKB 2004a/. Analyses of the organic carbon content of the Milos and the Wyoming bentonite are shown in Table 5-1, where the weight percentage values are recalculated to the mass of organic material. The gross formula for organic material used is CH_2O.

Table 5-1. Amount of organic material in different bentonite clays.

Bentonite material	Organic carbon (weight %)	Organic material (weight %)	Organic material (kg/tonne of bentonite)
Milos Ca^{2+}	0.24	0.6	6
Wyoming Na^{+}	0.20	0.5	5

5.4 Wood

The main components of wood are cellulose and lignin /Fries 1973/. Cellulose is linear polymer of D-glucose with beta 1,4-linkage (Figure 5-2). Lignin, on the other hand, is a polymer with aromatic structures (Figure 5-3).

In wood there are so called secondary compounds present that are produced by the tree. A characteristic compound for pine tree is pinene, a terpenoid. Tannin is another compound produced by trees and the structure is shown in Figure 5-4 /Hagerman and Butler 1994/.

5.5 Degradation of organic material in construction materials

5.5.1 Concrete

After hardening, superplasticizers are strongly bound and immobilised within the hydrated phases of the Portland cement /Onofrei et al. 1992/, although relatively little is known about their precipitation in an insoluble form /Atkins and Glasser 1992/. It is possible that superplasticizers could decompose in a repository, if submitted to a radiation field /Gascoyne 2002/.

The additives in concrete are strongly bound to the concrete particles. As long as the concrete structures are intact these compounds are stuck. If the structures are removed there will be dust of concrete and this will increase the risk for release of the additives to the ground water. Naphthalene sulfonates have been shown to be degraded in aerobic environments /Brilon et al. 1981/.

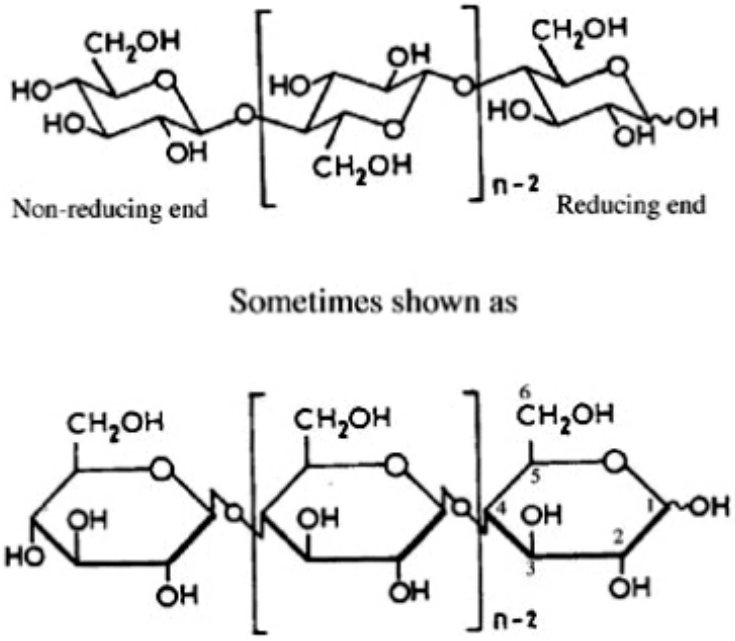


Figure 5-2. *The cellulose subunits.*

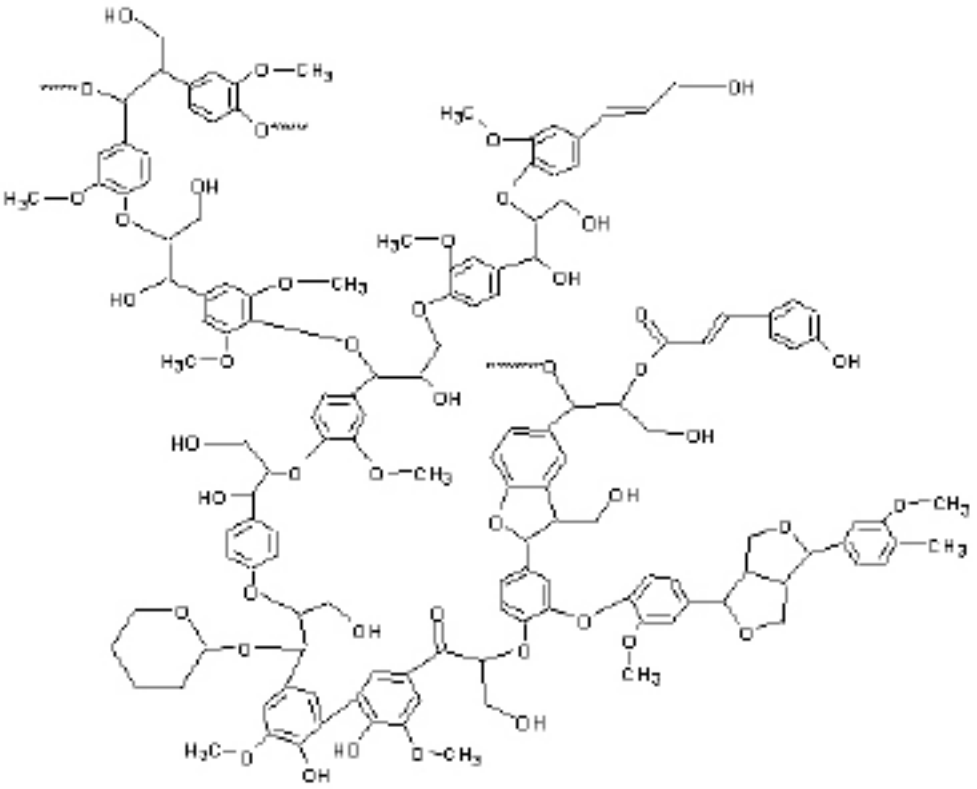


Figure 5-3. *Part of the lignin molecule.*

5.5.2 Asphalt

Most of the components in asphalt are large organic molecules and with low water-solubility. The most soluble organic molecules are the BTEX-group; benzene, toluene, ethyl-benzene and xylenes, all which are biodegradable at slow but significant rates. None of these compounds will be found in large quantities in asphalt.

5.5.3 Bentonite

The organic material in bentonite is assumed to be mainly formed by humic substances. These compounds will probably be bound to clay particles and trapped in the bentonite. A calculated problem, presently under extensive investigation, is the potential oxidation of organic material in the bentonite to carbon dioxide and hydrogen sulphide by sulphate reducing bacteria.

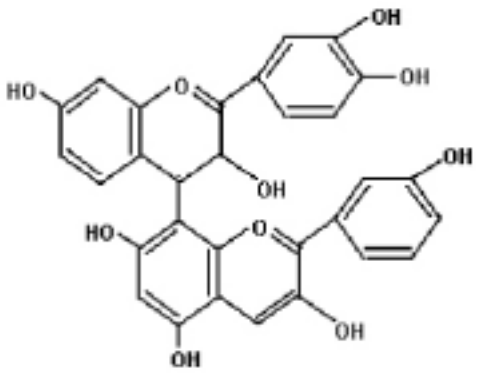


Figure 5-4. *Example of a tannin.*

Humic and fulvic acids have many carboxylic and hydroxyl groups. These properties make them possible complexing agents. In conclusion, the lack of data on organic material in bentonite merits a more thorough investigation of the amounts and composition of this organic material.

5.5.4 Wood

The cellulose part of wood is readily degraded by both bacteria and fungi. These organisms have extra-cellular cellulolytic enzymes, which break the bonds in cellulose /Perry et al. 2002/. Furthermore, cellulose easily degrades under alkaline conditions, commonly occurring at nuclear repositories build up with cement. The main degrading reactions of cellulose as well as the main degradation products can be found in section 8.6.5.

Lignin, on the other hand, is only degraded by a special type of fungi, the white rot fungi (bacidiomycetes). The degradation involves action of oxygen, peroxides and the enzyme ligninase. The fungi do not utilize the lignin in their metabolism but other microorganisms can use the phenolics degradation products as substrate /Perry et al. 2002/.

Secondary compounds that are produced by trees, for example pine tree tannins, are slowly biodegradable. Their chemical structure with many hydroxyl-groups makes them potential complexing agents. For example, sawdust was traditionally used to decrease clogging by iron precipitates in drainage systems because of the ability of tannins to bind iron.

Most of wood constructions will probably be removed before closure of the repository. A source of wood material that might be more problematic to get rid of is sawdust from construction work that has ended up in ditches or become mixed with gravel.

6 Diesel and emissions from diesel engines

Diesel is a distillation product made from crude oil. It is defined by the temperature interval used in the distillation, 150°C–350°C. By this diesel is a very complex mixture of compounds with different properties. The largest part of diesel is alkanes but there are also poly aromatics (PAH), alkyl-benzenes, branched or unsaturated aliphatic hydrocarbons and sulphur. The exact composition depends on the type of diesel used. The diesel in Sweden with the highest environmental specification is called MK-1 diesel, see Table 6-1 /Swedish National Road administration 2002/.

In complete combustion the products are carbon dioxide and water. The combustion in diesel engines is generally not complete. Unless efficient filters and catalysts are installed there will be particles in the emission from diesel engines. They have a size between 0.1 and 0.3 μm and are mostly soot (carbon) from the engine. They also consist of water, sulphuric acid and condensed hydrocarbons.

6.1 Other particles from vehicles

Particles can also come from tires. These are mostly rubber and some of the rubber contains PAH (poly aromatic hydrocarbons). The chemical name of natural rubber is isoprene. The rubber in tyres is cross-linked with sulphide bridges to enhance the elastomeric properties /Swedish National Encyclopedia 1992b/

Particles from brake linings can be deposited on the rock walls and in ditches. These particles are mostly metal, mainly copper, and do not contain organic material /Johansson et al. 2004/.

6.2 Degradation of diesel and its emissions

If a diesel spill occurs in a repository during construction, most of it will be pumped out with the infiltrating groundwater. Some of the diesel can stick to surfaces of rock material in ditches etc but it will most probably be biodegraded in presence of oxygen and water. The hydrocarbons have very low solubility in water and there will be a two-phase system if diesel and water are in contact. Since it is an equilibrium system there will be a slow partitioning of hydrocarbons into water during a long time. The components in diesel are different kinds of hydrocarbons and most of them are degraded by bacteria. Also in anaerobic environments, diesel hydrocarbons are degraded by sulphate- and/or iron-reducing bacteria /Meckenstock et al. 2000, Annweiler et al. 2002, Eriksson et al. 2005/.

Table 6-1. Composition of MK-1 diesel.

Compound	MK-1 diesel
Poly aromatic hydrocarbons (PAH)	Maximum 200 ppm often below 80 ppm
Aromatic hydrocarbons	Maximum 5 weight%
Benzene	Not detectible
Olefins	Not detectible
Sulphur	Maximum 10 ppm often 1 to 5 ppm
Oxygenates	Not added
Cykloaliphates naphtenes	Not regulated up to 50 weight%

Condensed hydrocarbons, PAH, are large molecules and are probably more slowly degraded especially in anaerobic systems than aromatic and aliphatic hydrocarbons are, even though anaerobic degradation of PAH has been reported /Annweiler et al. 2002/.

The organic material from diesel will probably have a negligible influence on the nuclear waste except as oxygen consuming carbon compounds in microbial degradation. Rubber particles will generally not be degraded by microorganisms.

7 Detergents and lubricants

During the construction of the repository detergents and lubricants will be used at many places.

7.1 Detergents

Among degreasing agents and detergents, surfactants are the most widely used ingredients in detergents. The two most common surfactant groups are linear alkylbenzene sulphonates (LAS) and alkyl phenol ethoxylates (APE) (see Figure 7-1 (a) and (b) respectively). LAS are the quantitative most important tensides for household and industry.

Also vegetable tensides (based on plants) are available.

7.2 Hydraulic oils and lubricants

As discussed later in section 10, the main sources of hydrocarbons at the repository are diesel oil and hydraulic and lubricating oils (see Figure 10-1 and Figure 10-2). Oil spills usually contain a complex mixture of aliphatic hydrocarbons, PAH's and cyclic hydrocarbons.

Lubricants are widely used for all kinds of vehicles and machines. There are both mineral and vegetable lubricants and also synthetic ones. The main components are fats and oils. The chemical structure of fats is shown in Figure 7-2. Different additives are added to the lubricants.

Dispersants keep sludge, carbon and other deposit-precursors suspended in oil. Detergents keep the engine parts clean from deposits, rust/corrosion inhibitors prevent or control oxidation of oil, formation of varnish and sludge, retard corrosion, and prevent viscosity increase**.** Extreme Pressure (EP), anti wear and friction modifiers form protective film on the engine parts and reduce wear and tear. Metal deactivators forms surface films so that metal surface does not catalyze oil oxidation. Pour Point Depressant lowers freezing point of oils assuring free flow at lower temperatures. Anti-foamants reduces foam in crankcase and blending /Leugner 2005/.

Lubricating oils are products that have a broad profile in the C18–C40 with nearly no resolved alkanes being present. Common types of lubricating oils include crackcase oil, transmission fluid, hydraulic fluid and cutting oil. In some hydraulic fluids, the PAH concentrations can be very low, in comparison with most of the other refined products. However, as stated by /Wong and Wang 2001/, lubricant oils can also become a important source of PAH when degrading.

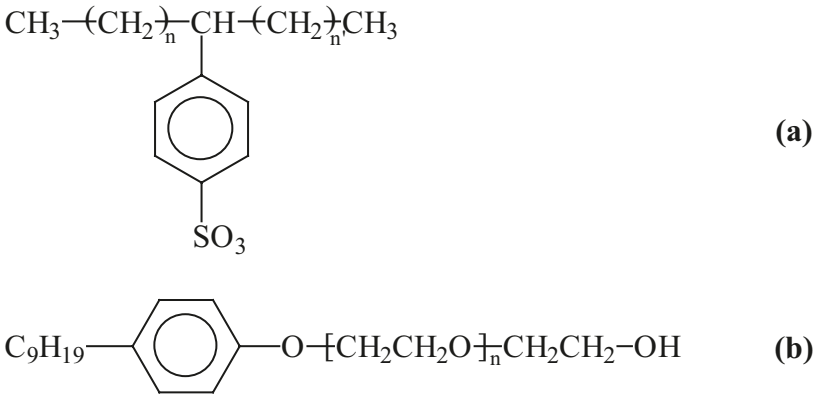


Figure 7-1. *Molecular formula of generic (a) LAS and (b) APE.*

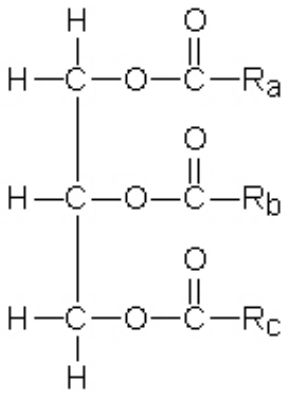


Figure 7-2. *Lipid molecule with a glycerol backbone and the ester linkages to three fatty acids Ra, Rb and Rc.*

7.3 Degradation of detergents and lubricants

7.3.1 Detergents

The natural degradation of LAS appears to be very efficient under oxic conditions, achieving percentages of 95–99%. The breakdown of LAS surfactants involves the degradation of the straight alkyl chain, the sulphonate group, and finally the aromatic group /Scott and Jones 2000/.

On the other hand, APE are less biodegradable than LAS. Estimated biodegradation ratios are quoted between 0–20% /Swisher 1987, in Scott and Jones 2000/. In addition, restrictions on the use of APE have arisen since the discovery that their breakdown products are more toxic to aquatic organisms than the APE themselves. Despite of this, APE are still among the most widely used non-ionic surfactants /Snyder et al. 2001/.

The biodegradation of APE leads to the shortening of the ethoxylate chains to alkyl phenol carboxylates leading ultimately to nonyl and octyl phenols (see Figure 7-3). Nonyl phenol (NP) is approximately 10 times more toxic than its ethoxylate precursor.

Many of the tensides and emulsifiers that were used earlier had long and heavily branched non-polar chains. Those products are to a low extent biodegradable and some, for example alkylphenol ethoxylates, have degradation products that are very stable /Swedish National Encyclopedia 1995/.

Nowadays there are several emulsifiers and tensides available on the market, made from vegetables or produced by microorganisms. These products are biodegradable and do not produce long-lived metabolites.

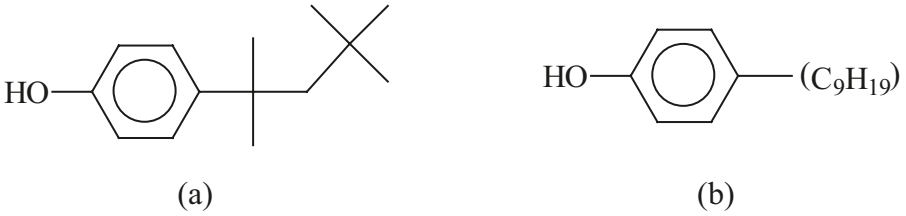


Figure 7-3. *Molecular formula of APE degradation products: a. p-t-Octylphenol and b. p-Nonylphenol.*

7.3.2 Lubricants

Lubricants can also be mineral or vegetable based. The vegetable fats and oils are more easily degraded but also mineral oils will be degraded but slowly.

The degradation is fastest in oxygenated environment and the tensides, emulsifier and lubricants will be part of the pool of organic material that contributes to oxygen consumption in the repository after the closure.

From all organic compounds found in oils or refined petroleum products, the monoaromatic hydrocarbons are found to be the most water soluble constituents /Eganhouse et al. 1996/. As a consequence, benzene and its alkylated derivatives are the hydrocarbons most frequently found in groundwater. Once groundwater moves away from the oil source, microbial degradation is the dominant process controlling the fate of these compounds /Eganhouse et al. 1996 and Massias et al. 2003/.

It should be noted that there is no single strain of bacteria with the metabolic capacity to degrade all the components found within crude oil. In nature, biodegradation of a crude oil typically involves a succession of species within the consortia of microbes present /Venosa and Zhu 2003/. Degradation of petroleum involves progressive or sequential reactions, in which certain organisms may carry out the initial attack on the petroleum constituent; this produces intermediate compounds that are subsequently used by a different group of organisms, in the process that results in further degradation.

The characterisation of bacterial communities that grow efficiently in presence of hydrocarbons have been the subject of decades of academic and industrial research /Zobell 1946, Atlas 1977, Foght et al. 1990, Pelletier et al. 2004/. Results were applied to the development of commercial fertilizers which have all in common the addition of nutrients to oily residues and the induction of optimal conditions for Hydrocarbon Degrading Bacteria (HDB). HDB have been found active in most marine environments including in the Arctic Ocean.

Generally, saturated n-alkanes are the most readily degradable components in a petroleum mixture /Zobell 1946, Atlas 1981/. Biodegradation of n-alkanes with molecular weights up to C44 has been demonstrated.

As previously stated, aerobic conditions are generally considered necessary for extensive degradation of oil hydrocarbons in the environment since major degradative pathways for both saturates and aromatics involve oxygenases /Atlas 1981, Cerniglia 1992/. Many studies have shown that oxygen depletion leads to sharply reduced biodegradation activities in marine sediments and in soils /Atlas 1981, Hambrick et al. 1980/.

Although anaerobic oil degradation has been shown in some studies to occur only at negligible rates /Atlas 1981/, recent studies have shown that anaerobic hydrocarbon metabolism may be an important process under certain conditions /Head and Swannell 1999/. The biodegradation of some aromatic hydrocarbons, such as BTEX compounds, has been clearly demonstrated to occur under a variety of anaerobic conditions. Studies have also demonstrated that in some marine sediments, PAHs and alkanes can be degraded under sulfate-reducing conditions at similar rates to those under aerobic conditions /Caldwell et al. 1998, Coates et al. 1997/. The importance of anaerobic biodegradation of oil in the environment still requires further studies.

Nevertheless, the oil left in the holes may be limited. One option is the use degradable hydraulic oil and lubrication greases. Most of these oils are based on biological oils and alcohols from the mineral oils. The use of degradable hydraulic oils and lubrication greases is an option not disregarded in the SKB repository /SKB 2004b/ since true biological oils based on rape-oil degrade in nature within a few weeks, synthetic oils within a few months and mineral oils within several years.

8 Organic materials from human activities

8.1 Tobacco products

Smoking will be prohibited in the repository both during construction and the deposition phase. Remnants from smoking will, therefore, not be present in the repository. However, snuff is widely used in Sweden and will certainly be used by the personnel during construction and deposition periods, especially if smoking is prohibited. Instructions should be given how to take care of the tobacco when it is used. Still a significant amount of used snuff will certainly be dropped.

Snuff is made of dried and ground tobacco plant leaves. Then water and sodium chloride are added to the tobacco. To keep the humidity in the snuff, propylene glycol is added and as a pH regulator sodium carbonate is used. The main part of the leftover of snuff is the plant leaf mixed with saliva from the user. A portion of snuff has a weight of about 1 g. Nicotine is the main predominant alkaloid component in the tobacco plant. It is a tertiary amine composed of a pyridine and a pyrrolidine ring. Nicotine may exist in two different three dimensionally structured shapes or stereoisomers. Tobacco contains only (S)-nicotine (also called l-nicotine), which is the most pharmacologically active form /Pool et al. 1985/. The nicotine content of this is 8–10 mg. When it has been used only 10–20% of the nicotine is left, that is between 0.8 and 2 mg. The nicotine molecule is shown in Figure 8-1. Although the major alkaloid in tobacco is nicotine, there are other alkaloids in tobacco. Those components include nornicotine, anabasine, myosmine, nicotyrine, and anatabine. They make up 8 to 12 percent of the total alkaloid content of tobacco products /Piade and Hoffmann 1980/. In some varieties of tobacco, nornicotine concentrations exceed those of nicotine /Schmeltz and Hoffmann 1977/.

The majority of the tobacco is plant cell wall material. This is made of pectin acid and small amounts of galactane and arabane. It also consists of polymerisation products of hexoses: glucose, galactose and mannose. To this polymerisation products of uronic acids are present: glucuronic acid, galacturonic acid, and of some pentoses. Some parts of the leaf are made of cellulose /Fries 1973/.

8.2 Dust from human skin and hair

The dust that comes from the human skin basically consists of dead cells from the outermost cell layer of the skin. It is composed of keratin, a threadlike protein compound /Swedish National Encyclopedia 1992c/. Hair is a special development of the keratin layer of the skin. It differs from skin by its higher sulphur content in the keratin /Swedish National Encyclopedia 1992a/. Dust from humans consequently mostly consists of protein compounds.

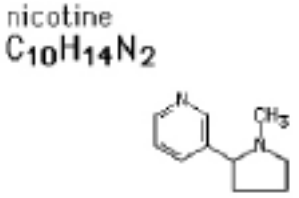


Figure 8-1. *The nicotine molecule.*

8.3 Fibres from clothes

The fabrics used in working clothes are made of synthetic fibres and/or cotton. Polyester is the mostly used synthetic fibre. Its chemical structure is show in Figure 8-2. Refined and bleached cotton fibre is composed of cellulose up to 99% (see cellulose in section 8.6.5).

8.4 Urine

The construction personnel have to be informed about the importance to keep the tunnel clean from waste of different kinds. There will be portable toilets available at convenient distances in the tunnel during construction but some urination will probably take place in out-of-the-way parts. The main organic components of urine are: urea, creatinin, ammonia, uric acid, amino acids and other inorganic components such as sodium, chloride, sulphate or carbonate /Lehninger 1982/.

8.5 Plastics and paper

Plastics are man-made materials that come from fractions of natural gas or crude oil changed chemically into solid form. These are the building blocks of plastics and they form chemically linked subunits called monomers. The long chains of monomers form polymers that compose plastics. There are two basic types of plastic: *thermosetting* and *thermoplastics*. *Thermosetting* plastics are set to a permanent shape and cannot be softened. These plastics are used primarily for multiple use items, such as dishes and furniture. *Thermoplastics* are soft when exposed to heat and pressure and harden when cooled. Thermoplastics are the most common type of plastic and are used to make a variety of products.

Table 8-1 lists some of the most common types of thermoplastics, and their common uses.

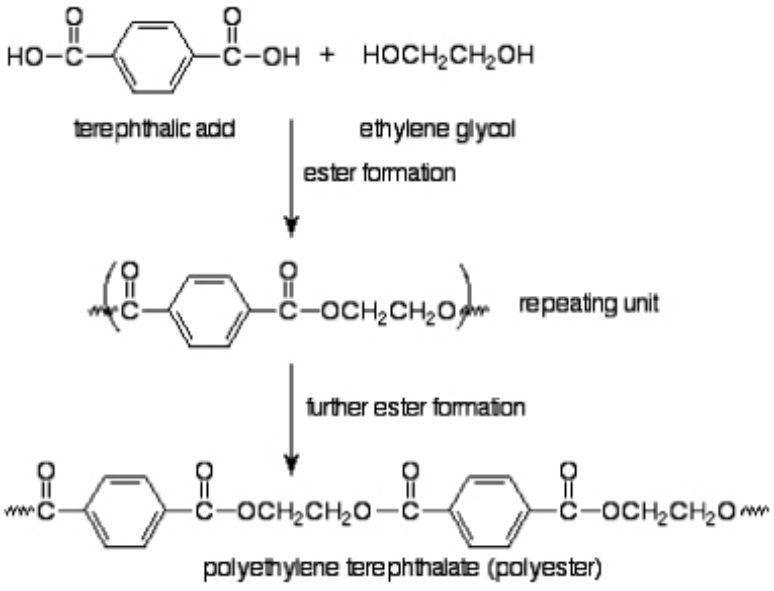
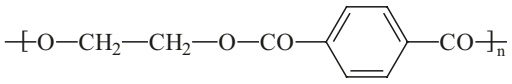
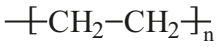
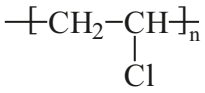
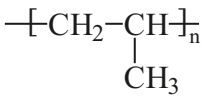
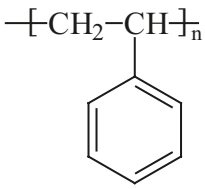


Figure 8-2. *Example of a polyester polymerisation reaction.*

Table 8-1. Most common types of thermoplastics.

Plastic type		Common uses	Formulae
Polyethylene Terephthalate (PET)		soft drink containers	
Polyethylene PE	High Density Polyethylene (HDPE)	milk crates, milk jugs and beverage bottles	
	Low Density Polyethylene (LDPE)	trash bags and other films	
Polyvinyl Chloride (PVC)		Insulation, pipes, some food containers, bottles.	
Polypropylene (PP)		Pipes, screw-on cap	
Polystyrene (PS)		packing materials, plastic utensils...	

Paper is made of cellulose. Cellulose is a relatively common material in the context of low and intermediate level radioactive repositories, due to its presence in daily use objects such as tissues, clothes or paper. However, its presence entails an important risk to the repository security, since the complexation capacity of polyhydroxy ligands has been largely described in the open literature.

8.6 Degradation of organic material from human activities

8.6.1 Tobacco products

The remaining tobacco from snuff is mainly plant leaf and it will be easily degraded by microorganisms, and by that contribute to the oxygen consumption in a closed repository.

The destruction of nicotine by microorganisms was investigated by /Batham 1927/ who observed an increase in the nitrate content of soil to which nicotine had been added. He assumed that this increase was due to the conversion of the alkaloid to nitrate by soil bacteria. The quantitative destruction of nicotine in a synthetic medium by individual species of bacteria was studied by /Bucherer and Enders 1942, in Hylin 1958/. They isolated three organisms in pure culture. /Wada and Yamasaki 1953/ reported the destruction of nicotine by a microbe as well and further characterisation and classification of this microorganism was performed by /Tabuchi 1954/. In addition, /Hylin 1958/ described several organisms which have been isolated in pure culture from tobacco seeds and from soil. Nicotine decomposing bacteria have been described by several investigators /Sguros 1954, Conn and Dimmick 1947, Weber 1935, Wenusch 1942, 1943, Bucherer 1942, 1943, Hylin 1958, Frankenburg and Vaitekunas 1955, Wada and Yamasaki 1953, 1954/ and they have been reported to be both, aerobic and anaerobic depending on the microbial species.

The ability to use nicotine as source of carbon and nitrogen seems to be shared by relatively few microorganisms since the toxicity of this substrate inhibits the adaptation of large numbers of bacteria to its use as a metabolite.

Some degradation products have been identified to be products of nicotine microbial degradation. Among them, 6-hydroxynicotine and 6-hydroxy-3-succionoylpyridine have been reported /Hylin 1958, Frankenburg and Vaitekunas 1955/. In addition, the oxidation of nicotine may produce 3-carboxylic pyridine acid or nicotinic acid.

8.6.2 Dust from skin and hair

The proteins in skin and hair will be degraded by microorganisms in the repository both by aerobic and anaerobic bacteria.

8.6.3 Fibres from clothes

The cellulose fibres will be degraded by microorganisms, both bacteria and fungi. Polyesters on the other hand are relatively resistant to biodegradation.

8.6.4 Urine

Urine contamination in the repository has a positive effect on most biodegradation of organic material, as it constitutes an additional nitrogen source. Nitrogen is generally a limiting nutrient.

The high amount of biodegradable substrate triggers rapid microbial growth, which strongly alters the chemical composition of urine. One of the dominating reactions is the decomposition or hydrolysis of urea. This microbially catalyzed reaction produces ammonia and increases the pH to above 9.

Urea is the major component of urine. The release of urea to the soil is known to affect the soil N-cycle. Urea hydrolyses rapidly, producing ammonia and releasing OH^- and can be broken down with the help of the enzyme urease, producing the alkaline product of ammonia and carbonate. Urease is a large heteropolymeric enzyme that catalyzes the hydrolysis of urea using a bimetallic nickel centre. This enzyme occurs in such different organisms and among the species and micro-organisms able to degrade urea in this process there are bacteria, algae, fungi and higher plants. Its primary function is allowing the organism to use urea as a nitrogen source. Urease, as any enzyme, is a catalyst which function is the increase of the chemical reaction rate without being affected itself.

During the urea hydrolysis process an unstable intermediate product forms to that rapidly degrades to ammonia and carbon dioxide. This intermediate product is $H_2NCOONH_4$ (ammonium carbamate) although due to its unstable character, the transformation of urea in soil essentially can be written with the following overall reaction:

$$H_2N\text{-}CO\text{-}NH_2 + 3\ H_2O \rightarrow 2\ NH_4^+ + OH^- + HCO_3^- \qquad \text{equation 3}$$

During the hydrolysis, soil pH can increase to pH > 7 because the reaction requires H^+ from the soil system.

8.6.5 Plastics and paper

In the last years, a series of biodegradable thermoplastics have been emerged. A plastic is known as biodegradable when living organisms (such as fungi, bacteria, algae…) can attack the chemical structure of the polymer to convert it into food The susceptibility of plastic to biodegradation depends on the chemical structure, so that polyethylene or polyesther are just slightly biodegradable, while polyurethanes are considerably biodegradable. A biocompatible

polymer is one that does not damage any living organism, either by chemical means or because of its own biodegradability.

As example can be given for the degradation of an aliphatic polyester with high melting point, poly tetra methylene succinate, that was degradable by some soil bacteria in aerobic environment /Pranamuda et al. 1995/. Also polyurethane, polyester polyurethanes and polyether polyurethanes were reported to be degraded by microorganisms and especially fungi in an aerobic environment /Nakajima-Kambe et al. 1999/. The environment in a repository will be depleted in oxygen in a relative short time after closure and there are limited supplies of the important nutrients nitrogen and phosphorous. Because of that, plastic degradation will probably be very slow. Plastics will therefore remain in the repository for a considerable length of time, unless removed.

Paper left in the repository might be degraded by microorganisms. Cellulose easily degrades under alkaline conditions, without needing the presence of microorganisms. This is a common process assumed to occur at nuclear repositories containing concrete as part of the engineering barriers. The three main degrading reactions are: i) the peeling off reaction ii) the base-catalysed cleavage of glycosidic bonds (alkaline hydrolysis) and iii) formation of non-reacting end groups through chemical transformation of reducing end groups to meta-saccharinate, which in fact are inter-related /Van Loon and Glaus 1998, Glaus and Van Loon 2004/.

Isosaccharinic acid (ISA) is the main product of anaerobic cellulose degradation formed at room temperature /Van Loon and Glaus 1998/ ISA is a general term for 3-deoxy-2-C-(hydroxymethyl)-D-aldonic acids showing both α and β diastereoisomers. Its structural formula is schown in Figure 8-3.

Furthermore, among the degradation products of cellulose, ISA has been identified conclusively as a key component, being one of the most responsible organics influencing on the speciation and mobility of radionuclides in a repository of radioactive waste.

In general, mass balances for carbon show that the large majority of reactions products found in solution can be explained by formation of ISA and other low-molecular weigth carboxylic acids. On the other hand, as described elsewhere /Motellier and Charles 1998, Glaus et al. 1999/, some other degradation products of cellulose can be identified at alkaline pH. Thus, among others, these include glycolic acid, lactic acid, acetic acid, formic acid, as well as metasaccharinate, although all of them represent only 10% of the total dissolved organic compounds. All of them are acids with important complexation capacity. Table 8-2 shows the degradation kinetics of cellulose considering a final analysis time of 239 days.

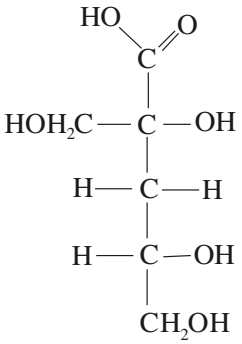


Figure 8-3. *α-Isosaccharinic acid.*

Table 8-2. Degradation kinetics of cellulose. Products concentration referred to the total DOC content (in %). Data from /Glaus et al. 1999/.

Analytes	7 days	40 days	62 days	119 days	181 days	239 days
Formic	0.60	1.22	1.09	1.19	1.30	1.30
Acetic	1.80	2.66	2.12	2.39	1.93	2.07
Glycolic	0.37	0.71	0.66	0.70	0.83	0.85
Pyruvic	0.20	0.23	0.17	0.11	0.13	0.10
Glyceric	0.46	1.68	1.27	0.90	1.05	0.94
Lactic	1.22	1.79	1.51	1.60	1.63	1.59
Threonic	1.59	1.77	1.32	0.94	0.99	1.16
Isosaccharinic	56.6	85.0	76.1	74.0	78.1	77.1
DOC	123	317	471	685	784	910

/Glaus and Van Loon 2004/ reported an extensive work were the degradation of pure cellulose and cotton cellulose at the conditions of an artificial cement pore water (pH=13.3) has been measured at 60° and 90°C for reaction times between 1 and 2 years. An interesting observation reported by those authors is the chemical instability of α-isosaccharinic acid at 90°C due to its hypotetically fragmentation induced by its sorption on $Ca(OH)_2$. Carbon mass balances showed that α-isosaccharinic acid is thereby transformed to other low-molecular weight carboxylic acids, which would reduce the concentration of organic compounds that strongly complex radionuclides.

9 Organic material from blasting and/or rock-drilling

Depending on the method used for construction, blasting or rock-drilling machine, a certain amount of debris from the activity will be left.

9.1 Blasting

Paper and plastic material from cables and detonators are typical leftovers from blasting. See section 8.5.

A study made in Canada showed that blasting left nitrate on rock surfaces and in the ground water /Stroes-Gascoyne and Gascoyne 1998/. Even if nitrate is not an organic material it can affect organic material since it is a crucial nutrient for microorganisms. A supply of extra nitrate will increase the possibility for degradation of the organic material left in a repository. Nitrate is also an electron acceptor for nitrate-reducing microorganisms and will be consumed quickly when the repository starts to get anaerobic, see section 2.2.2.

9.2 Rock-drilling

Drilling-machines may leave spills of various hydrocarbons as discussed above (see section 6).

10 Estimation of the amounts of stray materials left in the repository system

10.1 Background

The description of the initial state of the engineered parts of the repository system is one of the main bases for the SR-Can safety assessment. The initial state of each sub-system composing the repository system is described by a set of variables, selected to allow an adequate description of the long-term evolution of the component in question in the safety assessment. Stray materials, including organics, of relevance in the three different sub-systems of the barriers are defined below/SKB 2006/:

1. **Buffer:** in the deposition holes the canister will be surrounded by a buffer of bentonite. Two different types of bentonite are selected as reference in SR-Can. One is a natural sodium bentonite from Wyoming (MX-80) and the other is a natural calcium bentonite from Milos (Deponit CA-N).

   The *deposition holes* are assumed to be filled with groundwater between drilling and emplacement, draining is therefore the first step /SKB 2006/. This means that water soluble stray materials are expected to be pumped out.

   Deposition holes are expected to be carefully cleaned prior to the emplacement of the buffer and canister. To limit the amount of oil left in the holes one option is to use degradable hydraulic oils and lubrication greases. Most of these oils are based on biological oils and alcohols from mineral oils. Hence, limited amounts that have not been quantified are expected.

2. **Backfill of deposition tunnel:** the deposition holes are drilled in the floor of the deposition tunnels. Three backfill concepts are analyzed in SR-Can:
   - *Case A.* To backfill the entire tunnel section with pre-compacted blocks made of a mixture of 70 wt-% crushed rock and 30 wt-% bentonite and bentonite pellets.
   - *Case B.* Another concept is to place prefabricated blocks of 100% natural Friedton clay in the tunnel.
   - *Case C.* To in situ compact a mixture of 30 wt-% bentonite and 70 wt-% crushed rock in the tunnel.

   The chemical state of the backfill is defined by the material composition and by the pore water composition and the occurrence of structural and stray materials in the deposition tunnel. According to the backfill pore geometry described in /SKB 2006/, the porosity of the three different sub-systems can be calculated assuming a final total saturation of the system (see Table 10-1).

Table 10-1. Backfill pore geometry /from SKB 2006/ and calculated porosity. The void ratio is related to the porosity by the relation: $\phi = \frac{e}{1+e}$.

	Case A	Case B	Case C
Comments	**78% of the cross-section assumed to be filled with blocks, 20% with pellets and 2% is void**	**78% of the cross-section assumed to be filled with blocks, 20% with pellets and 2% void**	**the average void ratio is given by the average dry density**
Void ratio (*e*)			**0.42**
Blocks	**0.23**	0.35	
Pellets	1.45	1.45	
Calculated porosity (φ)*			
Blocks	0.187	0.259	
Pellets	0.592	0.592	
Total porosity	**0.284**	**0.340**	**0.296**

*calculated in this work.

Figure 10-1 shows the relative amounts of different organic stray materials expected in the deposition tunnels. Plastic materials, originating from detonators and their cables together with hydraulic and lubricating oils are the main organic components likely to be present in deposition tunnels.

The distribution of the expected stray materials in the deposition tunnels of both Forsmark and Laxemar is nearly the same considering the type and relative amounts of the different stray materials.

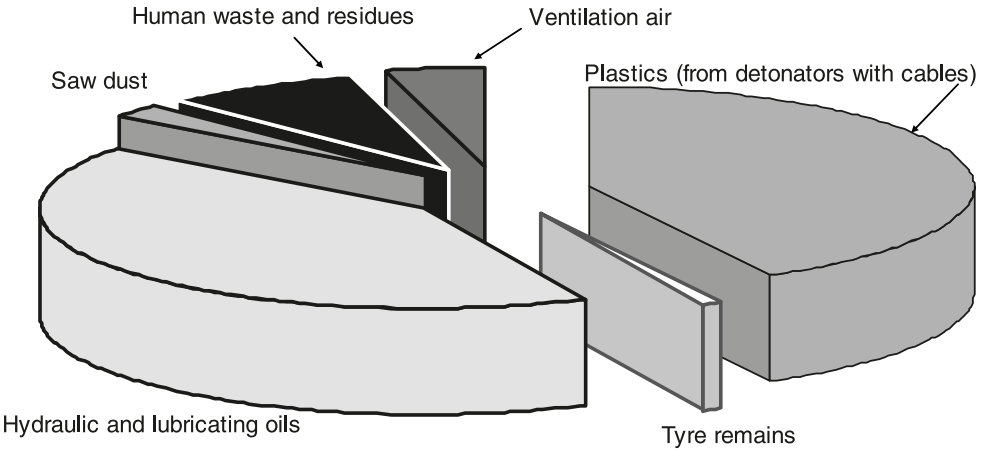
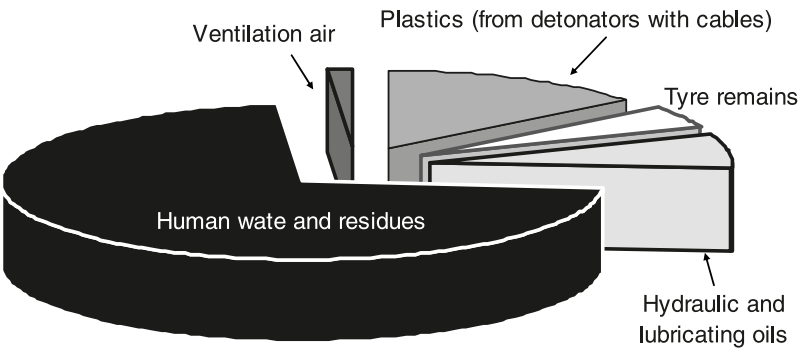


Figure 10-1. *Relative amounts of the different stray materials left in deposition tunnels. Data from /SKB 2006/.*



main tunnel and other repository cavities

Figure 10-2. *Relative amounts of the different stray materials left in other repository cavities. Data from /SKB 2006/.*

3. **Backfill of other repository cavities:** repository cavities other than deposition tunnels as can be the access ramp, shafts, central area and tunnels can be backfilled with the same material as the deposition tunnels.

   The backfill geometry is determined by the dimensions of the different cavities and is detailed in /SKB 2006/. Concerning the backfill concept, the concept applied for the deposition tunnels may be applied also in this case (Case A, B and C, described in the previous sub-section).

   Stray materials will be present in these cavities in the form of spillage and waster products from machine use, contaminants from blasting, human refuse and materials introduced via the ventilation air, etc. Figure 10-2 shows the relative amounts of different organic stray materials expected in the main tunnel and other repository cavities. In this case, human wastes are one of the main organic materials expected. Detonators with cables and hydraulic and lubricating oils follow the list of expected organic materials in the remaining repository cavities.

10.2 Estimated total amounts

The amounts of stray material left in the repository are very much dependent on requirements on stripping and cleaning of the repository cavities before the backfilling. These requirements may be detailed at later stages /SKB 2006/.

Still, an estimation of the amount of stray materials in the deposition tunnels as well as in other repository cavities is provided in /SKB 2006/.

The estimation of amounts of stray materials in the deposition tunnels has been done in amount per metre of tunnel (g/m), and total amounts (in kg) in both Laxemar and Forsmark areas, see Table 10-2 and Table 10-3.

The estimation of total amounts of stray materials left in other cavities has been given in /SKB 2006/ and, although they are more general than for the deposition tunnels, the inventory is judged to be comprehensive and include all potential stray materials.

Table 10-2. Summary of the estimated amounts of stray materials left in the deposition tunnels. Data from /SKB 2006/.

Material	Component	Deposition tunnels		
		Amount per metre tunnel (g/m)	Total amount (kg)	
			Forsmark [1]	Laxemar [2]
Detonator with conductor	Aluminium	0.8	40	50
	Plastic	5	200	300
Explosives	NO_x	0.2	10	10
	Nitrate	50	2,000	3,000
Bolts	Steel	1,000	50,000	60,000
Concrete constructions	Concrete	40	2,000	2,000
Tyre wear	Rubber	0.1	5	7
Exhausts	NO_x	–		
	Particles	–		
Detergents and degreasing compounds		0		
Hydraulic and lubrication oil		5	200	300
Diesel oil		–		
Battery acid		–		
Metal chips		0.1	5	6
Wood chips	Wood	0.3	10	20
Corrosion products	Rust	80	4,000	5,000
Urine	Urea	0.8	40	50
Other human waste	Organics	–		
Ventilation air	Organics	0.4	20	20

[1] Forsmark – Length of deposition tunnels 47,503 m.
[2] Laxemar – Length of deposition tunnels 60,620 m.

Table 10-3. Estimates of stray materials left in the other cavities. Data from /SKB 2006/.

Material	Component	Total amount (kg)
Detonator with conductor	Aluminium	20
	Plastic	100
Explosives	NO_x	4
	Nitrate	1,000
Bolts	Steel	50,000
	Concrete	30,000
Road beds	Concrete	3,000
	Aphalt	1,000
Concrete constructions	Concrete	3,000
Tyre wear	Rubber	30
Exhausts	NO_x	600
	Particles	20
Detergents and degreasing compounds		*
Hydraulic and lubrication oil		50
Diesel oil		*
Battery acid		*
Metal chips		2
Wood chips	Wood	3
Corrosion products	Rust	200
Urine	Urea	300
Other human waste	Organics	500
Ventilation air	Organics	10

* finite, not quantified, amount.

10.3 Evolution with time: degradation processes

The main organic compounds left as stray material in a repository are carbohydrates and hydrocarbons. The presence of water is crucial for all degradation. When the bentonite has gained its eventual swelling pressure the flow of water will be dramatically reduced over the areas where the stray materials will be found. The exception is compounds that are water soluble and have been transported with the groundwater flow during construction and filling up phase of the repository. The main part of the degradation will occur during the first 100 years. Below follows a description for respective group of material.

10.3.1 Degradation of carbohydrates

Urea

As described in section 8.6.4, urea will be hydrolysed and degraded into ammonium and carbon dioxide very fast. The degradation process starts immediately and the ammonium will be consumed by microorganisms. By the time of closure only a small fraction will be left. This fraction will be degraded in a time frame of weeks to months.

Other human waste

Materials like hair, skin, fibres from clothes and some snuff are included here. The materials will be disposed randomly in small doses and by that they will have a large surface area. These materials are biologically degradable and the decomposition will start immediately. By the time of closure only a small amount will be left and this will be degraded in about 1–5 years.

Organics from ventilation

This material has small size and a large surface area to volume ratio. This enhances degradation. The materials are mostly biological and will be degraded in about 1–5 years.

Wooden chips and sawdust

Degradation of wood is dependent on specialised fungi and oxygen. Larger pieces are more difficult to degrade because of small surface area to volume ratio. There are several examples of wood that have been preserved for very long time. One extreme example is the fossil wood Dunarobba in Italy, which is 1.5 million years old. This wood was buried in sediment and clay, which protected it from degradation, presumably by reduction of the flow of water and by that also transport of electron acceptors and nutrients. Another example is mosses. In mosses in Sweden intact wood can be found that has been deeply buried for up to several thousand years. The explanation for this is that no electron acceptors other than carbon dioxide have been present and therefore no degradation has occurred. Carbon dioxide can only be used as electron acceptors by methanogens and acetogens and they cannot use long chained carbohydrates as substrate.

A situation with almost no transport of water is comparable with the repository situation when the saturated bentonite clay is fully saturated.

How long wood can be intact therefore depends on the function of the bentonite. If there is no flow it can persist for hundred thousands of years.

One group of compounds present in wood is the tannins (see section 5.5.4). These compounds are resistant to degradation. The molecular structure includes many hydroxyl-groups making them possible as complexing agents.

10.3.2 Degradation of hydrocarbons

Plastics

Degradation of plastic is very much depending on the size of the pieces. Small pieces and dust of plastic will be degraded faster than large pieces due to the size of the exposed surface area. Important factors for degradation are also flow of water and by that the transport of nutrients and electron acceptors. Degradation of plastic will be fast during the operational phase of the repository because of available flowing water and oxygen. Plastics left close to bentonite in the closed and saturated repository will probably be left intact for several thousands of years.

Rubber

Rubber is even less degradable than plastics. Remains of rubber dust from tyres are very small but degradation in groundwater is probably infinitesimal. If some degradation occurs it is dependent on flowing water, as all other degradation processes.

Rubber left in or in close connection to bentonite will probably be intact for several thousands of years.

Hydraulic and lubrication oil

These compounds are more soluble in water than plastics and rubber although the solubility is low. During the operational phase and the first years when water is flowing and oxygen is present there will be degradation of hydraulic and lubrication oils, especially if so-called biodegradable types are used. Also under anaerobic conditions there will be degradation as long as there is a flow of water.

Asphalt

The more soluble compounds in asphalt will be degraded as long as there is flowing water in the repository. Most of the heavy hydrocarbons will remain in the asphalt and not degrade for several thousands of years.

10.3.3 Time scale of degradation for organic materials in the deposition tunnels in Forsmark and Laxemar

Calculations on the degradation of organic materials have been done by classifying the different types of substances according to three categories (carbohydrate, hydrocarbon and surface active substances) as well as taking into account the following assumptions:

i) **Deposition holes.** Since the expected amounts of the chemical substances in the stray materials in the deposition holes are negligible or a limited amount not quantified, they are disregarded here.

ii) **Deposition tunnels.** The total potential volume of water assumed to fill the deposition tunnel cavities (see Table 10-4) has been calculated by taking into account both, the total volume of the systems as well as the total porosity of the different backfill concepts calculated in Table 10-1.

   From information given in Table 10-2, it is possible to calculate the expected amounts of stray materials to be left in the deposition tunnels classified according to three categories (carbohydrate, hydrocarbon and surface active substances) as well as the estimated concentration (in kg/m^3) of these substances.

The classification of these three categories includes:

– carbohydrate substances coming from humus, wood chips, ventilation air, and other human wastes
– hydrocarbons coming from oils, degreasing compounds, plastics, rubber, etc
– surface active substances coming from hydrocarbons, as well as degreasing compounds and detergents. In this case, the total amounts are zero or a limited amount not quantified.

In Table 10-5 an estimation has been made on how much of the different carbohydrates and hydrocarbons will be degraded in the deposition tunnels during the first 100, 1,000, 10,000 and 120,000 years in Forsmark, Table 10-5a and b, and in Laxemar, Table 10-5c and d.

iii) **Other repository cavities.** The total volume of water assumed to fill the main tunnel and the other repository cavities (see Table 10-4) has been calculated by taking into account both, the total volume of the systems as well as the total porosity of the different backfill concepts calculated in Table 10-1. The data in Table 10-3 has been used to estimate the total amounts according to the three categories described above. Table 10-6a and b show estimated amounts of carbohydrates and hydrocarbons in other cavities after degradation for up to 120,000 years.

Table 10-4. Calculated volume of water to fill the deposition tunnels as well as other cavities in Forsmark and Laxemar assuming total saturation for the different backfill concepts under study.

	Forsmark			Laxemar		
Total length of deposition tunnels (m) /SKB 2006/	47,503			60,620		
Total volume of deposition tunnels (m^3) /SKB 2006/	1,306,333			1,667,089		
Total volume of main tunnel and other cavities (m^3) /SKB 2006/	865,000			1,020,000		
	Forsmark Case A	**Case B**	**Case C**	**Laxemar Case A**	**Case B**	**Case C**
Total volume of water in deposition tunnels (m^3)*	370,998	444,153	386,674	473,453	566,810	493,458
Total volume of water in main tunnel and other cavities (m^3)*	245,660	294,100	256,040	289,680	346,800	301,920

* calculated in this work.

Table 10-5a. Estimation of the amount of carbohydrate material left after different periods of time in the deposition tunnels in Forsmark.

Compound	Amounts left (kg)	Left after 100 years (kg)	Left after 1,000 years (kg)	Left after 10,000 years (kg)	Left after 120,000 years (kg)	Left (kg)
Urea	40	0	0	0	0	0
Other human waste	0	0	0	0	0	0
Organics from ventilation	20	0	0	0	0	0
Wooden chips and sawdust	10	7.5	7.5	7.5	7.5	7.5

Table 10-5b. Estimation of the amount of degraded hydrocarbon material for different periods in the deposition tunnels in Forsmark.

Compound	Amounts left (kg)	Left after 100 years (kg)	Left after 1,000 years (kg)	Left after 10,000 years (kg)	Left after 120,000 years (kg)	Left (kg)
Plastics	200	200	200	150	150	150
Rubber	5	5	5	4.5	4.5	4.5
Hydraulic and lubrication oil	200	100	0	0	0	0

Table 10-5c. Estimation of the amount of carbohydrate material left after different periods of time in the deposition tunnels in Laxemar.

Compound	Amounts left (kg)	Left after 100 years (kg)	Left after 1,000 years (kg)	Left after 10,000 years (kg)	Left after 120,000 years (kg)	Left (kg)
Urea	50	0	0	0	0	0
Other human waste	0	0	0	0	0	0
Organics from ventilation	20	0	0	0	0	0
Wooden chips and sawdust	20	15	15	15	15	15

Table 10-5d. Estimation of the amount of hydrocarbon material left after different periods of time in the deposition tunnels in Laxemar.

Compound	Amounts left (kg)	Left after 100 years (kg)	Left after 1,000 years (kg)	Left after 10,000 years (kg)	Left after 120,000 years (kg)	Left (kg)
Plastics	300	275	250	225	225	225
Rubber	7	6.5	6	5	5	5.25
Hydraulic and lubrication oil	300	150	150	150	150	150

Table 10-6a. Estimation of the amount of carbohydrate material left after different periods of time in the other cavities in Forsmark and Laxemar.

Compound	Amounts left (kg)	Left after 100 years (kg)	Left after 1,000 years (kg)	Left after 10,000 years (kg)	Left after 120,000 years (kg)	Left (kg)
Urea	300	0	0	0	0	0
Other human waste	500	0	0	0	0	0
Organics from ventilation	10	0	0	0	0	0
Wooden chips and sawdust	3	2.5	2.5	2.5	2.5	2.5

Table 10-6b. Estimation of the amount left hydrocarbon material for different periods in the other cavities in Forsmark and Laxemar.

Compound	Amounts left (kg)	Degraded after 100 years (kg)	Degraded after 1,000 years (kg)	Degraded after 10,000 years (kg)	Degraded after 120,000 years (kg)	Left (kg)
Plastics	100	90	80	75	75	75
Rubber	30	28	25	21	21	21
Hydraulic and lubrication oil	50	25	0	0	0	0
Asphalt	1,000	950	900	800	800	800

For carbohydrates it assumed that compounds that can be degraded will do so during the first 100 years, if there is enough flowing water. The remaining compounds will probably be left after 120,000.

The degradation of hydrocarbons will in general be somewhat slower than degradation of carbohydrates. Also for hydrocarbons the more easily degraded compounds will be degraded during the first 100–10,000 years, the rest will be left after 120,000 years.

From the tables above the total amount of carbohydrates and hydrocarbons that will be degraded have been calculated and shown in Table 10-7a–c.

Table 10-7a. The total amount and the amount of degraded organic material in the deposition tunnels in Forsmark.

Substance	Total amount (kg)	Left (kg)	Degraded (kg)
Carbohydrates	70	7.5	62.5
Hydrocarbons	405	162	313

Table 10-7b. The total amount and the amount of degraded organic material in the deposition tunnels in Laxemar.

Substance	Total amount (kg)	Left (kg)	Degraded (kg)
Carbohydrates	90	15	75
Hydrocarbons	607	380.25	226.75

Table 10-7c. The total amount and degraded organic material in other cavities in Laxemar or Forsmark.

Substance	Total amount (kg)	Left (kg)	Degraded (kg)
Carbohydrates	813	2.5	819.5
Hydrocarbons	1,180	896	284

Some of the organic material is insoluble in water. When calculating a possible concentration of organic material in groundwater in a repository, the insoluble matter has to be subtracted before the calculations are made. Here the estimated amounts of degraded organic material are used to calculate the highest amounts and concentrations of the different substances (carbohydrate, hydrocarbon and surface active substances) that can occur in deposition tunnels, Table 10-8, and in other repository cavities, Table 10-9. The concentrations are obtained using the volumes of water for the different cavities (see Table 10-4).

According to the information presented in previous tables, the type of organic materials expected in the repository systems are mainly hydrocarbons in the deposition tunnels and carbohydrates in other repository cavities in both areas, Forsmark and Laxemar (see Figure 10-3). The estimated average concentrations would never exceed $1.7 \cdot 10^{-4}$ kg/m^3 (0.17 mg L^{-1}) of hydrocarbons in the deposition tunnels and $8.4 \cdot 10^{-4}$ kg/m^3 for carbohydrates (0.84 mg L^{-1}), assuming a total saturation in the porewaters and an even distribution of the organic materials. At 500 m depth the DOC (dissolved organic carbon) content in granitic groundwater is 0.5–2 mg L^{-1}.

Table 10-8. Summary of the estimated amounts and concentrations of degradable organic materials in the stray materials left in the deposition tunnels, assuming total saturation of the system.

Substance	Estimated total amount (in kg) in Forsmark	Estimated total amount (in kg) in Laxemar	Estimated concentration (in kg/m³) in Forsmark			Estimated concentration (in kg/m³) in Laxemar		
			Case A	Case B	Case C	Case A	Case B	Case C
Carbonhydrate[1]	62.5	75	$1.68 \cdot 10^{-4}$	$1.41 \cdot 10^{-4}$	$1.62 \cdot 10^{-4}$	$1.58\ 10^{-4}$	$1.23 \cdot 10^{-4}$	$1.52 \cdot 10^{-4}$
Hydrocarbon[2]	313	227	$8.44 \cdot 10^{-4}$	$7.05 \cdot 10^{-4}$	$8.09 \cdot 10^{-4}$	$4.79 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$
Surface active substances[3]	0	0	0	0	0	0	0	0

[1)] humus, urine, wood chips, organics, other human wastes, ventilation air,
[2)] hydraulic oil, lubrication oil, degreasing compounds, detergents, plastics, rubber, diesel oil, soot,
[3)] hydrocarbon with surface active substances (degreasing compounds and detergents).

Table 10-9. Summary of the maximum estimated amounts of degradable organic material in the stray materials left in other repository systems.

Substance	Estimated total amount (in kg) in main tunnel and other repository cavities	Estimated concentration (in kg/m³) in Forsmark			Estimated concentration (in kg/m³) in Laxemar		
		Case A	Case B	Case C	Case A	Case B	Case C
Carbonhydrate[1]	811	$3.30 \cdot 10^{-3}$	$2.76 \cdot 10^{-3}$	$3.16 \cdot 10^{-3}$	$2.80 \cdot 10^{-3}$	$2.34 \cdot 10^{-3}$	$2.68 \cdot 10^{-3}$
Hydrocarbon[2]	284	$1.16 \cdot 10^{-3}$	$9.66 \cdot 10^{-4}$	$1.11 \cdot 10^{-3}$	$9.80 \cdot 10^{-4}$	$8.19 \cdot 10^{-4}$	$9.41 \cdot 10^{-4}$
Surface active substances[3]	0	0	0	0	0	0	0

[1)] humus, urine, wood chips, organics, other human wastes, ventilation air,
[2)] hydraulic oil, lubrication oil, degreasing compounds, detergents, plastics, rubber, diesel oil, soot,
[3)] hydrocarbon with surface active substances (degreasing compounds and detergents).

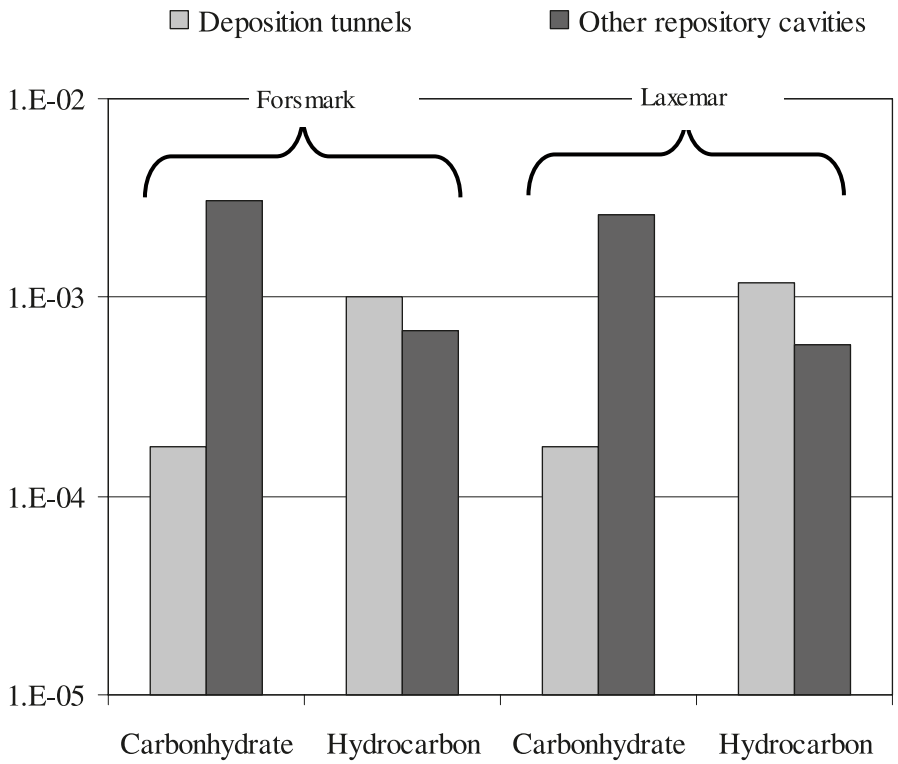


Figure 10-3. *Estimated total amounts of chemical substances in stray materials at the deposition tunnels and other repository cavities in Forsmark and Laxemar.*

The main source of hydrocarbons are oils (hydraulic, lubricating, diesel, etc) and degreasing compounds. Excavation with drill and blast is associated with some spillage. Spillage from charging depends on how explosives are handled and on the type of explosive used. Not all explosives may detonate due to disturbances in the initiation of the holes and the total not detonated amount of explosives may be as high as 10–15% of the total charged weight i.e. around 200 tones of spillage of explosives for excavation of all deposition tunnels. A rough estimate has been reported to be that 10% of the oil and explosive spillage is left in the deposition tunnel, i.e. around 1 m^3 of hydraulic oil for all deposition tunnels and less for lubrication grease, and 20 tones of explosives /SKB 2004b/. In any case, the estimated hydrocarbon concentrations never would exceed $1.7 \cdot 10^{-4}$ kg m^{-3}.

In the main tunnel and other repository cavities, the most abundant organic substances are carbohydrates coming from human wastes. In this case, the estimated concentration is $8.4 \cdot 10^{-4}$ kg m^{-3} of carbohydrates

Amount and concentrations of organic material in microbial biofilms

The dominant biofilm found in tunnel environments in granitic rock is iron-oxidizing bacteria (BIOS: **b**acteriogenic **i**ron **o**xide**s**). Using the estimation of the organic component in such biofilm (see section 3.2.2), 75 g m^{-2}, in deposition tunnels, the total amount of organic material from BIOS can be calculated see Table 10-10. It is assumed that 5% of the tunnel surfaces are covered with BIOS. Tunnel lengths are available for deposition tunnels only. It can be assumed that the concentrations in the other cavities will be in the same range. The tunnel walls will probably be cleaned from BIOS before backfill of at least of the deposition tunnels. The calculations are therefore large uncertainty margins.

Table 10-10. Summary of the estimated amounts and concentrations of degradable organic materials in the BIOS left in the deposition tunnels, assuming total saturation of the system.

Substance	Estimated total amount (in kg) in Forsmark	Estimated total amount (in kg) in Laxemar	Estimated concentration (in kg/m³) in Forsmark			Estimated concentration (in kg/m³) in Laxemar		
			Case A	Case B	Case C	Case A	Case B	Case C
Organic material in BIOS	980	1,250	$2.64 \cdot 10^{-3}$	$2.21 \cdot 10^{-3}$	$2.53 \cdot 10^{-3}$	$2.64\ 10^{-3}$	$2.20 \cdot 10^{-3}$	$2.52 \cdot 10^{-3}$

The concentration of organic material from BIOS in the deposition tunnels in Forsmark and Laxemar will be approximately 2.5 mg L^{-1}. The concentrations are in the same range as the natural content of organic material in granitic groundwater, approximately 0.5–2 mg L^{-1}.

A comparison of the data in Table 10-8 with the values in Table 10-10 also shows that the organic material in BIOS could be higher than the estimated amount from stray materials in the deposition tunnels.

11 Summary and conclusions

A compilation of the origin and composition of organic material possibly left in a repository are found in Table 11-1. Recommendations of precautions and actions for the different material are listed as well. As a brief summary of the work presented in this document, the different categories of organic material of relevance for the repository are:

1. Microorganisms. Their effect would be mainly a reduction of the redox potential in the initial stages after the repository closure. They may contribute to the depletion of the oxygen entrapped due to the repository construction. This effect would not jeopardize the stability of the repository.

   If the dominating microorganisms in the anaerobic environment are sulphate-reducing bacteria, oxidation of organic material would lead to formation of HS^-. The produced sulphide can corrode copper under anaerobic conditions, if it reaches the canisters.

   Another effect of microorganisms would be the increase of the complexing capacity of the groundwater due to excreted metabolites. The impact of these compounds is not yet clear, although it will surely not be very important, due to the low amounts of the excreted substances.

2. Materials in the ventilation air. Their effect will probably be a contribution to the maintenance of reducing conditions in the area, although it is likely that this effect will be minimal or negligible.

3. Construction materials. Among them we can highlight organic materials present in concrete, asphalt, bentonite and wood. The most important compounds from the repository safety perspective will be those hydrocarbons from asphalt that may contribute to decreasing the redox potential around the repository, and the products of degradation of cellulose. This last category of compounds may contribute to enhance the complexing capacity of the groundwater around the repository and it is recommended to minimize the amount of cellulose left in the repository.

4. Fuels and engine emissions. No important effects from these organics in the repository are expected, although the presence of aromatic compounds and PAHs in groundwater is not desirable by itself, they are of no consequence for the long-term performance of the repository.

5. Detergents and lubricants. The same reasoning as for fuels and engine emissions can be applied in this case. The amount of detergents should be minimized, although in the amounts that they are expected to occur, no important impact is foreseen.

6. Materials from human activities. Among them, the ones having potentially a more important effect are fibres from clothes, due to the presence of cellulose, and therefore it is recommended to minimise human-related wastes, although no large amounts of these materials are expected to be present after the repository closure.

The previous information is presented in a more systematic fashion in Table 11-1.

The effects that organic substances can have in the repository will always depend on the amounts present in the repository after closure. The estimated average concentrations are below $1.7 \cdot 10^{-4}$ kg/m^3 (0.17 mg L^{-1}) of hydrocarbons in the deposition tunnels and less than $8.4 \cdot 10^{-4}$ kg/m^3 (0.84 mg L^{-1}) of carbohydrates, assuming a total saturation in the pore water and an even distribution of the organic materials. This should be compared to the organic material found in groundwater at natural circumstances. At 500 m depth the DOC (dissolved organic carbon) content usually are approximately 0.5–2 mg L^{-1}.

Table 11-1. Organic material in a repository for HLW. Source, composition, possible effect and recommended action.

Categories of organic material	Chemical components	Effect in the repository after closure	Recommended action:
Growth of microorganisms	Biological compounds, EPS: polymers, excreted metabolites.	Oxygen consuming E_h lowering because of action as substrate for groundwater microorganisms. Possible increase of the complexation capacity due to the excreted metabolites.	None Study of the amount of excreted metabolites. Is it enough as to provide important complexing capacity?
Organic material in ventilation air	Biological compounds in seeds, spores, pollen.	Oxygen consuming E_h lowering because of action as substrate for groundwater microorganisms.	Minimize. Not foreseen to be important, due to the low amount of compounds introduced by this via.
Construction materials			
Concrete	Lignosulfonates, lignosulphates, sulfonated naphthalene sulfonated, formaldehyde, acryl sulfonate, alkyl sulfonate, phenol ethoxylates.	Strongly bounded to concrete particles. Possible decomposition in radiation field /Gascoyne 2002/. Probably no effect on the repository.	None
Asphalt	Heavy hydrocarbons and compounds containing oxygen, sulphur and nitrogen atoms.	Some leakage of low molecular hydrocarbons to groundwater of which some are biodegradable and by that E_h lowering.	Remove
Bentonite clay	Thought to be humic and fulvic acids, humine but not examined.	Function as substrate for microorganisms. Lowering the Eh but can increase hydrogen sulphide production in the bentonite buffer. Possible effect onto Cu canister.	None
Wood	Cellulose lignin secondary products like tannins and terpenes.	Cellulose is both, easily degraded by many microorganisms and easily degraded under alkaline conditions, commonly occurring at nuclear repositories build up with cement. Lignin is degraded by white rot fungi. Tannins and terpenes are very slowly decomposed and can act as complex binding agents. In summary, these species enhance the complexing capacity of the media.	Remove
Fuels and engine emissions			
Diesel	Diesel: *n*-alkanes, PAH, alkyl benzenes, aromatics, branched and unsaturated aliphatic hydrocarbons, cyclo-aliphatic naphtenes.	Diesel hydrocarbons are easily degraded with oxygen although condensed hydrocarbons (PAH) are slowly degrades. Also in anaerobic conditions degradation occurs. Oxygen consumption and E_h lowering effects.	Minimize and if possible pump out.
Engine emissions	Carbon soot, water, sulphuric acid, condensed hydrocarbons.	Condensed hydrocarbons can be degraded with oxygen but also by some anaerobic microorganisms.	Minimize

Rubber from tires	Isoprene cross-linked with sulphur bridges.	Not easily degraded. Probably no effect on the repository.	Minimize
Detergents and lubricants	Alkylbenzene sulfonates, alkylphenol ethoxylates, vegetable tensides, C18–C40 alkanes.	The “old” tensides are often difficult to degrade but “new” vegetable ones are more readily degraded. Oxygen depletion.	Minimize and, if possible remove.
Organic material from human activities			
Tobacco products	Plant leaf components with nicotine, nornicotine, anabasine, myosmine, nicotyrine and anatabine.	Increase in the nitrate content of groundwater.	Minimize
Cigarettes			Prohibit
Snuff	Including glycerol, sodium chloride and sodium carbonate.	Biodegradable. The amount can be easily minimized by restrictions.	Minimize
Dust from skin and hair	Protein	Biodegradable. No large effect expected.	None. Unavoidable
Fibres from clothes	Polyesters Cellulose	Polyesters will stay but probably not affect the repository. Cellulose is both, biodegradable and easily degrades under alkaline conditions, commonly occurring at nuclear repositories build up with cement. Not expected to be very important.	Remove
Urine	Urea, creatinin, ammonia, uric acid, amino acids.	Urine is degradable and functions as a nitrogen source in the oxygen consuming and E_h lowering degradation in the repository. Its degradation and the consequent urea hydrolysis can increase the soil pH. The spreading should be minimized mainly by hygienic reasons. Expected effect not very important.	Minimize
Paper and plastic waste	Cellulose and the plastic polymers (see Blasting below).	Cellulose will be biodegraded. Some plastics will be degraded and other not depending on the composition. Can be avoided by restrictions.	Remove
Blasting and/or rock-drilling			
Paper	Cellulose	Biodegradable. Large quantities can be removed. Small stuff can be left.	Remove
Plastics	Polyethylene terephatalate, polyethylene, polyvinylchloride, polypropylene, polystyrene.	Most of these plastics are not biodegradable. There are so called bio-plastics that are produced by microorganisms and these are more or less biodegradable.	Remove

Three processes are deemed to have the largest possible impact on the performance of the repository:

i) Increase of the reducing capacity and decrease of the redox potential in the short-term, and increased rate of depletion of the oxygen trapped during the repository operation stage.

ii) Increase in the complexing capacity of the groundwater due to the presence of organic complexants, which is expected to be a process of more relevance in the long-term. Many organic molecules with complexing capacity, such as short organic acids like acetate are, however, oxidised as a consequence of microbial metabolism. The acetate concentration in ground water is below detection limit of methods available. The amount of organic material in ground water is usually a few mg L^{-1}. Between 25 and 75% of this material is non-humic material, i.e. short chained acids (see for example /Nissinen et al. 2001/).

iii) Production of HS^- from oxidation of short organic acids by sulphate reducing bacteria using sulphate as electron acceptor. The produced sulphide can corrode copper canisters if the sulphide can come in contact. Appendix A presents calculations of the maximum sulphide concentration possible from the concentration of organic material estimated in this report. The concentrations of sulphide are in the same range as those found in natural groundwaters at the sites.

By and large, the decrease of the O_2 concentration is positive and, therefore, no specific measures need to be taken against substances only having this effect. The increase of the complexing capacity, though, can be relevant if the products of degradation of the organic matter coexist with radionuclides in the long-term or if they can have influence in decreasing the performance of the engineering barriers.

Since the addition of organic material to the groundwater from stray materials left in the repository is small compared to the organic content in natural groundwater the results from all three of the processes induced by the additional organic material above are of minor importance for a repository (see also Appendix A).

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Appendix A

Scoping calculations of the degradation of organic material in a HLW repository

The calculations in this section are based on the data for carbohydrates in Table 10-2, Table 10-3, Table 10-8 and Table 10-9.

Aerobic degradation

If the carbohydrate chemical composition is set as $(CH_2O)_6$, a carbohydrate with 6 carbon atoms, the following calculations on **oxygen consumption** can be made:

The chemical reaction for aerobic biodegradation of carbohydrates is as follows:

$$(CH_2O)_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \text{(A1)}$$

In aerobic metabolism about 50% of the consumed organic material is converted to biomass and 50% is used in energy transformations and by that reduce oxygen. In Table A-1 calculations of the required oxygen gas amounts are presented for different parts of a repository.

Anaerobic degradation

If the same amount of organic material is assumed to be degraded anaerobically, the following calculations can be made. We assume that all carbohydrates are fermented to acetate and dissolved inorganic carbon.

$$(CH_2O)_6 + 2\ H_2O \rightarrow 2\ CH_3COO^- + 2\ HCO_3^- + 4\ H^+ + 2\ H_2 \quad \text{(A2)}$$

For each mole of carbohydrate 2 moles of acetate are formed. The acetate can be used by sulphate reducing bacteria if the conditions are such that these bacteria predominate. The degradation would be as follows:

$$CH_3COO^- + SO_4^{2-} \rightarrow 2\ HCO_3^- + HS^- \quad \text{(A3)}$$

In equation (A3) it can be seen that the molar ratio is one for acetate and hydrogen sulphide in this reaction. The amounts of hydrogen sulphide that can be produced in the different parts of a repository are listed in Table A-2.

The sulphide concentration in granitic groundwater varies from below the detection limit of the sulphide analysis, < 0.01 mg L^{-1}, up to approximately 7 mg L^{-1}. Organic material from stray materials could give an increase in sulphide concentration that does not exceed the highest concentrations measured in natural systems.

Table A-1. Calculations of the concentration of oxygen that can be reduced by biodegradation of the assumed carbohydrates left in the deposition tunnels, and other cavities.

Location	Amount of carbohydrate (mg L^{-1})	Concentration of carbohydrate (µM)	Used in energy transformation (µM)	Oxygen reduced (µM O_2)	Oxygen reduced (mg L^{-1} O_2)*
Deposition tunnels	0.17	0.94	0.47	2.82	90
Other cavities	3.3	18	9	54	1,728

* At a temperature of 25°C and a pressure of 1 bar the volume of one mole gas is 22.4 L.

Table A-2. Calculations of the concentration of sulphide that can be produced by anaerobic biodegradation of the assumed carbohydrates left in the deposition tunnels, and other cavities.

Location	Amount of carbohydrate (mg L^{-1})	Concentration of carbohydrate (μM)	Acetate produced in fermentation (μM)	HS^- produced in sulphate reduction (μM)	HS^- produced in sulphate reduction (mg L^{-1})
Deposition tunnels	0.17	0.94	1.88	1.88	0.062
Other cavities	3.3	18	36	36	1.2

Anaerobic degradation of organic material in BIOS

Calculations on the sulphide production from organic material in BIOS (**b**acteriogenic **i**ron **o**xide**s**) are presented in Table A-3. The amounts of organic matter are taken from Table 10-10. The stoichiometry is based on equations (A2) and (A3).

The highest concentration of hydrogen sulphide possible from the anaerobic degradation of BIOS in the deposition tunnels via sulphate-reduction is 0.99 mg L^{-1}. This is in the range of sulphide amounts in natural ground waters and will not exceed the highest concentration found of 7 mg L^{-1}.

A comparison of the data in Table 10-8 with the values in Table 10-10 shows that the organic material in BIOS could be higher than the estimated amount from stray materials in the deposition tunnels.

Table A-3. Calculations of sulphate reduction with BIOS.

Location	Amount of carbohydrate (mg L^{-1})	Concentration of carbohydrate (μM)	Acetate produced in fermentation (μM)	HS^- produced in sulphate reduction (μM)	HS^- produced in sulphate reduction (mg L^{-1})
Deposition tunnels	2.64	15	30	30	0.99