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Discussion on the $^{14}CH_4$ gas formation and release from SFR1 repository

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Förord

Denna rapport motiverar kravet på högt pH i de förvarsdelar i SFR där kol-14-innehållande avfall deponeras. Rapporten visar vilka processer som i annat fall styr uttransport av kol-14 från förvaret.

Resonemanget som är helt hypotetiskt visar att stora delar av allt kol-14, 10 % eller mer, skulle kunna föras upp till biosfären under en tidsperiod av hundratals till tusentals år om inte pH i avfallet kan hållas så högt att metanbildande mikrober är inaktiva.

Säkerhetsanalysen SR-PSU visar att avfallet i de förvarsdelar som innehåller kol-14 kommer att ha ett pH-värde som uppgår till 12,5 eller högre under minst 22 000 år. Kol-14 har en halveringstid på 5 700 år och har avklingat till 1/16-del efter 22 800 år.

Viktiga omständigheter som nämns i rapporten och som ytterligare förstärker uppfattningen om att kol-14 inte kan transporteras upp till biosfären är den långsamma uttransporten (diffusionskontrollerad) genom avfallsbehållarna och utfällning av kalciumkarbonat i det höga pH-värdet.

Abstract

In the SFR repositories for low and intermediate level waste hydrogen gas evolves due to corrosion of metals. The gas can carry with it volatile components that contain radioactive elements such as ^{14}C and radon. Volatile organic compounds can form from non-volatile components such as carbonate and cellulose *only if the reactions can be mediated by microbial catalysis*. The ^{14}C containing compounds can then also react to form volatile gases. Thermodynamically this is strongly favoured in the anaerobic environment with high pressure of hydrogen. The most favoured product is methane, which by itself can generate a sufficient pressure to overcome the hydraulic pressure at repository level. The escaping gas will carry with it the ^{14}C containing methane. In the hypothetical calculations it is found that *if rapid microbial catalysis is present* a considerable fraction of the radioactive carbon could escape with the gas during a few hundred years. However, there are many uncertainties, especially regarding the rate of microbial catalysis. Therefore pessimistic assumptions are made in the calculations to demonstrate the potential effects of microbal mediated CH_4 production. Should rapid microbially catalysed reactions occur the release of gaseous ^{14}C compounds might result in considerably larger activity release rates than reported in SKB, 2008.

Sammanfattning

I slutförvaret för låg- och medelaktivt avfall, SFR, utvecklas vätgas orsakad av metallkorrosion. Gasen kan lämna förvaret som gas och svepa med sig flyktiga föreningar vilka kan innehålla radionuklider som ^{14}C och radon. Flyktiga organiska föreningar kan bildas av icke flyktigt material, som karbonat och cellulosa, *endast om reaktionerna påskyndas av mikrobiell katalys*. Då kan även material som innehåller ^{14}C bilda flyktiga gaser. Dessa reaktioner är termodynamiskt starkt gynnade under rådande anaerobiska förhållanden med ett högt vätgastryck. Den mest gynnade reaktionsprodukten är metangas, vilken ensam kan bilda så högt partialtryck att det kan övervinna vattentrycket i det vattenmättade förvaret. Gasen som lämnar förvaret för med sig ^{14}C-metan. De hypotetiska beräkningsfallen visar att *om kraftig mikrobiell katalys* förekommer kan en väsentlig andel av det radioaktiva kolet lämna förvaret under några hundra år. Det finns dock många och stora osäkerheter, särskilt hur snabb den mikrobiella katalysen kan vara i förvarsmiljö. Därför har ett antal pessimistiska antaganden gjorts i beräkningarna för att visa på den eventuella effekten. Skulle den vara snabb kan utsläppet av gasformigt ^{14}C orsaka väsentligt större aktivitetsutsläpp än vad som redovisades i SKB, 2008.

Summary

The potential formation and release of radioactive elements by gases from the waste in SFR1 has been explored. The only radioactive element that can form substantial amounts of volatile compounds is ^{14}C. Organic and inorganic compounds in the repository vaults such as cellulose and carbonates can, aided by microbial catalysis, react with hydrogen that results from corrosion of metals. This forms mainly methane gas that escapes as gas. The gas will carry with it ^{14}C-methane. The gas will have high pressure set by the need for the gas to overcome the hydraulic pressure of the water in the water-saturated rock above the repository vaults. It is somewhat above 6 atm. at 50 m depth. Abiotic reaction rates are extremely slow and for the reactions to take place, they must be catalysed by microorganisms. The consequences of a hypothetical "what if" case is explored in which it is assumed that rapid microbial catalysis is present.

The methane formation is conditioned on that the ^{14}C containing compounds can migrate to regions where the microorganisms can live. These are too large to invade most waste forms and the compounds must therefore be released from the waste forms and migrate to the microorganisms. Microorganisms have sizes around one micrometre. By far most of the pores of non-fractured concrete are much smaller. In fractured concrete microbes can invade the fractures. Microorganisms can exist outside and between the waste packages in the repository vaults where porous cement has been used as infill. It is porous to allow gas to escape. Also other voids and fractures can host microorganisms.

Most of the ^{14}C in the wastes is bound in ion exchange resins. These are either mixed with bitumen or with cement in containers of different types. The bitumen-stabilised waste degrades very slowly and the release of ^{14}C containing compounds is very slow.

The compounds in resins in cement are expelled from the resin particles by intruding hydroxyl ions, OH^-, from the cement. All ^{14}C-containing compounds are released from the resin by this process. Some of the ^{14}C containing compounds are inorganic HCO_3^- and CO_3^{2-}. These react with $Ca(OH)_2$ in the cement and concrete and precipitate as solid $CaCO_3$. This is not readily accessible to microbial catalysis. Only a very small fraction in the containers with concrete stabilised waste can react to form methane. The small organic ^{14}C containing compounds on the other hand migrate to the outside of the waste form within years to tens of years. There they can react with hydrogen in the presence of the catalyst- the microorganisms *stipulated to exist.* Thermodynamically the reactions are very favoured but the environment for the development of microbial activity is not favourable as the pH is high due to the presence of cement and concrete in which there are large amounts of $Ca(OH)_2$ and alkali hydroxides.

Mass balance calculations of the availability of hydroxide to expel the ^{14}C containing compounds from the resins show that all can be expelled. It has also been explored by migration calculations how large amounts of carbonate in the cement and concrete can escape and if this also could act as a major source for non-active carbon to consume the hydrogen to form methane. This would decrease the rate of ^{14}C methane production and slow down its release because the more non-active carbon there is available that can consume the hydrogen the less ^{14}C can form methane. It was found that the rate of migration of carbonate from the concrete and cement is very low and would contribute little to hydrogen depletion. The largest source of carbon is from the cellulose in the waste although the carbonate in the porous cement could potentially contribute some carbonate.

Calculations also show that the various sinks for hydroxyl that potentially could lower the pH to make the environment less un-friendly for the microbes are not sufficient to do this.

Calculations have also been performed to assess if the ^{14}C containing compounds present in the resins could be or could form volatile compounds without reaction with hydrogen to methane. Only very small amounts of such compounds could escape with hydrogen gas in this form.

Assuming that the microbiologically catalysed reactions exist and are rapid, the following release rates of activity can be expected and are shown in Table S-1.

Table S-1. Rate of release of ^{14}C for three cases.

	Duration of release (Years)	All ^{14}C converts (Bq/yr)	Only organic ^{14}C converts (Bq/yr)	Only that in resin embedded in concrete converts (Bq/yr)
Silo	173	$1.85 \cdot 10^{11}$	$5.54 \cdot 10^{10}$	$2.10 \cdot 10^{10}$
1BMA	4,188	$1.77 \cdot 10^{9}$	$5.25 \cdot 10^{8}$	$2.0 \cdot 10^{8}$
2BTF	129	$1.0 \cdot 10^{10}$	$2.94 \cdot 10^{9}$	$1.5 \cdot 10^{8}$

The third column where all organic and inorganic^{14}C in all waste forms converts is only aimed to show an upper bound. The next column shows results assuming that the cement and bitumen conditioned wastes release organically bound ^{14}C. The rightmost column gives the results for the case where only the cement conditioned waste releases organically bound ^{14}C to form methane gas that escapes to the biosphere.

In the Silo that has little cellulose to generate non-radioactive methane there is a potential that the ion exchange resins might contain up to on the order of 20 times as much organic carbon as the cellulose if the resin is fully saturated with organic acids. No information on the utilisation of the resins and of the composition of bound species has been found, however.

The release can be compared with the release found in the previous analysis. Thomson et al. (2008) give the maximum^{14}C near-field release to be $2 \cdot 10^{7}$ Bq/yr from the Silo. This is similar to what is found in the earlier safety analysis (Lindgren et al. 2001, SKB 2008). In those analysis gas release was not considered with the mechanisms considered in the present report.

The dose consequences depend much on when the release occurs. If all the radioactive gas is released while the Baltic sea still is above the repository it has little effect on the dose. Should the release occur after a few thousand years when the land has risen and there remain lakes and mires the dose consequences could be several orders of magnitude larger than in previous safety analysis (Lindgren et al. 2001). The release from 1BMA was estimated to occur over more than 4,000 years. There are several uncertainties on when the release starts, and it cannot be affirmed that also the silo will release $^{14}CH_4$ over much longer times that the few hundred years shown in Table S-1.

The release results are entirely dependent on the assumption that microbial activity develops and that it causes rapid reaction between hydrogen and carbon containing compounds. It is outside the scope of this report to discuss the details of the possibility of and reaction rates of microbiologically mediated reactions.

It may be noted that the un-catalysed reactions rates are negligible at ambient temperature over the time scales of interest for this study covering tens to hundred thousand years.

In short: With the data and assumption used, our calculations show that if microbial catalysis cannot be ruled out a large fraction, 10%, or more of the radioactive carbon in the waste could escape to the biosphere within a few hundred or possibly a few thousand years if SKB's new gas generation data are used. If microbial catalysis could be ruled out negligible release of radioactive carbon would escape.

Contents

1 Introduction

The SFR1 repository for low and intermediate level radioactive waste contains nuclides that can be released from the waste form to the seeping water, which may carry them to the biosphere. This has been modelled and used in the previous safety analysis, SA, for the repository (SKB 2008). The repository construction and general properties of the wastes are described in that report. In the upcoming, new SA, SR PSU for SFR1, an additional transport pathway for radioactive gases, will also be explored. This report considers the formation of volatile ^{14}C compounds that could form and be carried by gas generated in the repository vaults by corrosion of iron and aluminium.

The ^{14}C in the repository is present in organic compounds and in carbonate. Most of the ^{14}C is present in the ion exchange resins that were used to clean the water in the nuclear power plants (Riggare and Johansson 2001). Details about the waste forms, their activity content, how they are packaged and in which parts of the repository they are deposited are described in Almkvist and Gordon (2007). These data are summarised in Appendix 1.

^{14}C in both inorganic and organic compounds can be transformed by microbial catalysis into volatile organic compounds such as CH_4, C_2H_6, low molecular weight acids such as formic acid and acetic acid and alcohols such as methyl and ethyl alcohol. The volatile compounds could be carried upward by gas that forms by corrosion of metals, as bubbles or gas streams through the engineered barriers and rock above the repository. During early times when the repository is still under the sea some of the gas could dissolve in the seawater. Under aerobic conditions in the sea these organic compounds may at least partly be oxidised and ^{14}C would form $^{14}CO_2$, which dissolves in the seawater. Non-degraded ^{14}C-compounds can partly stay dissolved in the water and partly vaporise to the atmosphere. At later times when the repository is no longer under the sea due to land rise the ^{14}C-compounds may migrate through an aerobic soil layer where organic compounds can be oxidised to carbon dioxide, which can be bound to form e.g. carbonates, biomass or be released to the atmosphere.

The gas generated in the repository is expected to have a much shorter residence time from the waste to the biosphere to carry the gaseous ^{14}C compounds than the water seeping in the rock because gas moves upward driven by strong buoyance forces whereas water moves only due to the hydraulic gradient if there is no gas present in it. Furthermore, the neutral volatile compounds in the gas do not react with or sorb on the rock or cement surfaces with the exception of gaseous CO_2. This will be shown to make up a negligible amount of the gas and the effect can be neglected.

During the work on this report it was found that there is a large number of different processes that influence the potential release of gas containing ^{14}C compounds. There is a large a number of different waste forms with different sizes and properties. The chemical forms of ^{14}C compounds bound in the waste are practically not known. The release of the compounds from the main waste form, the ion exchange resins, depends on the availability of hydroxyl ions. This depends on how much cement and concrete can supply the ion exchange with hydroxyl ions. This in turn depends on how much of cement is mixed with resin and how much and with what rate it can be released from the concrete constructions nearby. There are further uncertainties of how much hydroxyl there is in the different cements and concretes used in different waste forms and concrete constructions. Simple scoping calculations showed that there should be sufficient hydroxyl available to release all ^{14}C compounds from the resins.

Another major uncertainty is whether the released ^{14}C compounds will react with hydrogen gas formed by corrosion to form volatile methane that could be carried with the hydrogen gas from the repository. This is very much favoured thermodynamically but it needs to be catalysed by microbial activity. The high pH in cement and concrete is an unfriendly environment for microorganism. However, it was not ruled out in the previous SA (SKB 2008). A further complication is that the ion exchange resins can potentially act as sinks for hydroxide and thereby lower the pH. Also here there are considerable uncertainties because of lack of information but a lowering of pH does not seem to be likely because of the large amount of hydroxyl available. See chapter 8 where the acid neutralising capacity of the concrete and cement is discussed.

Hydrogen and organic matter reactions would also occur with other carbon containing matter such as cellulose and also with carbonate in the cement and concrete, when available. Should also the non-radioactive carbonate form methane, again thermodynamically favoured, a considerable decrease of the radioactive methane formation would take place. The availability and release rate of carbonate from cement and concrete were therefore also modelled but there are several uncertainties involved.

There are other potential sinks for hydrogen, namely sulphate and ferric iron in the cement and concrete. If these reactions were catalysed by suitable microorganisms, the amount of hydrogen that could form methane would decrease and the release rate of ^{14}C would decrease. There are considerable uncertainties involved when trying to assess the availability of sulphate and ferric iron but these will be exhausted after some time, see chapter 12.

Because of the above-mentioned complexities and uncertainties the report was structured so that in Chapter 5 a simple model is used to estimate the release rate of ^{14}C in a gas stream assuming that all of the organic ^{14}C bound in cement conditioned resins becomes available to form methane. The main source of non-radioactive carbon was assumed to be from cellulose that was deemed to be readily accessible for reaction with hydrogen. With the above as a main case a number of the assumptions are revisited. This is described in subsequent chapters. These assumptions were chosen to be on the cautiously conservative side.

This gave a framework for analysis of how a number of different mechanisms and processes could influence the assumptions underlying the example calculations and how this could influence the release rate.

2 Aims and scope

The main aim is to assess the potential release rate of gaseous ^{14}C.

The following questions are explored:

- How much potentially volatile ^{14}C-compounds are present in the waste?
- Under what conditions can volatile ^{14}C-compounds form?
- How much volatile ^{14}C-compounds can form?
- Under what conditions can sufficient amounts of gas be generated to carry the volatile compound?
- How much ^{14}C-compounds can be carried by such gas and at what rate?
- What are the major uncertainties concerning the above issues?

Many of these questions are expected to be difficult to quantify. It is notoriously difficult to predict the rates of reactions that are catalysed by microbes. We therefore assume as bounding cases that such reactions are either very fast reaching thermodynamic equilibrium or very slow and that no reaction takes place even if there is a positive driving force for the reaction. The use of equilibrium considerations and equilibrium data for the reactions are therefore essential. In addition we approach the problems by simple exploratory calculations based on mass balances and rates of transport in the materials in the repository vaults. The analysis is based on data from SFR1.

It is outside the scope of the present report discuss the likelihood of the presence of microbial activity. However, some observations in natural systems at high pH are discussed in Appendix 4. We study a "what if" case assuming that the microbial catalysis is rapid.

3 Reactions, thermodynamic data and kinetics

The ^{14}C is bound in a number of different compounds. Carbonate is the only inorganic form considered in this report. The carbonate can form different solids mainly with the abundant calcium in water and especially in the concrete in the repositories. Precipitates can form and incorporate the radioactive carbon. Activity in ion exchange resins conditioned in bitumen is released very slowly (SKB 2008). This is not the case for the ion-exchanged resins mixed with cement. Dissolving alkali hydroxides and portlandite, $Ca(OH)_2$, from the concrete and the cement used for conditioning the anion exchange resins in the repositories makes the pH very high and expels carbonate ions and anionic carbon acid compounds from the anion exchange resins. This is the largest source of ^{14}C in the repository. It makes the ^{14}C available to dissolve in the water in the waste.

Iron and aluminium react with water to produce hydrogen and dissolved or precipitated solid metal compounds. The type of iron precipitates that form determines how much gas evolves. A possible solid precipitate is $Fe(OH)_2$, which releases one H_2 molecule per one Fe atom reacted. Thermodynamically the expected final iron precipitate is magnetite Fe_3O_4, which given time, is expected to reform from $Fe(OH)_2$. In this process additionally 1/3 H_2 is released per iron atom. There is some uncertainty as to if magnetite will form under the conditions expected at SFR. It is assumed in the following that magnetite is the end product. These factors influence and determine the water chemistry in the repositories.

The mobility and volatility of organic ^{14}C containing compounds are also influenced by the water chemistry. At the high pH in the repositories the organic acids will dissociate and form anionic species, which are not volatile but are mobile and are not retarded by sorption and precipitation in the concrete. This is in contrast to carbonate, CO_3^{2-}, which reacts with calcium to precipitate $CaCO_3$.

When thermodynamics favour a reaction, kinetics will determine at what rate it occurs. The organic reactions will only occur at the low temperature in the repository vaults if catalysed by microorganisms. The development of microorganisms that can do this in turn is influenced by water chemistry and temperature and other factors such as availability of nutrients.

In the next sections thermodynamic data of importance for the present task is summarised.

3.1 Thermodynamic data

Thermodynamic data suitable to estimate equilibrium constants for our purposes (low temperature and pressure in water) can be found in many handbooks, textbooks and databases. In this report the computer code PhreeqC (Parkhurst and Appelo 1999) is used with its thermodynamic databases.

In addition, for simple illustrations and to facilitate gaining insights into which reactions and parameter data dominate the results some simplified calculations are also presented. This allows us to estimate when some possibly important organic compounds could play a role and when not. Some of the compounds are not included in the databases coupled to PhreeqC. Equilibrium constants for some organic compounds known to participate in the microbially mediated reaction of interest are taken from Al-Sheikh (2006) and have been checked against data in Weast and Astle (1980). They are derived from Gibbs' free energy data of formation, ΔG_f. Table 3-1 compiles the equilibrium data for 12 reactions of methane (from Al-Sheikh 2006).

The reaction formulas have been written in the three groups: formation, decomposition and oxidation of methane. We will discuss first formation of methane and then possible degradation and oxidation when the methane migrates and emerges into the biosphere. Table 3-2 gives the equilibrium constants for these reactions (From PhreeqC, Minteq database and Stumm and Morgan 1996).

It may be noted that in the pH range 6–10, the dominating carbonate species will be HCO^{-}. When $Ca(OH)_2(s)$ is present the pH will be larger and the dominating carbonate species is CO_3^{2-}.

Table 3-1. Equilibrium data for some reactions involving light organic compounds.

Reaction number	Reaction formula	ΔG_r^0 (kJ/mol) at 298 K at 1 atm. (g) in atm. (aq) in (mol/l) at water activity = 1. (upper value) Log¹⁰(*K*) Lower value
	Formation of methane	
1	From formic acid $HCOOH(aq) = \frac{1}{4}CH_4(g) + \frac{3}{4}CO_2(g) + H_2O(l)$	–65.68 +11.51
2	From acetic acid $CH_3COOH(aq) = CH_4(g) + CO_2(g) + H_2O(l)$	–55.65 +9.755
3	From methanol $CH_3OH(aq) = CH_4(g) + \frac{1}{2}O_2(g)$	+124.92 –21.90
4	From carbon dioxide $CO_2(g) + 4H_2(g) = CH_4(g) + 2H_2O(l)$	–130.79 +21.925[1]
	Decomposition of methane	
5	To ethane $CH_4(g) = \frac{1}{2}C_2H_6(g) + \frac{1}{2}H_2(g)$	+34.35 –6.021
6	To propane $CH_4(g) = \frac{1}{3}C_3H_8(g) + \frac{2}{3}H_2(g)$	+15.08 –2.643
7	To ethylene $CH_4(g) = \frac{1}{2}C_2H_4(g) + H_2(g)$	+84.85 –14.87
8	To acetylene $CH_4(g) = \frac{1}{2}C_2H_2(g) + \frac{3}{2}H_2(g)$	+115.39 –20.226
	Oxidation of methane	
9	By oxygen $CH_4(g) + 2O_2(g) = CO_2(g) + H_2O(l)$	–817.97 +143.37
10	By nitrate $CH_4(g) + \frac{8}{5}NO_3^- + \frac{8}{5}H^+ = CO_2(g) + \frac{4}{5}N_2(g) + \frac{14}{5}H_2O(l)$	–830.99 +145.66
11	By sulphate $CH_4(g) + SO_4^{2-} + H^+ = CO_2(g) + HS^- + 2H_2O(l)$	–63.43 +11.12
12	By iron(III) $CH_4(g) + 8Fe^{3+} + 2H_2O(l) = CO_2(g) + 8Fe^{2+} + 8H^+$	–464.34 +81.389

[1] The Minteq database attached to PhreeqC gives a value 21.94. This value is used in the PhreeqC calculations. The difference between the data has no practical impact for the purposes of this report.

Table 3-2. Gas solubility and some other equilibrium data.

Reaction number	Reaction formula	Log10(K) at 25°C
13	$H_2(g) = H_2(aq)$	–3.5, Log (mol/l/atm)
14	$CH_4(g) = CH_4(aq)$	–2.86, Log (mol/l/atm)
15	$CO_2(g) = CO_2(aq)$	–1.468, Log (mol/l/atm)
16	$CO_3^{2-} + H^+ = HCO_3^-$	10.329
17	$CO_3^{2-} + 2H^+ = CO_2(aq) + H_2O(l)$	16.681
18	$Ca^{2+} + CO_3^{2-} = CaCO_3(s)$	8.48
19	$Ca(OH)_2(s) + 2H^+ = Ca^{2+} + 2H_2O(l)$	22.675
20	$Fe(s) = Fe^{2+} + 2e^-$	14.9
21	$Al(s) = Al^{3+} + 3e^-$	85.78

Table 3-3. Iron reaction equilibrium data.

Reaction	Log K	Delta-H (kJ/mol)	
$Fe^{2+} + 2e^{-} = Fe(s)$	–14.9		(Stumm and Morgan p 445)
	–13.8	–21.29	(Stumm and Morgan) From G-values in Table 3A
$Fe(OH)_2(s) = Fe^{2+} + 2OH^{-}$	–16.3	19.9	(Stumm and Morgan) From G-values in Table 3A
$Fe_3O_4 + 8H^{+} = 4H_2O + Fe^{2+} + 2Fe^{3+}$	4.24	–213.72	(Stumm and Morgan) From G-values in Table 3A
	3.74	–209.5	Minteq

It is seen that there are some differences in the equilibrium data in Table 3-3. These uncertainties do not influence the results much in the present context. Using the above data in PhreeqC calculations shows that whichever of the solid iron phases that finally form the resulting equilibrium pressure will be larger than 500 atm in the temperature range 0 to 25°C. The other data needed are taken from the PhreeqC and Minteq databases.

3.2 Reaction rates

The un-catalysed reactions rates of the reactions in Table 3-1 are negligible at ambient temperature over the time scales of interest for this study; tens to hundred thousand years. Many of these reactions are, however, known to be catalysed by microorganisms. The formation of methane in anaerobic digesters is catalysed by microbes and used commercially to produce biogas. Methane is also formed in deep groundwaters by reactions of hydrogen with carbon dioxide. Oxygen is known to be a strong and rapid oxidant of organic matter. Sulphate and nitrate reducing bacteria are known to catalyse the oxidation of organic matter including methane and the other organic substances in Table 3-1 (Stumm and Morgan 1996, Pedersen 2000). Many of the compounds in Table 3-1 are also found in groundwaters. Several are intermediary compounds used by the microorganism to live and to produce other substances.

Several microbially mediated reactions rates have been measured under well-defined laboratory conditions. However, there are few instances, where such information has been successfully used to predict reaction rates in-situ. The in-situ conditions may be very different than those in the laboratory. In SKB (2008) it was concluded that microbial activity could not be ruled out in the conditions expected in SFR. Under favourable conditions for the microorganisms the overall reaction rates can be very rapid.

In the calculations it is *stipulated* that the central reaction, the methane formation, takes place and rapidly reaches equilibrium in the repository. It is also assumed that the rate of formation of volatile carbon compounds from cellulose and carbonate is the same for radioactive ^{14}C as for stable ^{12}C.

4 Modelling

4.1 Overview

Volatile components with ^{14}C can be carried out of the repository vaults by advection and diffusion, dissolved in the water or as components in gas. To emerge with gas the total gas pressure must overcome the hydraulic pressure in the repository and the compounds must be volatile. Some of the ^{14}C containing compounds could possibly be volatile in the waste already. Some may form by chemical reactions. Both cases are considered.

In analysing the conditions, mechanisms and reactions and doing the calculations it was found that there are many uncertainties that have to be accounted for and addressed. It was at first contemplated to set up a model including "all" the relevant mechanisms and processes and to define the data needed to make simulations for the release of the radioactive carbon by gas generated by corroding metals. With such a model a number of simulations could then be made for different conditions. Uncertainties could be handled by varying the values of the parameters that are subject to the uncertainties. This would be a conventional approach. However, it was decided that for the present report the model would have to be too complex and that it would lead to too many cases to study. It could rapidly become unwieldy and might obscure the key processes and not give the insights sought.

Instead we try to identify the main uncertainties and simplify the models as far as possible to highlight the most important processes and items. In this chapter a number of simplifying assumptions are made that are revisited later. This makes it possible to describe the main ideas and issues in a simple way. In subsequent chapters the assumptions and uncertain items and their impact are explored.

Figure 4-1 illustrates the sources of radioactive carbon, how part of it converts to gas, and how part of it can be bound in the waste and does not convert to gas. It also illustrates that non-radioactive carbon reacts to form gas. This impacts the release of the radioactive carbon.

One purpose of the figure is to facilitate for the reader to follow the complex and intertwined processes and mechanisms that sometimes can cause retention of the ^{14}C in the waste, in other circumstances can facilitate its release and formation of volatile components. These mechanisms and processes will be described in more detail in the report but are shortly mentioned below and explained how they impact on the overall process. The boxes will be described from left to right starting in the upper left hand corner.

Most of the radioactive carbon is contained in ion exchange resins. Some of the resin is mixed with bitumen, some with cement in barrels or cubic containers with 1.2 m sides. The containers can be either concrete with 0.1 m wall thickness or steel walls that are thinner.

The first **BOX** *"$^{14}C_{org}$ in resins in bitumen, NO ESCAPE"* shows that the waste that is mixed with bitumen is very resistant to degradation and will remain essentially intact over very long time. It is not studied in any detail in the present report as its contribution to activity release is deemed to be small compared to the other sources. However, the consequences of a "what if" calculation will be presented

The next **BOX "***$^{14}C_{org}$ in resins in cement "* accounts for the waste in cement. **BOX** "*$^{14}C_{org}$ some may NOT ESCAPE"* shows that some potentially could be retained but the other part will escape to the pore water in the cement and then diffuse out of the container to the porous cement outside the container, **BOX** *"$^{14}C_{org}$ dissolved in pore water"*. The amount and availability of hydroxyl ions in the cement and possibly in the container walls will determine what fraction escapes and what remains. It is therefore necessary to establish the hydroxyl amount available for desorption.

It is in the pore water of the porous concrete that microorganisms could catalyse the transformation of non-volatile ^{14}C compounds to volatile compounds that could escape with the hydrogen gas. **BOX** *$^{14}C_{org} + H_2 \rightarrow {}^{14}CH_4(gas)$"*. The remaining amount of hydroxyl will influence the pH of the porewater. The cement and concrete porewater pH initially can be very high. Very high pH is an unfriendly environment for development of microbial activity. It is therefore important to assess how the hydroxyl can be consumed and how much the pH could decrease.

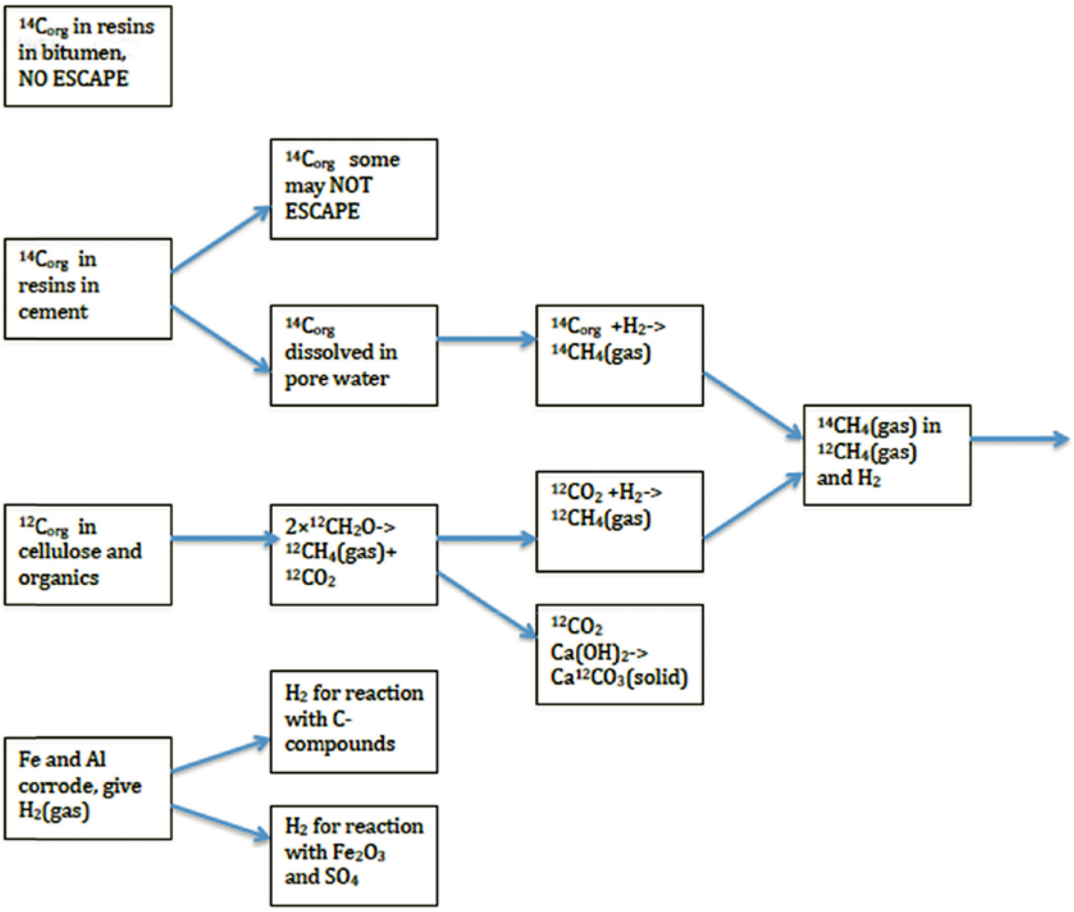

Figure 4-1. *Main sources and fates of* ^{14}C *compounds.*

The next **BOX** *"*$^{12}C_{org}$ *in cellulose and organics"* shows that there is carbon also in other waste. Not only radioactive carbon can generate volatile organic compounds. The **BOX** *"*$2\times{}^{12}CH_2O \rightarrow {}^{12}CH_4(gas) + {}^{12}CO_2$*"* shows that cellulose can degrade to carbon dioxide and volatile methane. The carbon dioxide can at least to a part react with hydrogen to form methane. **BOX** *"*$^{12}CO_2 + H_2 \rightarrow {}^{12}CH_4(gas))$". The methane can escape with other gases. Part of the carbon dioxide can bind to portlandite forming calcium carbonate, which has a low solubility at high pH and potentially can be bound in the cement/concrete.

The next **BOX** *"*$^{14}CH_4(gas)$ *in* $^{12}CH_4(gas)$ *and* H_2" shows that the radioactive methane is diluted in non-active methane and hydrogen as the gas escapes as a gas stream upward from the repository. It is therefore necessary to establish not only how much radioactive methane is produced but also how much hydrogen and non-active methane is produced. In addition there may be other gaseous organic compounds that also can be carried with the gas stream.

The next **BOX** "*Fe and Al corrode, gives* $H_2(gas)$" shows the gas generation from metal corrosion. It is this hydrogen that drives the process of methane production. This is shown by the next **BOX** *"*H_2 *for reaction with C-compounds"*. Hydrogen can also be oxidised by ferric iron and sulphate if suitable microorganism are present. This is shown by the next **BOX** *"*H_2 *for reaction with* Fe_2O_3 *and* SO_4^{2-}*"*. If these reactions were preferred to that with carbon less volatile compounds would form. The availability of Fe_2O_3 *and* SO_4^{2-}. must therefore also be assessed.

The figure tries to capture the essential processes. However, there are a number intertwined mechanisms and processes not shown in the figure that have to be explored and accounted for.

4.2 Form of ^{14}C compounds originally present in the waste

The ^{14}C is present in different waste forms and must first be released from the waste and enter the water to become mobilised (Lindgren et al. 2001). Some of the ^{14}C is in organic compounds and some is inorganic. It is assumed that the *inorganic* form is $^{14}CO_3^{2-}$ at the high pH expected.

It is not known in which compounds the *organically* bound ^{14}C exists. It is reasonable to assume that, as most of the ^{14}C resides in the ion exchange resins[1], the chemical interaction with the ion exchangers will play an important role.

There are no obvious cationic organic compounds. It is assumed that all of the ^{14}C is bound as anionic or non-charged compounds. The anionic compounds are expected to be mostly low molecular formic and acetic acids. These are not volatile in the high pH waters in the repository vaults because they exist as anions.

If present, non-charged species such as methane, ethane, ethylene and other low molecular weight alkanes and alkenes can be sorbed on or dissolved in the polymer resins that make up the cat- and anion exchangers (Kucukpinar and Doruker 2003). There is no information on the amount of such compounds in the waste. Any such compounds are deemed to be present in much smaller quantities than the acids because ion exchangers are specifically devised to have a high capacity for ionic compounds and not primarily as sorbents for gases.

In the repository the resins are either mixed with bitumen or cement. The bitumen itself and the embedded resins in it degrade very slowly (SKB 2008) and are not considered to release much of the bound species. In the cement embedded resins the anionic species will be readily released from the exchanger in the alkaline environment in the repository. The high pH will not specifically expel any non-charged compounds bound in the resins because they can be expected to be dissolved in the resin itself by *physical forces*. Furthermore the desorption and degassing of the non-charged species, if at all present will have been on-going ever since the ion exchange resin was removed from the equipment in the power plant. The radioactive gas should have been detected. It is assumed that non-charged species have either been desorbed by the time the repository is closed or that they are so strongly bound in the resins that they would only be released when the resins degrade. It is assumed that the resins do not degrade at a rate that must be seriously considered (Moreno et al. 2001).

4.3 Rate of escape from moulds and barrels with ion exchange resin

The concrete dissolves out large amounts of hydroxyl ions into the pore water and pH is very high. The ions are bound in the ion exchange resins by electrostatic forces. The anions will be desorbed by the hydroxyl ions, OH^-. As will be shown later there is a surplus of OH^- compared to the anions bound in the exchanger. The hydroxyl ions at the high pH will expel all anions bound in the resin. The rate determining mechanism for release of the anions to the free[2] water is diffusion in and out of the concrete boxes where the resin is embedded in cement. The rate of diffusion in the mm-sized resin particles is very rapid in comparison, because of the small particle size.

The ion exchanger in the moulds with at least 10 cm thick walls, 1.2 m cube and in the 200 l steel drums 90 cm high and 60 cm diameter, is embedded in either cement or bitumen. Also steel lined moulds and large concrete tanks are used (Almkvist and Gordon 2007). The organic anions released from the resin diffuse through the concrete walls of the moulds and through the walls of the corroded iron. The carbonate precipitates to form $CaCO_3$. This considerably slows down its escape.

Below, the rate of out transport of anions and neutral species out of the moulds and barrels with cement conditioned waste is assessed. The escape rate from the cement embedded waste is estimated by using a solution to the instationary diffusion equation, Fick's second law (Bird et al. 2007). It is thereby assumed that the compounds have been released from the resins by invasion of hydroxyl ions in the embedding cement.

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[1] A mixture of cat- and anion exchange resins is used to clean the water in the power plants.

[2] By free water is meant water that is mobile and present in voids large enough to host microorganisms.

The effective diffusion coefficient D_e in the concrete, which has a porosity of about 10% is on the order 10^{-11} m^2/s (Höglund 2001). For this porosity the pore diffusion coefficient D_p is 10 times larger as the relation between them includes the porosity ε.

$$D_e = D_p \varepsilon$$

A very simple way of estimating how rapidly the anions will escape to the water in the porous concrete outside the moulds is to consider the instationary diffusion from a sphere with radius r_o. This is a reasonable approximation if all anions are totally dissolved in the ion-exchange resin, the water in the conditioning cement and the concrete walls of the moulds at the initial time. This also presupposes that the amount of hydroxyl ions coming from the cement and concrete is sufficient to desorb the anions in the resin.

The amount of hydroxyl ions is as large or larger than the anion exchange capacity. The rate of transport in the resins is as fast for the hydroxyl inward as for the desorbed anions out of the resins because the hydroxyl is as mobile as other anions and its concentration is higher.

The sphere is a fair approximation of the mould and the barrel for the present purposes. The porous concrete in which microbes are assumed to exist surrounds the sphere. In the simple model the sphere is suddenly exposed to water into which the ions diffuse. If the concentration in the water is kept low by rapid microbially mediated reaction the solute in the sphere will be depleted as shown in Figure 4-2 for a spherical mould with radii 0.2 and 0.6 m, lower and upper curve respectively. It should be noted that in these calculations it was assumed that the diffusing solute already has filled the pores of the 10 cm thick walls, which may not the case. This would delay the first arrival of the anions to the surrounding water somewhat, on the order of years.

It is seen that a large fraction of the anions and neutral species can escape in a short time from the concrete filled moulds. Because of the low solubility of $CaCO_3$ the carbonate migrates much slower out from the moulds than the organic anions do. However, the consequences of a rapid escape will also be calculated.

The escape from the bitumen conditioned waste is much slower because bitumen has a very low water content, which slows down the in-diffusion of hydroxyl ions needed to expel the anions. The transport properties and long-term stability of bitumen in various environments is discussed in Eschrich (1980). That report indicates that there is less than 0.01% water in bitumen in which hydroxide and hydrophilic compounds could migrate.

For any neutral species the escape from the bitumen filled moulds and drums can be estimated in the same way. Diffusion data for methane and ethane have been measured at 25°C in Athabasca bitumen by Upreti and Mehrotra (2002) to be $8.1 \cdot 10^{-11}$ and $2.5 \cdot 10^{-10}$ m^2/s respectively. From a 0.2 m and 0.6 m diameter mould methane would be exhausted to more than 95% in 5 years and 50 years respectively. Ethane would escape three times faster. The escape rate from bitumen conditioned waste of anionic species is deemed to be negligible compared to that from concrete conditioned waste. However, the consequences of a rapid escape will also be calculated.

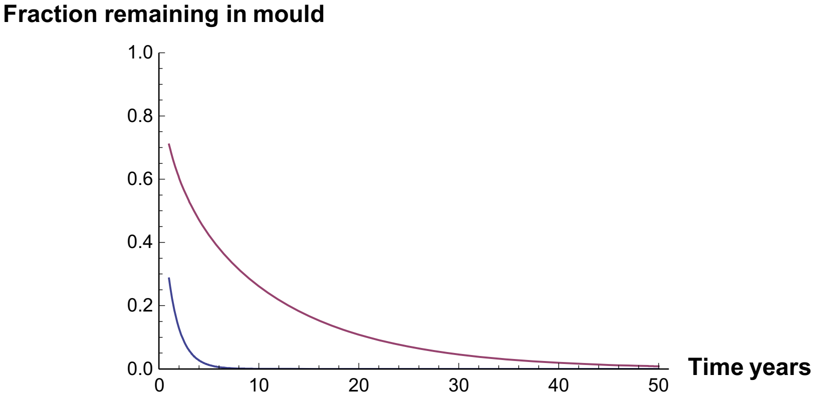

Figure 4-2. *Fraction of inventory remaining in sphere as function of time for 0.2 and 0.6 m (upper curve) radius sphere. Based on equation (8) in Carslaw and Jaeger (1959, p 234).*

4.4 Formation of volatile components

Even if there are no volatile carbon compounds to begin with, such can form by different reactions with hydrogen. Hydrogen is produced as a corrosion product between water and metallic iron and aluminium. Hydrogen is a very strong reducing agent. It can react with carbonate and with organic compounds and reduce them to compounds that contain more hydrogen. The thermodynamic driving force for such reactions is strong and at elevated hydrogen pressures many organic compounds would want to form mainly methane CH_4, which is very volatile. However, at the low temperatures in the repository, around 5–10°C such reactions, if not catalysed, are so slow that they can be neglected for the time of interest for the SFR repository. This may be concluded from e.g. the efforts to reduce unwanted impurities in biofuels. For example, to reduce acetic acid to methane sophisticated catalysts are needed and reaction temperatures of 150°C and pressures of 20 atmospheres are needed (Yu et al. 2011).

However, as there is a considerable gain in free energy in reactions where hydrogen reacts with light organic compounds (Table 3-1) microorganisms might develop that can utilise this energy for methane formation from not only the organic compound but also from the inorganic carbonate. However, it is not obvious that such microorganisms will develop in the hostile environment in the SFR repository where pH is expected be 12.5 to 13.5 or even higher. Also the temperature of 5–10°C is not the optimal for biochemically-mediated catalysis. We will later in the report quantify processes that could act as sinks for hydroxyl ions, which could lower pH and develop less unfavourable environment for microbes.

4.5 Biochemically catalysed reactions

In this "what if" case is assumed that if there is free energy to be gained microorganisms will adapt or develop to promote the reactions. These reactions will occur as long as there is a supply of hydrogen and there remain unreacted carbon compounds. Considered carbon sources in the repository are those bound in the ion exchangers, in concrete as carbonate, in the intruding water and in cellulose. All other organic material including the bitumen, resin, sludge, polymers etc. are assumed to give a negligible contribution. This is a conservative assumption because it neglects additional hydrogen consuming matter that would allow less hydrogen to react with the radioactive carbon. Hydrogen reactions with ferric iron and sulphate in the cement and concrete can also act as a sink and are considered in Chapter 12. Although there are considerable amounts of these oxidants the availability of them is deemed to be low.

It is assumed that all carbon including the ^{14}C reacts with the same rate. The fraction ^{14}C of all carbon in the gas will then be the same as that in the waste. The rate of escape will be governed by the rate of transformation of the available radioactive as well as stable carbon. It may be noted that the more available stable carbon, ^{12}C, there is present, the less ^{14}C will escape per produced hydrogen. This is assuming that they react with the same rate. The amount of available carbon will influence the release rate of ^{14}C activity.

The model is exemplified and illustrated by the following simple case where carbon dioxide reacts with hydrogen to form methane. Any other carbon source is treated in the same way.

The repository vault is modelled as well mixed (bio-) chemical reactors where the following main reaction is between hydrogen, carbon dioxide and methane according to the formula.

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O \tag{4-1}$$

The equilibrium constant for the reaction is

$$K=\frac{P_{CH_4}\, a_{H_2O}^2}{P_{CO_2}\, P_{H_2}^4} \tag{4-2}$$

P stands for partial pressure and a for activity. The activity of water is set to $a_{H_2O}=1$. The relation between the pressures of methane and carbon dioxide then is

$$\mathrm{P}_{CH_4} = KP_{CO_2}\mathrm{P}_{H_2}^4 \tag{4-3}$$

From Equations (4-2) and (4-3) the partial pressure of methane can be found if that of hydrogen and carbon dioxide is known. Similarly the equations for the equilibrium pressure of the other compounds can be defined.

However, the hydrogen and carbon dioxide pressures will depend on the rate of production of hydrogen, the rate of inflow of carbon dioxide (and its dissolved ionic species) and the rate of depletion of inventory of accessible carbon in the repository. In addition the concentration of all species will depend on the rate at which they are carried away by the out-seeping water and species contained in the gas effluent when this forms. In the same way the formation of the other organic volatile components in Table 3-1 e.g. ethane, can be described. However the different components will compete for the same carbon and accounting for a large number of reactions will generate a system of many simultaneous equations.

It will be shown, Chapter 11, that methane will by far dominate the produced compounds. To simplify the model only methane is used as the volatile gas that carries radioactive carbon.

4.6 Repository modelled as a reactor

It was shown above that the neutral and anionic organic compounds in the resins could "rapidly" escape the waste containers. The compounds then enter the water in voids or pores outside the containers where they are catalysed to react with hydrogen to form methane gas that escapes as gas. Under such circumstances one may approximate the complex geometry and processes by a simple stirred tank reactor in which all reactants are well mixed and where the reaction is instantaneous. Hydrogen gas is produced continuously. Reaction products leave the reactor as gas or with water flowing through the reactor. The water may also bring in carbon and other compounds of interest.

A mass balance of the reactor is illustrated in Figure (4-3).

The stirred tank reactor is used to simulate a case where hydrogen is added to the water by corrosion reactions. The repository is anaerobic i.e. devoid of oxygen. Organic matter and early reactions with metallic iron and aluminium will have scavenged any oxygen present at repository closure. The conditions are therefore favourable for formation of methane.

As long as there is a surplus of dissolved carbonate and organic compounds in the system the conversion rate is set by the rate of production hydrogen. Part of the methane dissolves in the water but part forms a gas together with remaining hydrogen and CO_2 gas, which also are partly dissolved. Hydrogen, CO_2 gas and methane will thus be present in water as well as in a gas if the pressure exceeds the hydrostatic pressure in the repository. In this example it is assumed that the water flowing in and out of the rector carries negligible amounts of reactants to and reaction products from the reactor. It will later, Chapter 10, be shown that this is a reasonable approximation.

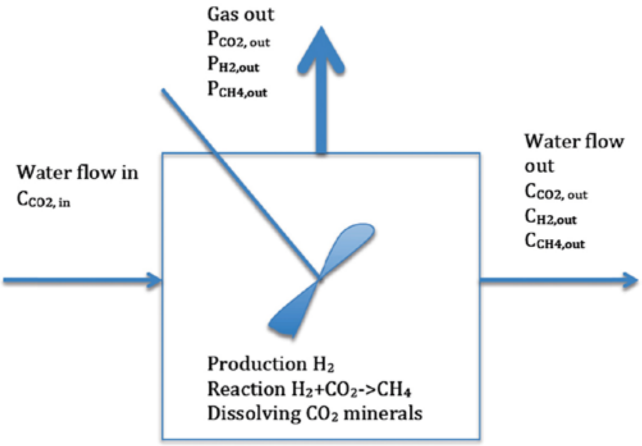

Figure 4-3. *Simplified illustration of a stirred tank reactor with inflow of water carrying reactants, outflowing water and gas carrying reaction products and reactions within the well-mixed reactor.*

A simple system of equations for steady state conditions is set down that describe the mass balance, MB, and equilibria involved

MB H_2: $m_{H2} = V_{water}(c_{H_2} + 2c_{CH_4}) + \frac{V_{gas}}{RT}(P_{H_2} + 2P_{CH_4}) + V_{water}\ m_{H_2O}$ (4-4)

V_{water} is volume of water, V_{gas} volume of gas, R the gas constant and T the temperature. m_{H_2O} comes from the reaction formula #4 in Table 3-1 that shows that half the reacted hydrogen forms water and thus $m_{H_2O} = 2m_{CH_4}$

Pressure condition: $P_{tot} = P_{H_2} + P_{CH_4} + P_{CO_2}$ (4-5)

P_{tot} is the hydrostatic pressure. The concentrations c_{H_2} c_{CH_4} and in the water are obtained from the solubility equilibria at pressure P_{H_2} *and* P_{CH_4} from Table 3-2 for hydrogen and methane. P_{CH_4} is related to the pressure of hydrogen and carbon dioxide.

There is a large amount of portlandite $Ca(OH)_2$ in the concrete and cement and this sets the pH to about 13 and above and the calcium concentration to 0.01 mol/l according to Equation #19 in Table 3-2. This in turn sets the maximum CO_3^{2-} concentration to $1.5 \cdot 10^{-6}$ mol/l as otherwise calcite precipitates according Equation #18 in Table 3-2. This in turn sets the CO_2 partial pressure P_{CO_2} to $4 \cdot 10^{-15}$ atm. as obtained from Equations #15 and #17 in the same table. These conditions are maintained as long as there remains available carbon for methane formation.

With V_{water}, R, T, P_{CO_2} and P_{tot} known V_{gas} and its composition can be solved as function of the amounts of hydrogen gas produced in the system m_{H_2}. The solution also shows at what amount of added hydrogen the pressure of the gas exceeds the hydrostatic and other pressures and bubbles start to form.

These simple equations are also used to cross check the more complicated system of equations in PhreeqC. Very similar results are obtained with the PhreeqC program, which also accounts for a large number of other complexes of the species involved as well as activity corrections.

The simulations show that:

1) When the reactions forming methane are fast the escaping gas will consist of practically only methane.
2) Carbon dioxide gas will not contribute to the escape of ^{14}C components because of its very low partial pressure.

This considerably simplifies the modelling of gas generation, pressure build up and gas release from the repositories.

If the production rate of hydrogen is low the hydrogen and any reaction products could dissolve in the water and be carried away with the water without any gas bubbles forming. Scoping calculations show that the corrosion rates would have be many orders of magnitude lower that those expected for this to happen. At high production rates gas can form even when it needs to do so against the hydraulic pressure at the depth of the repository. If the top of the repository is 50 m below the sea level (or water table in the ground) the gas pressure needs to rise to more than six atmospheres before any gas forms and can start to escape. Capillary forces in the fractures in the rock will also restrain the formation of gas flow paths, so the pressure needs to be somewhat higher that 6 atmospheres for the gas to start escaping. At high gas production rates the gas must also overcome the pressure drop needed to escape through the fractures in the rock.

Part of the volatile compounds formed remain dissolved and part of them form gas. The compounds will be released from the vaults with the rate that they can escape with the water and by the rate they can be volatilised and carried away by the gas. For simplicity, first a case where the only escape route is by gas is presented. In section 10 the rate of escape via only water is assessed and the rates are compared. Although the two escape routes are coupled and influence each other the simplification is sufficient for the present purposes and the two escape routes are treated separately.

For the Silo, where the flow through the intact Silo is small the release can also be by diffusion through the Silo walls and the surrounding bentonite clay. This can be estimated by the equivalent flow rate Q_{eq} (Lindgren et al. 2001). This accounts for the diffusion resistances in walls and bentonite and is smaller than the flowrate through and past the Silo.

When microbial activity has developed and converted all available carbonate and readily degradable organic matter to methane the $^{14}CH_4$ in the repository is mixed with the methane generated from all carbonate that also formed methane. It is thus considerably diluted because there is only on the order of totally about 250 g ($4.1 \cdot 10^{13}$ Bq) of ^{14}C in the entire SFR1 (Almkvist and Gordon 2007) and only part of this can react to methane. The total amount of available non-radioactive carbon only in the cellulose in the repository is more than 4 orders of magnitude larger, so there is a considerable dilution.

4.7 Mass balance based calculations

The rate of evolution of gas caused by corrosion of aluminium is not considered because the aluminium corrodes within a few years and it should be gone by the time the repository is closed. Only the hydrogen produced by iron corrosion is considered. The gas is allowed to escape when the pressure reaches 6 atmospheres, which is taken to be the pressure needed to overcome the hydraulic head about 50 m (5 atm.) and the atmospheric pressure.

The Silo contains the largest amount of ^{14}C. The 1BMA and 2BTF differ in amounts of carbonate content and rates of hydrogen production as well as amount of cellulose. 1BTF is not included here because it contains only a small amount of ^{14}C and it otherwise resembles 2BTF (Almqvist and Gordon 2007). The Silo contains 7,950 kg cellulose that can form $2.65 \cdot 10^5$ mol $^{12}CH_4$ if all carbon is turned to methane by reactions with hydrogen. The cellulose is by far the largest source of carbon available for reduction to methane. 1BMA contains more cellulose in relation to ^{14}C. The $^{12}CH_4$ will dilute the radioactive methane.

The following assumptions are used in the calculations:

- Reactions between carbon compounds and hydrogen are catalysed by microbes and are rapid.
- ^{14}C in the waste turns to methane with the following "what if "cases.
  1. All ^{14}C converts to methane.
  2. Only all organic ^{14}C coverts to methane.
  3. Only that in resins embedded in concrete converts to methane. Of these cases we consider this to be most likely case.
- Only cellulose supplies carbon to produce non-radioactive methane. The availability of carbonate in the concrete will be shown to be marginal in chapter 6.
- Only the hydrogen generated by iron corrosion forms methane and all hydrogen forms methane as long as there remains available carbon.
- No other sinks for hydrogen are active. Potential such sinks are sulphate and ferric iron. This is discussed in Chapter 12.
- All methane escapes as gas carrying ^{14}C in the same proportions of $^{14}C/^{12}C$ as in the waste.

The corrosion rate of iron, is 0.1 micrometre per year (SKB 2014). The activity inventory data is taken from Almqvist and Gordon (2007) appendices D, E, F. The data is summarised in Appendix 1. Other data used are given in Appendix 2. Table 4-1 summarises the results.

Table 4-1. Release rates of ^{14}C activity.

	Duration of release (Years)	All ^{14}C converts (Bq/yr)	Only organic ^{14}C converts (Bq/yr)	Only that in resin embedded in concrete converts (Bq/yr)
Silo	173	$1.85 \cdot 10^{11}$	$5.54 \cdot 10^{10}$	$2.10 \cdot 10^{10}$
1BMA	4,188	$1.77 \cdot 10^{9}$	$5.25 \cdot 10^{8}$	$2.0 \cdot 10^{8}$
2BTF	129	$1.0 \cdot 10^{10}$	$2.94 \cdot 10^{9}$	$1.5 \cdot 10^{8}$

4.7.1 Comments on the results

The amount of carbon that can be made available for transformation to methane is important for the release of $^{14}CH_4$ because it consumes hydrogen. It is shown later that the carbonate embedded in the concrete structures has to diffuse out of the structures and the rate of transport is very slow because of low calcium carbonate solubility and will contribute little. Should the concrete be severely fractured this is not valid as the microbes could live very near the resin particles. Carbonate in the porous concrete, if accessible, would decrease the release rate by about a factor of two in the Silo. The carbonate in the water *that fills* the repository vaults will precipitate on the surfaces of the concrete in contact with that water and can be made available to the microorganisms. It contributes marginally to hydrogen consumption and only in an initial stage. The anion exchangers will also release *organic* anions containing ^{12}C. This could be an important source of non-radioactive carbon to consume hydrogen. ^{12}C carbonate in the anion exchangers would not help because it would be immobilised as $CaCO_3$ in the cement. Especially in the Silo where there is little cellulose the contribution from the ion exchangers could be considerable. If all the anion exchange capacity fully were utilised by organic acids with one ^{12}C atom per charge this could supply 20 times more carbon than the cellulose in the Silo does. This would decrease the release rate by the same factor. However, no information has been found on the amount of non-active organic compounds in the resins. It is therefore neglected in order to be conservative.

Hydrogen that forms will rapidly migrate dissolved in water and possibly as gas to all locations can have carbon and microorganisms. Typical times involved are tens of years for hydrogen to migrate one metre. The microorganisms have a size much larger than the pores in the un-fractured concrete constructions and in conditioning cement. The microorganisms will have to develop and work in larger openings, fractures and in the pores in the porous concrete that is used as infilling between waste containers to ensure that gas can escape without damaging the concrete. The organic anions released from the resins will escape to mobile water within on the order of years. The amount of carbon carried by water that flows in and out of the repository vaults is a small fraction of the potentially available carbon already in the vaults discussed above and is neglected. The availability of carbonate in cement and concrete for methane formation is explored in section 6.

The hydrogen generated from aluminium is in itself sufficient to saturate all the water to an equilibrium pressure of 6 atm. and for bubbles to form. All aluminium corrodes in a few years and the hydrogen may well have dissipated as gas during the resaturation period. Thermodynamically practically all hydrogen can be converted to methane as long there is available carbon. This is assumed to be the case. Neglecting the aluminium it takes about 40 years before gas bubbles form. Thereafter it takes 173 years in the Silo for the available carbon to form methane and bring the ^{14}C with it in the gas that consists of practically only methane. Some methane remains dissolved in the water, to be flushed out later by the hydrogen that continues to be generated for additionally tens of thousands of years.

For 1BMA the duration of the release is much larger due to the larger amounts of cellulose. Carbonate in any porous concrete would decrease the release rate by a few percent at most. In 2BTF there is much less cellulose and the available carbon comes mostly from the water filling the tunnel and waste. The carbonate in the porous concrete could decrease the rate by up a factor of ten in 2BTF.

Another process has been considered. Cellulose can degrade without reaction with hydrogen to form CH_4 and CO_2. In Moreno et al. (2001) the rate of degradation of cellulose is discussed based on observations and modelling. This degradation is also mediated by microorganisms but is not caused by reaction with hydrogen. The proposed rate of gas generation is a fraction 0.005 per year. It would take about 200 years to degrade all cellulose.

Considering that the way of estimating the degradation in this report is different from that in Moreno et al. (2001) and is based on the rate of production of hydrogen and rapid reaction between cellulose and hydrogen, this is in surprising agreement with our results but is purely coincidental. The CO_2 can be reduced to CH_4 in a second step by reaction with H_2. It may therefore not seem to be important which cellulose degradation mechanisms are to be considered. It causes additional uncertainties, however, because the rate of gas production by the different mechanisms may differ.

4.7.2 Verifying simulation of gas evolution using PhreeqC

Simulations using PhreeqC of hydrogen gas evolution and reduction of carbon compounds to methane were performed to ensure that the simplified model gives reasonable results. These simulations differ from the calculations presented above in that involved components also can form complexes and that deviations from ideal conditions are accounted for by using activity coefficients for the different species and for water. It was found that these effects have a limited influence on the results. In the simulations it is assumed that magnetite Fe_3O_4 is the end product of the corroded iron. The alternative $Fe(OH)_2$ was also tested but resulted in insignificant differences except that the hydrogen gas production was somewhat smaller. The simulations confirmed that the simplifying assumption in the previous modelling were acceptable for the present purposes.

In the PhreeqC simulation described below it is assumed that by the time the microbial activity has fully developed the hydrogen from the aluminium corrosion has dissipated. The hydrogen from the much slower iron corrosion starts to build up and the available carbon, mostly cellulose, transforms rapidly to methane, consuming all hydrogen that is produced. The methane dissolves and accumulates in the water. It eventually builds up a sufficiently high concentration of methane gas of 6 atm to start to escape. After some time all the available carbon has reacted and no more methane is produced. However, the hydrogen that continues to be produced for a very long time slowly strips the methane that is dissolved in the water.

Figure 4-4 shows the partial pressure evolution up to 1,000 years of methane and hydrogen in the gas phase. The gas phase forms after about 40 years and consists of practically only methane. After about 200 years all carbon is gone and hydrogen begins to dissolve in the water. This agrees with the simpler calculations presented in Table 4-1.

Increasingly more hydrogen dissipates as the methane concentration in the water is depleted. After 1,000 years the gas contains 5% by volume methane and 95% hydrogen.

The simpler model and the PhreeqC results agree in all important respects.

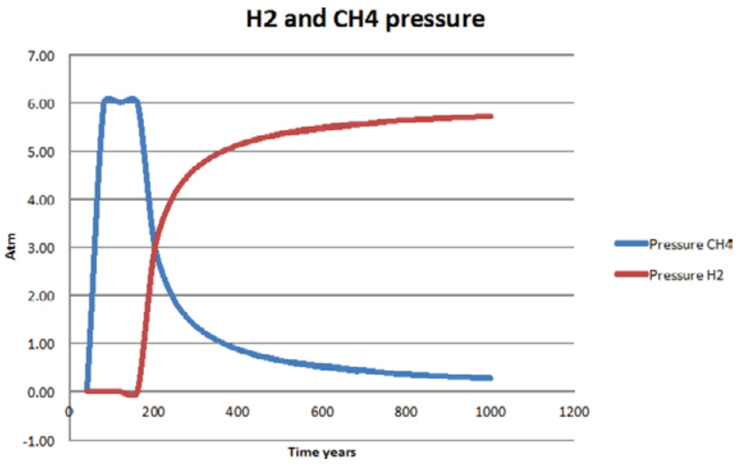

__Figure 4-4.__ Pressure of methane and hydrogen over time.

5 Availability of carbon for methane formation and ^{14}C dilution

One of the factors that have a strong impact on the rate of release of ^{14}C from the repository vaults is how much other carbon compounds there are that consume hydrogen. In the following sections the amounts and availability of carbon in various sources is explored.

5.1 Waste form types and waste inventories

The waste forms and their conditioning are described in detail in Almkvist and Gordon (2007). Most of the ^{14}C is bound in anion exchange resins. The resins are mixed with either cement or with bitumen in steel barrels or moulds that either can be made of steel or of 10 cm thick concrete walls. The moulds are typically 1.2 m cubes. There are also other minor amounts of wastes with scrap metal, sludge, cellulose, various organics, ashes etc. There are a large number of waste types. Besides the variations of sizes the ratios of resin to cement and resin to bitumen vary between different waste forms from different power plants. In the Silo there are 11 different waste forms. In the 1BMA there are 16 and in 2BTF there are 4 that are considered in this report. The properties of the waste forms are summarised in Appendix 1.

There are several sources of carbon. Carbonate and possibly other dissolved organic carbon molecules come in with the water that invades and fills up the repositories. Carbonate can be released from the concrete in the repository structures and fillings and from the cement used to mix with the ion exchange resins. It can also come from degrading cellulose and other readily degrading organic matter. Possibly also the bitumen, resins and other polymers can degrade in the anoxic environment in the repositories. The latter is not deemed to be likely during the few thousands to ten thousand years of interest in this report (Pedersen 2001, Moreno et al. 2001). There may also be considerable amounts of carbon bound as anions in the ion exchange resins.

In the Silo the amount of carbon in the concrete is comparable to that in cellulose. In the cement there is four times more carbon. This is not all available for reaction. In 1BMA cellulose dominates as a carbon source. The carbonate carried in by the water that fills the repositories gives the smallest contribution.

5.2 Release of carbonate from concrete

The solubility of carbonate in the high pH porewaters of cement is very low. The equilibrium concentration at 5°C of dissolved carbonate complexes is $1.5 \cdot 10^{-6}$ mol/l (From PhreeqC calculations). This implies that a carbonate ion will readily form calcite with the abundant portlandite, $Ca(OH)_2$. For the carbonate to be reduced to methane it needs to become available to the microorganisms, which cannot enter the pores of the concrete and cement. The microorganisms will be found in larger voids e.g. fractures in the structures and in the porous cement used to permit gas pathways to form. The hydrogen that evolves by corrosion of metals can readily enter the voids in the porous concrete. When the methane production starts the carbonate that leaches out of the concrete surrounding the voids reacts and new carbonate diffuses out from the concrete to replenish what has reacted. The low solubility of carbonate in the concrete/cement gives a low gradient to drive the diffusion. As the calcite, $CaCO_3$, in the concrete/cement dissolves and the carbonate diffuses out a dissolution front moves further into the concrete and the distance increases, which lowers the concentration gradient. A so-called moving boundary develops.

The rate of movement of the front v_f (m/s) can be assessed by the shrinking core model (Fogler 2006), which for linear diffusion results in the following expressions

$$v_f = \sqrt{\frac{D_e c_{sol}}{2 q_o t}} \qquad (5\text{-}1)$$

The out diffusion rate of carbonate J mol/m^2/s is

$$J = v_f q_o e = e\sqrt{\frac{D_e c_{sol} q_o}{2t}} \tag{5-2}$$

D_e is the effective diffusivity in concrete, c_{sol} the solubility of calcium carbonate, q_0 the concentration of calcite in the solid, both per l of pore water, t is the time and ε is the porosity of concrete.

For a solubility c_{sol} =1.5·10^{-6} mol/l pore water, calcite concentration q_0 =0.41 mol/l pore water, effective diffusivity 10^{-11} m^2/s and porosity 0.1, the flux J is shown as a function time in Figure 5-1a. The distance of the front into the concrete is shown in Figure 5-1b.

It is seen that over a hundred year period the calcite in the outermost 0.2 mm of the concrete will be able to dissolve and supply carbonate to the water. Considering that the concrete walls in the constructions are 10 cm thick or more less than a tenth of one percent of the total carbonate in the walls could become available in 100 years.

Table 5-1 summarises the potential carbon sources in the repository vaults. The carbon in porous concrete is much smaller than in cellulose. The carbon in cellulose and in porous concrete is assumed to be available for reaction with hydrogen. Only a small fraction of that in the concrete constructions can diffuses out to the porous concrete and is neglected.

5.3 Binding ^{14}C carbonate

About two thirds of the ^{14}C in the repository is carbonate (Almqvist and Gordon 2007). The carbonate is released from the resins embedded in cement. It precipitates as calcite in the cement. It is assumed that no microorganism can be present in the interfaces between the resin and the cement because of the very small pores in this mixture. The carbonate will be immobilised. In contrast inflowing non-radioactive carbonate with water will precipitate as calcite on the *surfaces* of cement containing materials and would be available to reactions with hydrogen. However, the amount is negligible as shown later in Chapter 10.

Table 5-1 Potential carbon sources in the repository vaults.

	In Cellulose (mol C)	In Porous concrete (mol C)	In Concrete (mol C)
Silo	2.65·10^5	1.64·10^3	3.89·10^5
1BMA	4.90·10^6	5.51·10^2	2.29·10^5
2BTF	5.53·10^3	4.98·10^2	6.66·10^4

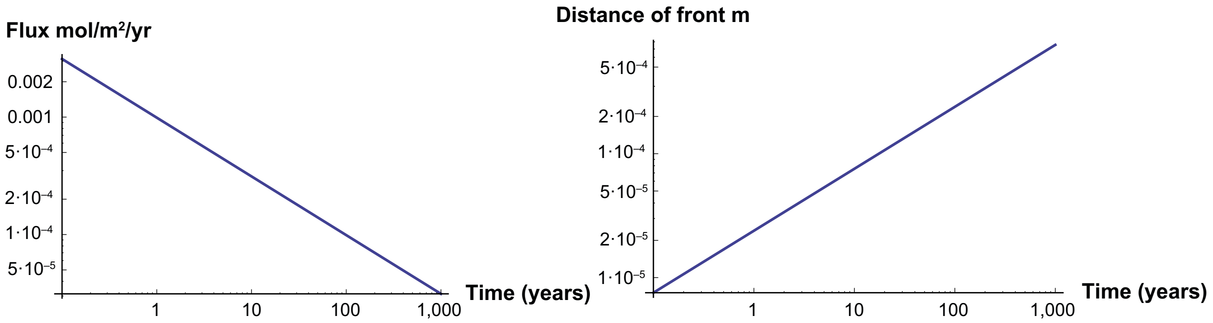

Figure 5-1 a and b. *Flux of carbonate out of concrete and distance of front into the concrete structure.*

6 Release of anions from resin

In the above examples it was assumed that all organic^{14}C in the anion ion exchange resin is released. This also implies that all ^{12}C bound as anions are released. In this section it is explored if there is sufficient hydroxide to expel the anions bound in the resins and if the hydroxide can be available at a rate that is not limiting for the overall release. It is assumed that the resins contain not only ^{14}C compounds but also other non-radioactive anionic organic or inorganic compounds. We have found practically no information on how much such compound there are in the resins. In the example calculations it was assumed that the resins do not have large proportion of the ion exchange sites filled with other *organic* compounds because these would generate more carbon available for non-radioactive methane formation. For the hydroxyl mass balance it is assumed that the full ion exchange capacity is utilised, i.e. filled with anions, but these may be inorganic. There is little information on if these are organic or inorganic except that in some PWR reactor resins most of the anion exchange capacity has been used by boric acid (Almkvist and Gordon 2007). In the Silo the amount of anion exchange capacity is much larger than the amount of carbon in cellulose.

Thus if information could be obtained on the amounts of organic anions bound in the resins this could be used in future calculations. If a large amount of organic anions are bound in the resin this could result in a considerable decrease in the release rate of ^{14}C, especially from the Silo.

Hydroxyl ions enter the anion exchanger and expel the same amount of charge of other anions. At the high pH in the cement this can be expected to be essentially a quantitative reaction. The ion exchange resins embedded in cement in the moulds are in direct contact with the cement. The transport distances from the cement and into the mm size resin particles are small and time for ions to move in and out of the resin particles is short.

The cement materials contain on the order of 0.5% sodium or potassium hydroxide and on the order of several up to 10% of portlandite, $Ca(OH)_2$. Höglund (2001) in one of his examples uses the value 3%. The sodium and potassium hydroxide will make the porewater, which makes up about 10% by volume of the concrete and cement very basic, pH well above 13. When these very soluble compounds have dissolved and the hydroxide ions have been consumed in the ion exchange process portlandite dissolves and maintains the pH at that set by the portlandite equilibrium as long as there still remains un-dissolved portlandite.

Table 6-1 shows the ratio of OH^- to that of the anion exchange capacity for the two waste packages in the Silo that contain the highest activity of ^{14}C. The same is shown for the 1BMA. Half of the resin is taken to be anion exchange resin, the portlandite content is 3% by weight of the dry cement and there is 0.5% alkali hydroxide. The anion- exchange capacity is taken to be 4.5 equivalents/kg anion resin (Helfferich 1995). Other data are taken from Appendix 1.

The amount of hydroxyl in the ion exchange resin is larger than the ion exchange capacity in all four packages. There is enough hydroxyl to expel all anions from the resin even if all ion exchange sites are filled with anions. All anions and thus all ^{14}C will be desorbed.

Table 6-1. Ratio of amounts of OH in cement and exchange equivalents in ion exchange resin in cement stabilised waste.

	Radioactivity (Bq)	Ratio cem/resin	Ratio OH/exchange capacity
Silo			
0.02	$8.39 \cdot 10^{11}$	8.5	2.0
R.16	$2.28 \cdot 10^{12}$	6	1.4
1BMA			
0.01	$1.89 \cdot 10^{11}$	8.5	2.0
R.01	$5.05 \cdot 10^{11}$	7.7	1.8

7 Sinks for hydroxyl that may exhaust $Ca(OH)_2$ and lower the pH

As long as there is $Ca(OH)_2$ the pH will be determined by the solubility of $Ca(OH)_2$, which is above 12.5 at 20°C in pure water. It is higher at lower temperatures. It was shown in the previous section that the anion exchangers could consume a large fraction of the hydroxyl in the cement in the moulds. This includes the sodium and potassium as well as the calcium hydroxides. Should there be additional sinks, the supply of $Ca(OH)_2$ could be exhausted and the pH would drop. The environment would become less unfriendly for microorganisms. This possibility is explored below.

7.1 Reactions considered that consume hydroxyl to lower the pH

The following scenario is considered. Ion exchange resins are embedded in a cement matrix. The ion exchange resins have equal amounts of cat- and anion-exchanger equivalents. The cement contains some sodium and/or potassium hydroxide, denoted MOH and some calcium hydroxide $Ca(OH)_2$. M stands for Na or K. These can release hydroxyl ions as well as cations.

$MOH \rightarrow M^+ + OH^-$ (7-R1)

$½Ca(OH)_2 \rightarrow ½Ca^{2+} + OH^-$ (7-R2)

The anion exchange resin denoted R_{an} can react reversibly

$R_{an}An + OH^- \leftrightarrow R_{an}OH + An^-$ (7-R3)

The formula shows the regeneration mode when the anion An^- is released when the exchanger is subject to high pH conditions such as are expected in the porewater in cement. An^- is a notation for the anions that were bound by the anion exchanger during operation in the nuclear power plant. This includes the anionic carbon molecules that contain the ^{14}C. Other acids can also take up a considerable amount of the capacity. For example resins from the PWR-reactors contain boric acid (H_3BO_3) up to 90 g/kg of resin (Almkvist and Gordon 2007). This is essentially all the exchange capacity the resin has.

The cation exchange resin can react according to

$R_{cat}H + M^+ \leftrightarrow R_{cat}M + H^+$ (7-R4)

The reaction is written in "water cleaning mode" when the resin in the "H"-form exchanges protons for cations, in this case exemplified by the cation M^+ generated by equation (7-R1).

We also consider the reaction

$H^+ \leftrightarrow H_2O - OH^-$ (7-R5)

(7-R5) in (7-R4) gives

$R_{cat}H + M^+ \leftrightarrow R_{cat}M - OH^- + H_2O$ (7-R6)

A molar capacity for OH^- uptake in the resins is set up below using equations (7-R3) and (7-R6). The exchange capacities N for the an- and cation exchangers in the resin as used in the power plants are nearly equal. To simplify we set $N_{an} = N_{cat} = N$. When one An^- is released from the anion exchanger it consumes one OH^-. When the cation exchanger takes on one M^+ it releases one H^+, which reacts with one OH^- to form water

The entire OH^- capacity of the two resins is

$N_{Capac,OH} = f_{an} \cdot N + (1-f_{cat}) \cdot N$ (7-1)

where f_{cat} and f_{an} are the fractions of cat- and an-ion exchange capacity utilised in the exchangers respectively during operation in the power plant.

When the an- and cation exchangers have been equally much utilised, irrespective of how much the OH^- , f_{cat}=f_{an}, the capacity is

$N_{Capac,OH} = N$ (7-2)

Should, as an extreme example, the anion exchange capacity be fully utilised e.g. by cleaning acidic water, as the example in the PWR mentioned above, but the cation capacity had not been used at all then f_{an}=1, and f_{cat}= 0 and

$N_{Capac,OH} = 2 \cdot N$ (7-3)

This capacity can be compared with the amount of hydroxyl that is available in MOH and $Ca(OH)_2$ in the cement in which the resins are embedded.

Another potential source of proton generating and thus hydroxyl consuming reaction is that from cellulose degradation. Although there is no or practically no cellulose in the waste packages in which resins are mixed with cement there is cellulose outside and nearby the waste package.

Cellulose, denoted CH_2O, can degrade by the following reaction

$2CH_2O + H_2O \rightarrow H_2CO_3 + CH_4$ (7-R7)

While there is still portlandite left in the cement the following reaction will take place

$H_2CO_3 + Ca(OH)_2(s) \rightarrow CaCO_3(s) + 2H_2O$ (7-R8)

The carbonic acid will be neutralised by reaction with portlandite and will not consume hydroxyl. As long as the portlandite is not exhausted by (7-R8) and the ion exchange reactions, cellulose degradation by the above mechanism does not contribute to pH lowering.

There are other potential sinks for hydroxyl namely some aluminium and iron complexes that bind hydroxyl at high pH e.g. $Al(OH)_4^-$ and $Fe(OH)_4^-$. This potential sink was explored using PhreeqC letting iron and aluminium corrode in water saturated with portlandite. It was found that only minor amounts of these and other complexes will form.

7.2 Examples

Below we explore at what resin to cement ratio the ion exchange sink for hydroxyl could deplete, first the sodium and potassium hydroxide in a first reaction, and the portlandite in a subsequent reaction. In these examples we take as before a central case with cement with 0.005 kg MOH and 0.03 kg $Ca(OH)_2$ per kg cement respectively (Höglund 2001) and ion exchange capacities of 5 eq/kg. The latter value is chosen to be in the upper range of typical ion exchangers (Helfferich 1995) in order to be conservative. In one kg of mixed an- and cation exchanges $N= N_{an} = N_{cat} = 2.5$ eq/kg. Taking the molar mass of MOH as the mean of sodium and potassium hydroxide to be 48 g/mol, one kg of cement contains 0.104 eq OH^-. The ion exchange capacity in one kg resin could exhaust 24.0 kg cement if MOH were the only source of hydroxyl and the an- and cation resins were equally much utilised, called case 1. When the anion exchanger is fully utilised and the cation exchanger not at all, 48 kg cement would be needed, called case 2. This implies that the very high pH set by MOH will not be maintained.

Once MOH is exhausted $Ca(OH)_2$ supplies hydroxyl. The combined amount of hydroxyl from MOH and portlandite is 0.91 eq/kg cement. 2.74 kg cement would supply the resin with OH^- to exhaust it in the case 1 and 5.48 kg in case 2. This suggests that $Ca(OH)_2$ in the cement will not be exhausted when the ratio cement/resin is larger than 5.48 even in case 2.

Should the cement contain two times less MOH and portlandite the value would grow by a factor of two to 5.48 and 11.0 kg respectively. In the last case pH would drop to below 12.5 to a value set by the solubility of complicated alumino-silicates in the cement. pH may drop to 10 and lower (Berner 1992).

An inspection of the table in Appendix 1 shows that the ratios of cement to resin ranges from 1.5 to 9.2. The three waste packages with ratios less than 2.6 contain very low amounts of ^{14}C compared to those with higher ratios. Excluding these the remaining ratios are 6.0–16.4. The package type R.16 in the Silo that contains the largest amount of ^{14}C activity, $2.28 \cdot 10^{12}$ Bq, has a ratio equal to 6. This makes up about 2/3 of all the activity in cement-stabilised resin in the Silo. The R.16 package would not be exhausted of OH^- under the conditions assumed above but could be exhausted if the cement contains less hydroxide. If only MOH is exhausted as the above data suggest will be the case for all ratios the pH will be set by $Ca(OH)_2$ solubility while this is not exhausted.

The cement in the waste package is not the only source of hydroxide. This is explored in the next section.

7.3 Other sources of hydroxyl than embedding cement

There is more cement in the concrete in the various constructions in the repositories that also may supply hydroxyl for desorption. This is explored below where other sources of hydroxyl and its availability for ion exchange are assessed. The table in Appendix 3 shows that there is a considerable amount of hydroxyl in the concrete compared to the amount of anion exchange capacity. The data in the table includes all ion exchange mass including that embedded in bitumen, which will not be a sink for hydroxyl, about half in the Silo and one third in 1BMA is bound in bitumen. Table 7-1 compares the hydroxyl amounts in the concrete and the anion exchange capacity.

7.4 Availability of hydroxide residing in the concrete constructions

The Silo has a mass $2.16 \cdot 10^7$ kg concrete and much more than half of the portlandite in it could be dissolving into the water *inside the Silo* if we consider that the outside of the Silo is exposed to clay and seeping groundwater that could dissipate the hydroxide in the outer half. The portlandite inside the Silo can dissolve only in the water inside the Silo. This water is in practice stagnant as a thick bentonite layer surrounds the Silo and there is very little flow through it.

Table 7-2 shows the solubility in pure water of portlandite at different temperatures calculated by PhreeqC with the Minteq database.

In the subsequent calculations the temperature is taken to be 5°C.

Table 7-1. Amounts of OH^- in concrete constructions and an-ion exchange capacities in waste. Data from Appendix 3.

	Concrete (kg)	Amount OH-mol[1]	Ion exchanger (kg)	Anion exchange capacity equivalents[2]
Silo	$2.16 \cdot 10^7$	$1.75 \cdot 10^7$	$2.45 \cdot 10^6$	$4.90 \cdot 10^6$
1BMA	$1.27 \cdot 10^7$	$1.03 \cdot 10^7$	$1.65 \cdot 10^6$	$3.30 \cdot 10^6$
2BTF	$3.70 \cdot 10^6$	$3.0 \cdot 10^6$	$8.06 \cdot 10^5$	$1.61 \cdot 10^6$

[1] Assumed that concrete contains 20% cement, and cement contains 0.5% MOH and 3% $Ca(OH)_2$.
[2] Assumed that half of the resin mass is anion exchanger with a 4 eq/kg.

Table 7-2 solubility and pH of saturated portlandite solution in pure water.

Temperature °C	0	5	10	20
mol/l $Ca(OH)_2$	$4.059 \cdot 10^{-2}$	$3.22 \cdot 10^{-2}$	$2.65 \cdot 10^{-2}$	$1.96 \cdot 10^{-2}$
g/l $Ca(OH)_2$	3.00	2.38	1.96	1.45
pH	13.55	13.28	13.04	12.61

The amount of hydroxyl ions totally present in all the concrete is larger than the amount of anions in the resin, Appendix 3. Much of the $Ca(OH)_2$ is bound in the concrete construction and must diffuse out of the walls to reach the anion exchange resin, which acts a sink for hydroxyl ions. The rate of out-diffusion can be assessed by a shrinking core model in the same manner as was done for calcium carbonate. Solubility data are taken from Table 7-2 and amounts of concrete from Appendix 3. Concrete porosity and diffusivity are taken to be the same as for calcite calculations.

Figure 7-1 a shows the flux of calcium hydroxide from a concrete structure when it is subjected to a sink of OH^- at the surface of the structure Figure 7-1b shows how the dissolution front of $Ca(OH)_2$ moves further and further from the surface with time.

It is seen in Figure 7-1a that the rate of out diffusion decreases with time. Figure 7-1b shows that after 100 years the dissolution front has progressed about 2 cm from the surface. Many of the moulds have 10 cm thick walls. This means that about 20% of the $Ca(OH)_2$ in the walls of the moulds would become available for ion exchange during the first 100 years. The hydroxyl ions in sodium and potassium hydroxides are depleted much faster as they have no solubility limitations.

Much of the $Ca(OH)_2$ in the thick walls of the Silo and construction walls 1BMA may not become available over the first hundred to thousand years but most of the alkali hydroxide will.

These examples serve to illustrate that most or all of the activity bound in the ion exchange resins could be released from the resins and made available to biochemical reactions. The examples also show that there is not sufficient capacity of the ion exchangers to deplete all $Ca(OH)_2$ in the cement embedding the resins, which could have led to a lowering of the pH below that set by the $Ca(OH)_2$ solubility. There can be a further slow release of hydroxide in the concrete constructions It is therefore not likely that the environment would become more friendly to microorganisms than that set by portlandite pH.

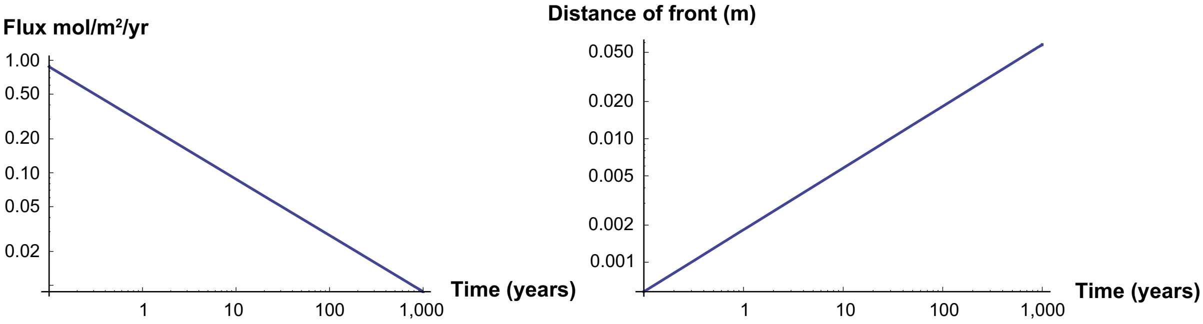

Figure 7-1. *a) Flux of $Ca(OH)_2$ over a surface with low concentration. b) Distance of receding dissolution front.*

8 Rate of escape of originally present volatile ^{14}C components

Although it is deemed improbable that more than a minute fraction of the organic compounds originally in the waste are volatile the degassing of such compounds is explored by an example.

Table 8-1 shows the solubility and carrying capacity of water for H_2 and CH_4 in the Silo, 1BMA and 2BTF if the individual gases are pure and were at 6 atm. pressure. This is meaningful because there are periods when either hydrogen or methane dominates in the gas. The concentration in the water is obtained by multiplying the pressure with Henrys constant Kh given in Table 8-1.

At 5°C the vapour pressure P_{CH_4} of methane above water with concentration c_{CH_4} is given by Henrys law with a constant K_H=2·10^{-3} mol/l, atm.,

$$P_{CH_4} = \frac{c_{CH_4}}{K_{H,CH_4}} \tag{8-1}$$

There will be an exponential decay of the amount of methane remaining in the water *m*. The volumetric gas flowrate in m^3/year is at the pressure in the repository, 6 atm. K_H is Henrys constant, *R* the gas constant, *T* the temperature in *K*, V_{water} the water volume in the repository and *t* the time.

$$m = m_o e^{-\frac{\dot{V}_{gas}}{K_H R T V_{water}}} = m_o e^{-0.0062\,\dot{V}_{gas}} \tag{8-2}$$

m_o is the amount in the water at time zero. The rate of hydrogen gas production from iron corrosion in the Silo is on the order of 70 Nm^3/year. This goes on for many thousands of years. From aluminium it is 800 Nm^3/year but only during a few years after which the aluminium is gone. We neglect this first time in the example below.

With V_{water}= 4,678 m^3 and $\dot{V}_{gas}$ =11.7 m^3/yr at 6 atm. half of the dissolved methane has been stripped in 12.4 years.

Other conceivable volatile organic compounds are ethane and propane. They have less than twice as large Henrys constants so they would be depleted somewhat more slowly. One needs to know the amount and kind of volatile compounds in order to assess if this can be an important escape mechanism for ^{14}C. This information has not been available. The hydrogen will also degas radon that dissolves out of the waste. If the radon is rapidly dissolved then it will be degassed with a rate that is about ten times smaller that methane because the Henry's constant is ten times larger.

Nitrogen and possibly helium present in the groundwater can have concentrations that are near the solubility at repository depth (Hallbeck and Pedersen 2008). When the water flows to shallower depths these may form bubbles. However, this effect will have marginal if any impact on the rate of release of the radioactive gases from the repositories.

Table 8-1. Solubility of gases at partial pressure of 6 atm. (Sander 1999)

	Kh at 25°C (mol/l/atm)	Dln(Kh)/d(1/T) (Kelvin)	Kh at 5°C (mol/l/atm)	mol/l water at 6 atm	Nm^3 per m^3 water
Gas					
H_2	7.80·10^{-4}	–500	8.80·10^{-4}	5.28·10^{-3}	1.18·10^{-1}
CH_4	1.40·10^{-3}	–1,700	2.11·10^{-3}	1.27·10^{-2}	2.84·10^{-1}
C_2H_6	1.90·10^{-3}	–2,400	3.39·10^{-3}	2.03·10^{-2}	4.56·10^{-1}
C_3H_8	1.40·10^{-3}	–2,700	2.69·10^{-3}	1.61·10^{-2}	3.61·10^{-1}
C_2H_4	4.70·10^{-3}	–1,800	7.26·10^{-3}	4.35·10^{-2}	9.75·10^{-1}
Rn	9.30·10^{-3}	–2,600	1.74·10^{-2}	1.05·10^{-1}	2.34
N_2	6.30·10^{-4}	–1,300	8.62·10^{-4}	5.17·10^{-3}	1.16·10^{-1}
He	3.70·10^{-4}	–360	4.04·10^{-4}	2.42·10^{-3}	5.42·10^{-2}

9 Impact of water flow through the repository vaults

The flowrate of water through the repository vaults is small and the turnover time of water is many hundreds to thousands of years. For our purpose we therefore can neglect the flows in and out for carrying dissolved species to and from the repository vaults because the main gas generation occurs during the first hundred to thousand years. Although some water may be expelled by the gas as it starts to form we consider the repository vaults to be open only to gas escape and in-seepage of sufficient water to generate the gas volume that escapes. However, below we explore if this assumption is reasonable.

Table 9-1 shows the water flowrates through the repository vaults (Moreno et al. 2001). As the gas will collect in the upper part of the excavations the water flowrates there will govern how much water is available to dissolve the generated gas. This is therefore included to represent the carrying capacity of the flowing water. The row denoted Q-equivalent is the carrying capacity of water flowing around the Silo when the diffusion resistances in the surrounding clay and in the thick walls of the Silo are accounted for. The rows with bold characters are used in the sample calculation below.

The flowing water carries dissolved substances to and from the repositories. The rate of flow of dissolved components is the product of the water flowrate and the concentration of the solute.

It is seen from Table 8-1 that if the gas consisted of only hydrogen to generate a pressure of 6 atm the volume of water needed to dissolve 1 Nm^3 of hydrogen is 0.118 m^3. For the Silo with water flow through and past the vault of 0.76 m^3 water/yr this means that 0.090 Nm^3 H_2 dissolved gas can be carried away per year. Thus if the hydrogen gas production is larger than 0.09 Nm^3/yr gas bubbles will form. Similarly if the gas consists of only CH_4 then 0.22 Nm^3 methane can be carried away per year.

With a corrosion rate of iron of 10^{-7} m/yr the hydrogen gas production is around 70 Nm^3/yr (Appendix 2). This is several hundred times larger than what the flowing water can carry away. Thus bubbles must form to allow the gas to escape.

It may also be noted that the inflow of carbonate by the water that flows through the repository vaults brings in negligible amounts of carbonate. See Table 9-2 column E. The amount of carbon as carbonate carried into the vault and the amount of carbon carried out of the repository as dissolved methane per year makes up a vanishingly small fraction of the amount of carbon in the repository. This shows that the assumption that water flow through the vaults has little impact used in the preceding chapters is valid.

Table 9-1. Flowrates through different parts of the repositories (Moreno et al. 2001)

Repository vault	Flowrate (m^3/yr) at time 2,000 years after closure
Silo: encapsulation	0.23
Silo: Filling on top:	0.53
Silo: Whole Silo	**0.76**
Silo: Q-Equivalent (R-01-18)	0.043
1BMA: Encapsulation	0.07
1BMA: Whole tunnel	**8.7**
2BTF:Encapsulation	2.4
2BTF: Whole tunnel	**6.7**

Table 9-2. In and outflow of carbon in the repositories. Data taken from table 5-2 in (Moreno et al. 2001)

	Vol mobile water (m^3)	Flowrate (m^3/yr)	Residence time (yrs)	Inflow C for 0.1g/l, (mol/yr)	Conc CH_4, 6 atm (mol/water)	Outflow CH_4 (mol/yr)	Available C (mol)	Fraction of C outflow per yr
Silo	1,334	0.76	$1.76 \cdot 10^{3}$	$1.25 \cdot 10^{-3}$	$1.27 \cdot 10^{-2}$	$9.62 \cdot 10^{-3}$	$2.46 \cdot 10^{5}$	$3.92 \cdot 10^{-8}$
1BMA	3,073	8.7	$3.53 \cdot 10^{2}$	$1.43 \cdot 10^{-2}$	$1.27 \cdot 10^{-2}$	$1.10 \cdot 10^{-1}$	$4.91 \cdot 10^{6}$	$2.25 \cdot 10^{-8}$
2BTF	23,700	6.7	$3.54 \cdot 10^{3}$	$1.10 \cdot 10^{-2}$	$1.27 \cdot 10^{-2}$	$8.48 \cdot 10^{-2}$	$4.44 \cdot 10^{4}$	$1.91 \cdot 10^{-6}$

10 Formation of other organic substances than methane

In Table 3-1 a number of other organic substances known to participate in biochemically mediated reactions are shown.

In this section we explore if these may play a role by not allowing formation of methane and so remain in solution. Those that are volatile would be desorbed from the water by hydrogen. On the other hand if the ^{14}C remains dissolved as neutral or anionic organic compounds it would not be retarded by sorption during the migration to the biosphere. It may also behave differently in the biosphere as to uptake in the biota.

It can be seen from the equilibrium constants in Table 3-1 that reactions #1 and #2 show that formic acid and acetic acid favours decomposition of these substances to methane because $\Delta G_r^0 << 0$. Except at extremely low P_{CO_2} only negligible amounts of these acids will form even if some microorganisms develop to use this reaction. Reactions #5 to #8 can generate these light organic compounds under high methane and low hydrogen pressure. All these substances except perhaps acetylene are found in deep groundwaters but in much lower concentrations than methane (Hallbeck and Pedersen 2008).

It is possible to incorporate these reactions in the models, including PhreeqC, but it is deemed to give little or no additional valuable information. Instead their concentrations or partial pressures are given in Table 10-1 under the conditions that were found in previous PhreeqC calculations, $pH=13.3$, $P_{CH_4} = 6$ atm., $P_{CO_2} = 3.76 \cdot 10^{-15}$ atm. and $P_{H_2} = 4.2 \cdot 10^{-4}$ atm. This applies when the biochemically catalysed reactions are rapid.

It is seen in the table that the other compounds will have vanishingly small concentrations. The simplifying assumption that methane will dominate is thus valid.

Table 10-1. Concentrations of other organic compounds.

From PhreeqC simulations for conditions	**pH**	**P_{CH_4}**	**P_{CO_2}**	**P_{H_2}**
Results from iron corrosion with portlandite and calcite in equilibrium	**13.20**	**6 atm**	**$3.76 \cdot 10^{-15}$ atm**	**$4.20 \cdot 10^{4}$ atm**
	logK	**K**	**Conc/press**	**Formula**
Formic acid	11.51	$3.24 \cdot 10^{11}$	$7.34 \cdot 10^{-23}$ Conc mol/l	Formic acid = P_{CH_4} $0.25 \cdot P_{CO_2}$ 0.75/K
Formate-	3.74	$5.50 \cdot 10^{3}$	$1.01 \cdot 10^{-27}$ Conc mol/l	Formate = 1/K·Formic acid/H^+
HAc	9.755	$5.69 \cdot 10^{9}$	$3.97 \cdot 10^{-24}$ Conc mol/l	Hac = $P_{CH_4} \cdot P_{CO_2}/K$
Ac^-	4.76	$5.75 \cdot 10^{4}$	$5.22 \cdot 10^{-30}$ Conc mol/l	$Ac^- = 1/K \cdot H_{ac}/H^+$
Ethane	–6.021	$9.53 \cdot 10^{-7}$	$7.78 \cdot 10^{-08}$ pressure atm	Ethane = $P_{CH_4} \cdot K/P_{H_2}$
Propane	–2.643	$2.28 \cdot 10^{-3}$	$9.62 \cdot 10^{-18}$ pressure atm	Propane = $K \cdot P_{H_2}/P_{CH_4}$
Etylene	–14.87	$1.35 \cdot 10^{-15}$	$3.71 \cdot 10^{-22}$ pressure atm	Ethylene = $K \cdot P_{CH_4}/P_{H_2}$
Acetylene	–20.226	$5.94 \cdot 10^{-21}$	$1.72 \cdot 10^{-29}$ pressure atm	Acetylene = $K \cdot P_{CH_4}/P_{H_2}$

11 Other potential scavengers for hydrogen

Besides the carbon containing compounds that consume and oxidise hydrogen to form methane also ferric iron compounds and sulphate can oxidise hydrogen. If this happens there will be less hydrogen to produce both radioactive and non-radioactive methane.

Both sulphate and ferric iron are present in cement. Almqvist and Gordon (2007) give an example of a “Degerhamn” cement that contains 4.6% by weight Fe_2O_3 and 2.2% SO_3, (SO_3 in water forms H_2SO_4). Ferric iron can be reduced to ferrous iron and sulphate to sulphide mediated by microbial catalysis. One Fe_2O_3 oxidises one H_2, one SO_3 oxidises four H_2 and one cellulose unit, CH_2O, oxidises two H_2.

In Table 11-1 the oxidising capacity of the cellulose is compared with the oxidising capacity of ferric iron and sulphate in the porous cement in the vaults. The ferric iron and sulphate are assumed to be readily available for microbial catalysis in the porous cement where it is assumed that the microbes can be present. This is in contrast to compact cement and concrete from which they are excluded because of their size.

It is seen that the oxidising capacity of the cellulose is orders of magnitude larger than either that of the ferric iron or sulphate. Should the sulphate and iron consume hydrogen before the ^{14}C-carbon and cellulose this would delay the start of $^{14}CH_4$ production and release.

Possibly some ferric iron and sulphate in compact cement and concrete could diffuse out to the porous cement and be made available for H_2 reaction. Table 11-2 shows the oxidizing capacity of sulphate and ferric iron in *all* cement and concrete in the vaults. In the Silo both the ferric iron and sulphate has a much larger oxidizing capacity than the cellulose. However, ferric iron minerals have low solubility in higher pH ranges (Stumm and Morgan 1996) and will impede its escape from the cement and concrete. The same applies to sulphate, which is bound in ettringite and or gypsum in cement. These also has a low solubility (Perkins and Palmer 1999).

Should all the amount of these substances become available then several cases can be considered. If cellulose reacts with the same rate as ferric iron and sulphate the release rate of ^{14}C methane would decrease by more than a factor of ten in the Silo, by half in 1BMA and by about two order of magnitude in 2BTF. If the reactions with ferric iron and sulphate are preferred compared to cellulose by the micro-organism the release of ^{14}C methane would be delayed but when these reducing agent are exhausted the release rate would be governed by the rate of production of hydrogen as if no hydrogen scavenging by sulphate and ferric iron had occurred. The case described in chapter 5 would still be valid but with delay. Other cases can also be considered. No detailed calculations have been made so far.

Table 11-1. Oxidation capacity of H_2 by sulphate and ferric iron in porous cement and cellulose.

	Porous cement in vault (kg)	Cellulose in vault (kg)	SO_4 in porous cement in vault (kg)	Fe_2O_3 in porous cement in vault (kg)	Consumed H_2 porous cement in vault (kg)	Consumed H_2 by SO_4 in porous cement (mol H_2)	Consumed H_2 by Fe_2O_3 in porous cement (mol H_2)
Silo	18,260	7,950	402	840	530,000	20,086	5,263
1BMA	6,117	147,000	135	281	9,800,000	6,729	1,763
2BTF	5,530	166	122	254	11,067	6,083	1,594

Table 11-2. Oxidation capacity of H_2 by sulphate and ferric iron in all cement and concrete.

	Cement and concrete total (kg)	Consumed H_2 by SO_4 in concrete, 80% ballast (mol H_2)	Consumed H_2 by Fe_2O_3 in concrete, 80% ballast (mol H_2)
Silo	21,600,000	4,752,000	1,245,113
1BMA	12,700,000	2,794,000	732,080
2BTF	3,700,000	814,000	213,283

Much more detailed investigations must be made to assess if and at what rate the ferric iron and sulphate within the compact concrete and cement can be made available for reducing hydrogen.

The sulphate and ferric iron ions can also be carried in by flow to the repository vaults. The pH of the water approaching the repository vaults is expected to be near neutral. Gaucher et al. (2005) in their calculations use pH 7.7 and 7.3 for fresh and saline groundwater respectively. The saline water has the higher concentration of sulphate $3.4 \cdot 10^{-3}$ M and $3.3 \cdot 10^{-5}$ M iron. Only a fraction of the ion is expected to ferric at the prevailing reducing conditions.

The water filling the vaults brings in sulphate and iron. The amounts hydrogen potentially oxidised in this way is shown in Table 11-3. Water volumes in the vaults are taken from Table 9-1.

The amount of hydrogen that can be oxidised by sulphate and ferric iron that is brought in by the infilling water is very small compared to what cellulose consumes.

Once filled there will be flow through the vaults. With the flowrates in Table 9-1 the influx of sulphate will be 2.6 mol/yr to the Silo, 30 mol/yr to 1BMA and 23 mol/yr to 2BTF. For the iron the influx is 100 times less. These amounts are totally negligible to the amounts that already are present in the vaults.

The start of CH_4 production would be delayed by the presence of sulphate and ferric iron.

Table 11-3. Oxidation capacity of H_2 by sulphate and ferric iron in water that fills the vaults.

	Water volume in vault (m^3)	Consumed H_2 by SO_4 in infilled water (mol H_2)	Consumed H_2 by Fe_2O_3 in infilled water (mol H_2)
Silo	9,900	8,415	82
1BMA	4,320	3,672	36
2BTF	23,700	20,145	196

12 Degradation of methane by oxygen and by other oxidants

The presence of hydrogen will make the environment very reducing. The hydrogen may reduce not only carbon dioxide as discussed in the preceding sections but also sulphate, nitrate and ferric iron, provided suitable catalysts are present. See reactions #9 to #12. This would use up the amount of hydrogen that could form methane. It is expected (Höglund 2001) that the amount of these substances is small in the repository. This is therefore not further pursued.

The gas with its hydrogen and methane that escapes the repository vaults and migrates upward to the biosphere may come in contact with sulphate, nitrate and ferric iron underway. The migration path up through the rock is short and fast and it is assumed that negligible degradation of methane takes place during the transit.

In the simulations presented the time when the microbial catalysis started is not specifically stated. If it starts early and is rapid, meaning within some hundred years the escaping gas will end up in the Baltic above the SFR at early times after closure, bubble up to the surface and escape into the air. Some of it may, however, be retained in the bottom sediments. If it starts later when the sea has receded the gas may come up in soils and sediment that are biologically active and the methane may be oxidised to carbonate and enter the bio-chain. This is outside the scope of this report.

The gas that reaches the seawater, covering SFR at early times after closure will either dissolve or reach the atmosphere and mix with it and disperse. On its way to the seawater it must, in some places at least, pass the bottom sediments. These may contain nitrate, sulphate and ferric iron if these substances have not yet reacted with other organic compounds in the sediments. Similarly the gas that reaches regions with soil after land rise will have the possibility to react and oxidise the methane with its ^{14}C to inorganic carbonate. It is outside the scope of this report analyse these processes. However, it cannot be ruled out that the short residence time of the methane in the aerobic region(s) will not allow it to be oxidised to carbon dioxide and permit it to enter the soil and water in the biosphere but to escape as gas to the upper atmosphere. The methane that escapes in this way will not contribute seriously the dose consequences.

13 Colloids with radioactive nuclides carried by gas

It is known that colloidal particles can attach to small gas bubbles and be carried by them upward in the water (Wan and Wilson 1994a, b). If the colloids have radioactive nuclides incorporated or attached to them these would rapidly be carried up to the biosphere.

The concentration of natural colloids in groundwaters is very low (Hallbeck and Pedersen 2008). For the colloids to carry radionuclides these would have to come from the interior of the repositories. It is very unlikely that solid particles will form colloids in the repositories or from the clay surrounding the Silo because of the high concentration of calcium. This will effectively cause any colloidal particles to become unstable and coagulate (Liu and Neretnieks 2010).

Furthermore, for any carrying capacity to develop the gas must form very small bubbles that together make up a large surface on which to attach the colloids. Such small bubbles are not likely to form initially in the repositories (Neretnieks and Ernstsson 1997). The bubbles that form are larger than the typical fracture apertures and the buoyancy forces of individual bubbles are not likely to be large enough to deform the bubbles against the surface tension to allow them to migrate by themselves through the fractures. To escape the bubbles must coalesce and form a much larger gas volume. The larger gas volume must then build up sufficient pressure to force itself through the fractures as a continuous gas stream. The originally large surface area of the bubbles decreases enormously and any attached colloids are detached and are not carried by the gas anymore.

14 Discussion and conclusions

If microbial activity develops that results in rapid catalysis of hydrogen reaction with inorganic and organic ^{14}C and ^{12}C compounds to methane considerable amounts of gas could form and carry radioactive ^{14}C with it by gas flow from the SFR1 repository to the biosphere. In this report it was *stipulated* as a “what if” case that microbial catalysis develops and is rapid.

The expected evolution of hydrogen by iron and aluminium corrosion will generate very favourable conditions for methane formation based on thermodynamic considerations. Gas with methane and hydrogen can readily attain sufficient pressure to form bubbles in SFR1 at the hydraulic pressure existing in a water-saturated repository. A situation where a large fraction of the carbon in the repository becomes methane at high enough pressure to escape can develop. The total amount of gas generated is essentially proportional to the amount of hydrogen that can be generated by corrosion of iron and aluminium.

We have assumed that ^{14}C components react with H_2 with the same rate as other carbon components. Accordingly there will be the same fraction ^{14}C in the reaction product, which is mostly methane. If only a fraction of the hydrogen reacts the escape of ^{14}C will be proportionally smaller.

The ^{14}C-methane is carried by ^{12}C-methane. The largest amount of ^{12}C is found in carbonate in the concrete. However, most of it is not available because of the slow out diffusion from the concrete structures. Degrading cellulose is therefore the largest readily available source of reactive carbon. The carbonate in the water that fills the repository vaults gives little addition of carbonate. There is much less carbonate in the porous concrete than in the cellulose. Inflow of carbonate with the water that constantly seeps through the repository vaults is negligible. The outflow of dissolved CH_4 with the water is also negligible in comparison with the gas flow.

Some hydrogen can be oxidised by sulphate and ferric iron, so decreasing the amount that can be used to generate methane. Such substances are present in porous cement, concrete and in the water that fills the vaults. The available amounts of these substances can only consume a minor fraction of the hydrogen.

If the resins or other waste forms contain ab- or adsorbed volatile compounds already and these can be assumed to be desorbed rapidly, they can be purged from the water by the hydrogen gas. The purging is a fairly rapid process and a considerable fraction of these volatile components could be expelled in tens of years. However, we have found no information of the existence or location of such volatile compounds and cannot estimate the rate of their release to the water.

The by far largest uncertainty is that of the microbial catalysis. The chemical conditions in the repositories are not favourable for microorganisms. If microbial catalysis develops the rate of reaction under the conditions in the repositories is also difficult to predict over the long times of interest.

Assuming that microbial catalysis is fast the potential impact of some other possibly limiting processes and uncertainties were also explored. It was found that although the cement and concrete compositions can vary as to how much hydroxyl can be released and how much carbonate is bound in the cement and concrete, the uncertainty in hydroxyl content does not impact the expulsion of the ^{14}C from the waste, nor does the uncertainty in carbonate in the cement much influence the capacity to dilute the ^{14}C in the escaping gas.

One uncertainty worth investigating is that concerning how much the anion and cation resins have been utilised and how much non-radioactive organic anions are present in the resins. In an extreme case this might decrease the release rate from the Silo by a factor of 20.

In short: With the data and assumption used, our calculations show that if microbial catalysis cannot be ruled out a large fraction, 10% , or more of the radioactive carbon in the waste could escape to the biosphere within a few hundred or possibly a few thousand years if SKB’s new gas generation data are used. If microbial catalysis could be ruled out negligible release of radioactive carbon would escape.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

Almkvist L, Gordon A, 2007. Low and intermediate level waste in SFR 1. Reference waste inventory 2007. SKB R-07-17, Svensk Kärnbränslehantering AB.

Al-Sheikh A A, 2006. Thermodynamic study on the formation, decomposition and oxidation of methane in the soil atmosphere. Saudi Journal of Biological Sciences 13, 115–122.

Berner U R, 1992. Evolution of pore water chemistry during degradation of cement in a radioactive waste repository environment. Waste Management 12, 201–219.

Bird R B, Stewart W W, Lightfoot E N, 2007. Transport phenomena. Rev. 2nd ed. New York: Wiley.

Brazelton W J, Morrill P L, Szponar N, Schrenk M O, 2013. Bacterial communities associated with subsurface geochemical processes in continental serpentinite springs. Applied and Environmental Microbiology 79, 3906–3916.

Carslaw H S, Jaeger J C, 1959. Conduction of heat in solids. 2nd ed. Oxford: Clarendon.

Eschrich H, 1980. Properties and long-term behaviour of bitumen and radioactive waste–bitumen mixtures. SKBF/KBS TR 80-14, Svensk Kärnbränsleförsörjning AB.

Fogler H S, 2006. Elements of chemical reaction engineering. 4th ed. Upper Saddle River, NJ: Prentice Hall.

Gaucher E, Tournassat C, Nowak C, 2005. Modelling the geochemical evolution of the multi-barrier system of the Silo of the SFR repository. Final report. SKB R-05-80, Svensk Kärnbränslehantering AB.

Hallbeck L, Pedersen K, 2008. Explorative analysis of microbes, colloids and gases. SDM-Site Forsmark. SKB R-08-85, Svensk Kärnbränslehantering AB.

Helfferich F G, 1995. Ion exchange. New York: Dover.

Höglund L O, 2001. Project SAFE. Modelling of long-term concrete degradation processes in the Swedish SFR repository. SKB R-01-08, Svensk Kärnbränslehantering AB.

Kucukpinar E, Doruker P, 2003. Molecular simulations of small gas diffusion and solubility in copolymers of styrene. Polymer 44, 3607–3620.

Lindgren M, Pettersson M, Karlsson S, Moreno L, 2001. Project SAFE. Radionuclide release and dose from the SFR repository. SKB R-01-18, Svensk Kärnbränslehantering AB.

Liu L, Neretnieks I, 2010. Interaction between colloidal particles. Literature review. SKB TR-10-26, Svensk Kärnbränslehantering AB.

Moreno L, Skagius K, Södergren S, Wiborgh M, 2001. Project SAFE. Gas related processes in SFR. SKB R-01-11, Svensk Kärnbränslehantering AB.

Neretnieks I, Ernstsson M-L, 1997. A note on radionuclide transport by gas bubbles. In Gray W J, Triay I R (eds). Scientific basis for nuclear waste management XX: symposium held in Boston, Massachusetts, USA, 2–6 December 1996. Pittsburgh, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 465), 855–862.

Parkhurst D L, Appelo C A J, 1999. User's guide to PHREEQC (version 2): a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, Colorado.

Pedersen K, 2000. Microbial processes in radioactive waste disposal. SKB TR-00-04, Svensk Kärnbränslehantering AB.

Pedersen K, 2001. Project SAFE. Microbial features, events and processes in the Swedish final repository for low- and intermediate-level radioactive waste. SKB R-01-05, Svensk Kärnbränslehantering AB.

Pedersen K, Nilsson E, Arlinger J, Hallbeck L, O'Neill A, 2004. Distribution, diversity and activity of microorganisms in the hyper-alkaline spring waters of Maqarin in Jordan. Extremophiles 8, 151–164.

Perkins R B, Palmer C, 1999. Solubility of ettringite (Ca6[Al(OH)6]2(SO4)3 · 26H2O) at 5–75°C. Geochimica et Cosmochimica Acta 63, 1969–1980.

Riggare P, Johansson C, 2001. Project SAFE. Low and intermediate level waste in SFR-1. Reference Waste Inventory. SKB R-01-03, Svensk Kärnbränslehantering AB.

Sander R, 1999. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry. Mainz, Germany: Max-Planck Institute of Chemistry.

Schrenk M O, Brazelton W J, Lang S Q, 2013. Serpentinization, carbon, and deep life. Reviews in Mineralogy and Geochemistry 75, 575–606.

SKB, 2008. Safety analysis SFR 1. Long-term safety. SKB R-08-130, Svensk Kärnbränslehantering AB.

SKB, 2014. Data Report for the Safety Assessment SR-PSU. SKB TR-14-10. Svensk Kärnbränslehantering AB.

Sleep N H, Meibom A, Fridrikson T, Coleman R G, Bird D K, 2004. H_2-rich fluids from serpentinization: geochemical and biotic implications. Proceedings of the National Academy of Sciences 101, 12818–12823.

Stumm W, Morgan J J, 1996. Aquatic chemistry: chemical equilibria and rates in natural waters. 3rd ed. New York: Wiley.

Thomson G, Miller A, Smith G, Jackson D, 2008. Radionuclide release calculations for SAR-08. SKB R-08-14, Svensk Kärnbränslehantering AB.

Upreti S R, Mehrotra A K, 2002. Diffusivity of CO_2, CH_4, C_2H_6 and N_2 in Athabasca bitumen. The Canadian Journal of Chemical Engineering 80, 116–125.

Wan J, Wilson J L, 1994a. Colloid transport in unsaturated porous media. Water Resources Research 30, 857–864.

Wan J, Wilson J L, 1994b. Visualization of the role of gas–water interface on the fate and transport of colloids in porous media. Water Resources Research 30, 11–23.

Weast R C, Astle M J (eds), 1980. CRC Handbook of chemistry and physics: a ready-reference book of chemical and physical data. 61st ed. Cleveland, OH: CRC Press.

Yu W, Tang Y, Mo L, Chen P, Lou H, Zheng X, 2011. One-step hydrogenation–esterification of furfural and acetic acid over bifunctional Pd catalysts for bio-oil upgrading. Bioresource Technology 102, 8241–8246.

Appendix 1

Waste types and 14C contents

Appendix 1 lists the different types of waste containers/types in the Silo, 1BMA and 2BTF. The information is taken from SKB R-07-17. The number of waste packages in the vaults, the mass of ion exchange resin in each package, mass of cement, steel, concrete and bitumen in each container as well as total volume and void volume, mass of cellulose and 14C activity is show. In addition the derived quantities cement to resin ratio, amount of hydroxyl in cement and concrete and the amount of iron are listed.

Data from R-07-17.

Silo

Type	**# of this type for full repository**	**Resins (kg)**	**Cement (kg)**	**Steel (kg)**	**Concrete (kg)**	**Bitumen (kg)**	**Volume (m^3waste)**	**Void (m^3)**	**Cellulose+ Organic (kg)**	**14C (Bq/type)**	**14C (Bq total)**		**Resins (total kg)**	**Cement to resin ratio**	**mol OH in cement**	**mol OH in concrete**	**Sum**	**mol Fe**	**mol AnMinus in resin**
B.04	1,000	33	302	40			0.19	0.02		$2.0\cdot10^{7}$	$2.0\cdot10^{10}$		33,000	9.2	$3.15\cdot10^{4}$	$1.62\cdot10^{4}$	$4.77\cdot10^{4}$	$5.41\cdot10^{5}$	$7.43\cdot10^{4}$
B.06	1,840	50		40		150	0.2	0.03		$5.8\cdot10^{7}$	$1.07\cdot10^{11}$		92,000		0	$2.98\cdot10^{4}$	$2.98\cdot10^{4}$	$9.95\cdot10^{5}$	$2.07\cdot10^{5}$
F.18	1,132	600		400		960	1.53	0.17		$2.3\cdot10^{9}$	$2.6\cdot10^{12}$		679,200		0	$1.84\cdot10^{5}$	$1.84\cdot10^{5}$	$6.12\cdot10^{6}$	$1.53\cdot10^{6}$
O.02	2,623	130	1,100	290	1,340		0.85	0.15		$3.2\cdot10^{8}$	$8.39\cdot10^{11}$		340,990	8.5	$3.01\cdot10^{5}$	$3.08\cdot10^{5}$	$6.09\cdot10^{5}$	$1.03\cdot10^{7}$	$7.67\cdot10^{5}$
C.02	1,636	130	1,100	290	1,340		0.85	0.15		$2.5\cdot10^{8}$	$4.09\cdot10^{11}$		212,680	8.5	$1.87\cdot10^{5}$	$1.92\cdot10^{5}$	$3.80\cdot10^{5}$	$6.41\cdot10^{6}$	$4.79\cdot10^{5}$
C.24	222				2,000		0.99	0.01	35	$1.5\cdot10^{8}$	$3.33\cdot10^{10}$	scrap metal	0		0	0	0	0	0
R.02	371	130	1,000	290	1,340		0.85	0.15		$1.5\cdot10^{8}$	$5.57\cdot10^{10}$		48,230	7.7	$3.86\cdot10^{4}$	$4.36\cdot10^{4}$	$8.23\cdot10^{4}$	$1.45\cdot10^{6}$	$1.09\cdot10^{5}$
R.16	3,928	250	1,500	425			1.615	0.085		$5.8\cdot10^{8}$	$2.28\cdot10^{12}$		982,000	6.0	$6.14\cdot10^{5}$	$6.77\cdot10^{5}$	$1.29\cdot10^{6}$	$2.26\cdot10^{7}$	$2.21\cdot10^{6}$
S.04	249	65	170	77			0.2	0.01		$1.6\cdot10^{5}$	$3.98\cdot10^{7}$		16,185	2.6	$4.41\cdot10^{3}$	$7.77\cdot10^{3}$	$1.22\cdot10^{4}$	$2.59\cdot10^{5}$	$3.64\cdot10^{4}$
S.11	60	667	1,300	425			1.615	0.085	3	$9.1\cdot10^{5}$	$5.46\cdot10^{7}$	sludge + cell	40,020	1.9	$8.13\cdot10^{3}$	$1.03\cdot10^{4}$	$1.85\cdot10^{4}$	$3.45\cdot10^{5}$	$9\cdot10^{4}$
S24	155		404	275	1,340		0.95	0.05				smoke detectors	0		$6.52\cdot10^{3}$	$1.73\cdot10^{4}$	$2.38\cdot10^{4}$	$5.76\cdot10^{5}$	0
								Total in Silo	$7,95\cdot10^{3}$		$6.35\cdot10^{12}$		$2,44\cdot10^{6}$						
Sum										In resins with cement	**$3.64\cdot10^{12}$**	cf Table 6.2c	$1.36\cdot10^{6}$		**$1.19\cdot10^{6}$**	**$1.27\cdot10^{6}$**	**$2.46\cdot10^{6}$**	**$4.24\cdot10^{7}$**	**$3.76\cdot10^{6}$**

Data from R-07-17 continued.

1BMA

Type	# of this type for full repository	Resins (kg)	Cement (kg)	Steel (kg)	Concrete (kg)	Bitumen (kg)	Volume (m^3 waste)	Void (m^3)	Cellulose+ Organic (kg)	14C Bq/ type	14C Bq total		Resins (total kg)		mol OH in cement	mol OH in concrete	Sum	mol Fe	mol AnMinus in resin
B.05	4,188	50		50		150	0.2	0.03		$2.9\cdot10^{7}$	$1.21\cdot10^{11}$		209,400		0^{0}	$8.49\cdot10^{4}$	$8.49\cdot10^{4}$	$2.83\cdot10^{6}$	74,250
F.05	1,712	130		32		95	0.195	0.02		$1.7\cdot10^{7}$	$2.91\cdot10^{10}$		222,560		0	$2.22\cdot10^{4}$	$2.22\cdot10^{4}$	$7.40\cdot10^{5}$	207,000
F.15	11	375	575	425			1.53	0.17		$1.0\cdot10^{7}$	$1.1\cdot10^{8}$		4,125	1.5	$6.59\cdot10^{2}$	$1.90\cdot10^{3}$	$2.55\cdot10^{3}$	$6.32\cdot10^{4}$	1,528,200
F.17	1,343	650		400		820	1.615	0.085		$2.0\cdot10^{8}$	$2.69\cdot10^{11}$		872,950		0	$2.18\cdot10^{5}$	$2.18\cdot10^{5}$	$7.26\cdot10^{6}$	767,227.5
F.23	399			462	1,356		1.615	0.085	600	$4.5\cdot10^{7}$	$1.8\cdot10^{10}$	Various organics, variants	0		0	$7.47\cdot10^{4}$	$7.47\cdot10^{4}$	$2.49\cdot10^{6}$	478,530
O.01	675	130	1,100	290	1,340		0.85	0.15		$2.8\cdot10^{8}$	$1.89\cdot10^{11}$		87,750	8.5	$7.73\cdot10^{4}$	$7.94\cdot10^{4}$	$1.57\cdot10^{5}$	$2.65\cdot10^{6}$	0
C.01	68	130	1,100	290	1,340		0.85	0.15		$1.8\cdot10^{8}$	$1.22\cdot10^{10}$		8,840	8.5	$7.79\cdot10^{3}$	$7.99\cdot10^{3}$	$1.58\cdot10^{4}$	$2.66\cdot10^{5}$	108,517.5
O.23	579			274	1,340		0.95	0.05	97	$3.3\cdot10^{7}$	$1.91\cdot10^{10}$	sludges. cellulos	0		0	$6.43\cdot10^{4}$	$6.43\cdot10^{4}$	$2.14\cdot10^{6}$	2,209,500
C.23	167			274	1,340		0.95	0.05	97	$3.5\cdot10^{7}$	$5.85\cdot10^{9}$	sludges. cellulos	0		0	$1.86\cdot10^{4}$	$1.86\cdot10^{4}$	$6.18\cdot10^{5}$	36,416.25
R.01	1,686	130	1,000	274	1,340		0.85	0.15		$3.0\cdot10^{8}$	$5.06\cdot10^{11}$		219,180	7.7	$1.76\cdot10^{5}$	$1.87\cdot10^{5}$	$3.63\cdot10^{5}$	$6.24\cdot10^{6}$	90,045
R.10	129		800	274	1,340		0.9	0.1		$9.2\cdot10^{7}$	$1.19\cdot10^{10}$	sludge	0		$1.08\cdot10^{4}$	$1.43\cdot10^{4}$	$2.51\cdot10^{4}$	$4.78\cdot10^{5}$	0
R.15	154	250	1,500	425			1.615	0.085		$2.6\cdot10^{8}$	$4\cdot10^{10}$		38,500	6.0	$2.41\cdot10^{4}$	$2.65\cdot10^{4}$	$5.06\cdot10^{4}$	$8.84\cdot10^{5}$	0
R.23	564			274	1,340				144	$4.9\cdot10^{7}$	$2.76\cdot10^{10}$	celulose + organics + scrap	0		0	$6.26\cdot10^{4}$	$6.26\cdot10^{4}$	$2.09\cdot10^{6}$	3,764,486.25
R.29	698		1,600	160	1,600		1.53	0.17		$6.6\cdot10^{5}$	$4.61\cdot10^{8}$	Evaporator conc.	0		$1.16\cdot10^{5}$	$4.53\cdot10^{4}$	$1.62\cdot10^{5}$	$1.51\cdot10^{6}$	0
S.09	905		280	77						$1.8\cdot10^{5}$	$1.63\cdot10^{8}$	sludge	0		$2.64\cdot10^{4}$	$2.83\cdot10^{4}$	$5.46\cdot10^{4}$	$9.42\cdot10^{5}$	0
S.23	353			113	1,340		0.95	0.05	29	$1.7\cdot10^{7}$	$6\cdot10^{9}$	Sludge, Cellulose	0		0	$1.62\cdot10^{4}$	$1.62\cdot10^{4}$	$5.39\cdot10^{5}$	0
								Total in 1BMA	$4.03\cdot10^{5}$	$1.55\cdot10^{9}$	$1.26\cdot10^{12}$		$1{,}66\cdot10^{6}$						
Sum										In resins with cement	$\mathbf{8.36\cdot10^{11}}$				$\mathbf{4.39\cdot10^{5}}$	$\mathbf{9.52\cdot10^{5}}$	$\mathbf{1.39\cdot10^{6}}$	$\mathbf{3.17\cdot10^{7}}$	$\mathbf{9.26\cdot10^{6}}$

Data from R-07-17 continued.

2BTF

Type	# of this type for full repository	Resins (kg)	Cement (kg)	Steel (kg)	Concrete (kg)	Bitumen (kg)	Volume (m^3 waste)	Void (m^3)	Cellulose+ Organic (kg)	14C Bq/ type	14C Bq total	Resins (total kg)	mol OH in cement	mol OH in concrete	Sum	mol Fe	mol AnMinus in resin
B.07	194	1,466		647			2.2	3.8		$9.8 \cdot 10^7$	$1.9 \cdot 10^{10}$		0	$5.09 \cdot 10^4$	$5.09 \cdot 10^4$	$1.70 \cdot 10^6$	$6.4 \cdot 10^5$
S.13	390									$4.0 \cdot 10^4$	$1.56 \cdot 10^7$	Ashes	0	0	0	0	0
F.99:2	18									$2.0 \cdot 10^5$	$3.6 \cdot 10^6$	steel	0	0	0	0	0
O.99	20	130		1,221					8.3	$1.6 \cdot 10^7$	$3.2 \cdot 10^8$		0	$9.90 \cdot 10^3$	$9.90 \cdot 10^3$	$3.30 \cdot 10^5$	$5.85 \cdot 10^3$
Sum									166	In resins with cement	**$1.94 \cdot 10^{10}$**		**0**	**$6.08 \cdot 10^4$**	**$6.08 \cdot 10^4$**	**$2.03 \cdot 10^6$**	**$6.46 \cdot 10^5$**

Appendix 2

Corrosion and gas generation rates

	Water vol (Tot m^3)	Water vol that can flow	Amount concrere (kg)	Fraction $CaCO_3$	$CaCO_3$ (kg)	$CaCO_3$ (mol)	HCO_3 (mol)	CH_2O (kg)	CH_2O (mol)	Available C (mol)	Available C (mol/water)	Radioactivity (Bq C-14 total)	Radioactivity (Bq C-14 organic)	Bq in resins in cement
Silo	4,678	1,334	$2.16\cdot10^{7}$	0.0018	$3.89\cdot10^{4}$	$3.89\cdot10^{5}$	$2.19\cdot10^{3}$	$7.95\cdot10^{3}$	$2.65\cdot10^{5}$	$2.67\cdot10^{5}$	$5.71\cdot10^{-2}$	$3.20\cdot10^{13}$	$9.60\cdot10^{12}$	$3.64\cdot10^{12}$
1BMA	4,035	3,073	$1.27\cdot10^{7}$	0.0018	$2.29\cdot10^{4}$	$2.29\cdot10^{5}$	$5.04\cdot10^{3}$	$1.47\cdot10^{5}$	$4.90\cdot10^{6}$	$4.91\cdot10^{6}$	1.22	$7.40\cdot10^{12}$	$2.20\cdot10^{12}$	$8.36\cdot10^{11}$
2BTF	23,700	23,700	$3.70\cdot10^{6}$	0.0018	$6.66\cdot10^{3}$	$6.66\cdot10^{4}$	$3.89\cdot10^{4}$	$1.66\cdot10^{2}$	$5.53\cdot10^{3}$	$4.44\cdot10^{4}$	$1.87\cdot10^{-3}$	$1.30\cdot10^{12}$	$3.80\cdot10^{11}$	$1.94\cdot10^{10}$
	R-07-17 Tables 4-2c, 5-2c and 6-2c													

	Fe (kg)	Fe (mol)	Fe/l water (mol/l)	H_2 from Fe (mol/l)	Al (kg)	Al (mol)	Al/water (mol/l)	H_2 from Al (mol/l)		Comment: Fe → magnetite → 1.33 mol H_2/mol Fe
Silo	$3.83\cdot10^{6}$	$6.86\cdot10^{7}$	$1.47\cdot10$	$1.95\cdot10$	$5.99\cdot10^{2}$	$2.22\cdot10^{4}$	$4.74\cdot10^{-3}$	$1.42\cdot10^{-2}$		
1BMA	$2.76\cdot10^{6}$	$4.94\cdot10^{7}$	$1.22\cdot10$	$1.63\cdot10$	$7.26\cdot10^{3}$	$2.69\cdot10^{5}$	$6.66\cdot10^{-2}$	$2.00\cdot10^{-1}$		
2BTF	$6.34\cdot10^{5}$	$1.14\cdot10^{7}$	$4.79\cdot10^{-1}$	$6.37\cdot10^{-1}$	$2.54\cdot10^{3}$	$9.41\cdot10^{4}$	$3.97\cdot10^{-3}$	$1.19\cdot10^{-2}$		
	R-07-17 Tables 4-2c, 5-2c and 6-2c									

	Fe area (m^2)	Corr rate (m/yr)	mol (Fe/yr)	mol (H_2/yr)	Nm^3 (H_2/yr)	mol/l (H_2/l/yr)	time (yr for H_2)		Al area (m^2)	Corr rate (m/yr)	mol (Al/yr)	mol (H_2/yr)	mol/l (H_2/l/yr)	Nm^3 (H_2/yr)	time (yr for H_2)
Silo	$1.66\cdot10^{5}$	10^{-7}	$2.34\cdot10^{3}$	$3.11\cdot10^{3}$	$6.97\cdot10$	$6.65\cdot10^{-4}$	$2.2\cdot10^{4}$		$1.13\cdot10^{2}$	10^{-3}	$1.13\cdot10^{4}$	$3.39\cdot10^{4}$	$7.25\cdot10^{-3}$	$7.59\cdot10^{2}$	1.96
1BMA	$1.26\cdot10^{5}$	10^{-7}	$1.78\cdot10^{3}$	$2.36\cdot10^{3}$	$5.29\cdot10$	$5.85\cdot10^{-4}$	$2.09\cdot10^{4}$		$1.05\cdot10^{3}$	10^{-3}	$1.05\cdot10^{5}$	$3.15\cdot10^{5}$	$7.81\cdot10^{-2}$	$7.06\cdot10^{3}$	2.56
2BTF	$3.69\cdot10^{4}$	10^{-7}	$5.2\cdot10^{2}$	$6.92\cdot10^{2}$	$1.55\cdot10$	$2.92\cdot10^{-5}$	$1.64\cdot10^{4}$		$1.40\cdot10^{3}$	10^{-3}	$1.40\cdot10^{5}$	$4.20\cdot10^{5}$	$1.77\cdot10^{-2}$	$9.41\cdot10^{3}$	$6.72\cdot10^{-1}$
	R-07-17 Tables 4-2c, 5-2c and 6-2c								**R-07-17**	**Tables 4-2c, 5-2c and 6-2c**					

	Time to exhaust available Carbon	Release of 14C by gas			Time for gas	Basic data					
		All 14C avalable	**All organic 14C**	**Only 14C in resins in cement**							
	Assume 2 H_2 per C as main source is CH_2O (Years)	**(Bq/yr)**		**(Bq/yr)**	**Bubble to form (Years)**	**Navogadro** **T1/2 14C**	**$6.02\cdot10^{23}$** **5.730**	**Ro Fe = $7.87\cdot10^{6}$** **Ro Al = $2.7\cdot10^{6}$**		**M iron** **M Al**	**55.85** **27**
Silo	173	$1.85\cdot10^{11}$	$5.54\cdot10^{10}$	$2.1\cdot10^{10}$	36	Lambda s-1	$3.84\cdot10^{-12}$			M $CaCO_3$	100
1BMA	4,188	$1.77\cdot10^{9}$	$5.25\cdot10^{8}$	$2\cdot10^{8}$	41			Kh H_2	$8.80\cdot10^{-4}$	M HCO_3	61
2BTF	129	10^{10}	$2.94\cdot10^{9}$	$1.5\cdot10^{8}$	829	HCO_3 in W		Kh CH_4	$2\cdot10^{-3}$	M CH_2O	30
						0.1 g/l	0.1				
						R-01-08					

Factor H_2 per C = 2.02.
Weighting factor accounting for that CO_2 uses $4H_2$ and CH_2O uses $2H_2$ to form CH_4.

Appendix 2 lists the information used to calculate the rate of hydrogen production, amounts of carbon in calcite, water and cellulose, total ^{14}C activity, activity in organics and resins in cement. Amounts of iron and aluminium used to calculate hydrogen generation rates are given. Other derived quantities including release rates of ^{14}C activity from the three vault types are listed for the cases if all activity can be converted to methane, only the organic or only that from cement condition containers can be released. Data are taken from SKB R-07-17. The columns and rows in the table are identified as in an excel sheet for reference. Below are comments on some cells. Other cells are deemed to be self-explanatory.

C5:C7	All water in the vault
D5:D7	Water that enters the vault at closure
I5:I7	Mobile water in vault
K5:K7	Amount of HCO_3^{2-} carried in by invading water
L5:L7	Amount of cellulose in vault
M5:M7	Amount of carbon available to form methane
O5:O7	Amount of ^{14}C in organic compounds
P5:P7	Amount of ^{14}C in cement embedded resins
I18:I20	Time for all iron react at constant rate
Q18:Q20	Time for all aluminium to react at constant rate
C26:C28	Time for all carbon to form methane
EFG26:EFG28	Release rate of activity
H26:H28	Time before gas bubbles form

The cement in the concrete contains considerable amounts of carbonate, 0.9% of cement by mass, R-01-08. The fraction of cement in concrete is about 20%.

Appendix 3

Ion exchange capacity and hydroxyl amounts

Appendix 3 compiles data used to calculate amounts of hydroxyl available to expel anions from the anion exchangers. Also the sink for consuming hydroxyl in the cellulose degradation reaction to potentially lower the pH is calculated. Data are taken from R-07-17, R-01-08 and R-01-11.

	Water vol (Tot m^3)	**Amount concrere (kg)**	**Fraction ($CaCO_3$)**	**$CaCO_3$ (kg)**	**$CaCO_3$ (mol)**	**Mass of Na and KOH (kg)**	**Mean (mol OH)**	**pH if all dissolves**	**Mass of $Ca(OH)_2$ (kg)**	**OH (mol)**
Silo	**4,678**	**$2.16\cdot10^{7}$**	**0.0018**	$3.89\cdot10^{4}$	$3.89\cdot10^{5}$	$1.08\cdot10^{5}$	$2.25\cdot10^{6}$	13.7	$6.48\cdot10^{5}$	$1.75\cdot10^{7}$
1BMA	**4,035**	**$1.27\cdot10^{7}$**	**0.0018**	$2.29\cdot10^{4}$	$2.29\cdot10^{5}$	$6.35\cdot10^{4}$	$1.32\cdot10^{6}$	13.5	$3.81\cdot10^{5}$	$1.03\cdot10^{7}$
2BTF	**23,700**	**$3.7\cdot10^{6}$**	**0.0018**	$6.66\cdot10^{3}$	$6.66\cdot10^{4}$	$1.85\cdot10^{4}$	$3.85\cdot10^{5}$	12.2	$1.11\cdot10^{5}$	$3\cdot10^{6}$
	R-07-17	**R-07-17**	**R-01-08**							
			9% of cement cement 20% of concrete				0.5% of concrete			3% of concrerte

	Amount tot ion X-Chang. (kg)	**Amount An-ion X-Chang. as mol OH**	**Amount Cellulose (mol CH_2O)**	**Amount C in Porous concr (mol)**	**Amount H^+ To react w OH (mol)**	**Sum OH consuming (mol)**	**Sum of OH (mol)**	**Surplus OH times**
Silo	**$2.45\cdot10^{6}$**	$5.51\cdot10^{6}$	$2.65\cdot10^{5}$	$1.83\cdot10^{5}$	$5.3\cdot10^{5}$	$6.04\cdot10^{6}$	$1.98\cdot10^{7}$	3.3
1BMA	**$1.65\cdot10^{6}$**	$3.71\cdot10^{6}$	$4.9\cdot10^{6}$	$6.12\cdot10^{4}$	$9.8\cdot10^{6}$	$1.35\cdot10^{7}$	$1.16\cdot10^{7}$	0.9
2BTF	**$8.06\cdot10^{5}$**	$1.81\cdot10^{6}$	$5.53\cdot10^{3}$	$6.8\cdot10^{4}$	$1.11\cdot10^{4}$	$1.82\cdot10^{6}$	$3.39\cdot10^{6}$	1.9
	R-07-17	4.5 eq/kg		**R-01-11 and**				
	half of all is anion resin	Helfferich Half an-ionX		**R-01-08**				

Appendix 4

A note on observations of microbial activity in hyper-alkaline media

Neretnieks 2013-06-23

A central assumption in the present report is that microorganisms are present and active in the porewaters in the cement/concrete constructions in the SFR repository. The pH is very high because the concrete contains sodium-, potassium-, and calcium- hydroxide. As discussed earlier the first two can generate pH up to about 14 initially and the much more abundant $Ca(OH)_2$ can maintain pH at around 12.5 for a long time. So high pH is not a very friendly environment to microorganisms but it is not necessarily assured that they cannot live and catalyse reactions that otherwise would be extremely slow.

The key question is whether significant microbial activity and microbial growth can occur in hyper-alkaline water under ambient conditions.

A natural analogue to conditions in cementitious repositories has been extensively studied in the Maqarin Natural Analogue Project. In some springs in Jordan the pH is 12.5 and above due to the presence of $Ca(OH)_2$. The activity and growth of microorganisms in the waters were studied (Pedersen et al. 2004). A short summary of this work and findings are given below.

Waters from several springs and in boreholes in the area were collected. The chemical composition and the number of unattached microorganisms in water from seven different locations were determined. The attachment of microorganisms to sterile surfaces was also studied and their surface density determined. The diversity of the microbes was explored using 16S ribosomal deoxyribonucleic acid (rDNA) gene sequencing and comparison. Numerous combinations of culture media compositions were inoculated with spring seepage and groundwater and incubated. The in situ activities of unattached and attached microorganisms were studied using various radiolabelled carbon sources. Experiments were performed both under aerobic and anaerobic conditions. In the experiments under anaerobic conditions the electron acceptors used were FeOOH, MnO_2 and SO_4^{2-}. Carbon sources used were glucose, lactate, acetate, formate, and R2A agar culture medium. In many of these media activity and/or growth of microorganisms starting at pH 12.5 and higher was found and measured.

In several experiments under aerobic as well as under anaerobic conditions it was found that microorganisms multiplied. The cell population density grew to above 10^6 cells/ml in several anaerobic experiments with a maximum of $2.9 \cdot 10^6$. The number of generations was up to 10.5 in some experiments. In the anaerobic experiments, of most interest here, the starting pH was 12.5 to 12.7 but dropped by one to two units during the 150 to 300 day duration. Any of the four carbon sources could be used by the microorganisms but glucose was preferred. In the anaerobic experiments with any of the three electron acceptors gave similar results. The highest activity was found with glucose where one experiment gave a reaction rate of $18.6 \cdot 10^{-18}$ mol carbon/cell/h. In other experiments acetate gave $6.7 \cdot 10^{-18}$ and lactate $4.6 \cdot 10^{-18}$ mol/cell/h. These waters were sampled in November 1999. In similar experiments with water sampled in May 2000 much smaller rates were found. It was concluded that microorganisms could be active and grow under hyper-alkaline conditions.

The question explored next is whether such activity would be sufficient for the fast microbial catalysis assumed for the CH_4 production in SFR. The reaction of main interest there is the generation of methane by reaction of organic as well as inorganic compounds with hydrogen to form methane. This was not studied at Maqarin. If, however, it is assumed that there are reactants e.g. the abundant hydrogen in SFR and a carbon source, inorganic or organic, where microorganisms could utilise the released free energy for their growth, microorganisms will somehow adapt or develop to utilise this energy. If we further assume that they can reach the same population density and reaction rate as those in Maqarin an estimate of methane production rate in SFR can be made. The above data were specially chosen as examples of high cell populations and high reaction rates to explore what consequences it might have for the SFR-repository. A simple example is presented below.

Population density	$3 \cdot 10^6$ cells/ml
Reaction rate	$20 \cdot 10^{-18}$ mol carbon/cell/h
Water volume in silo	4,678 m^3

Assuming further that each carbon reacted forms methane and that the hydrogen in the methane is from H_2 the methane production and the hydrogen consumption is 2,460 mol CH_4/yr and 4,920 mol H_2/yr respectively in the silo. The hydrogen production in the silo is 3,110 mol H_2/yr. The production and consumption rates are comparable and it thus cannot be ruled out that microbial catalysis would lead to considerable production of methane by reaction with hydrogen.

Also H_2 and CH_4 are said to have been used as potential reactants but then no microbial activity was detected and there is no further information on this in the paper. This alone cannot be used as an argument for that it may not occur.

However, there are several assumptions that may be challenged and possibly tested experimentally. One is that the reaction rate used in the example above is some average over the pH range from the starting value 12.6–12.7 down to about 11.0 at the end of the experiment where up to 10.5 generations of microorganisms had participated. It may be argued that the reaction rate can have been much slower in the beginning when the pH was very high and increased as the pH dropped. In SFR conditions the pH would remain at about 12.5 for a very long time. Then the reaction could be much slower. The information in the experiments is not sufficient to explore this.

Another assumption is that the microbial population contains some microorganisms that can use hydrogen as the main reactant, alternatively that some existing microorganism could adapt to this. Hydrogen was mentioned to have been used in one experiment but not to have led to any measurable reaction. It cannot be ruled out that the time was too short or that the concentration (pressure) of hydrogen was too low. The hydrogen pressure will be very high, about 5 bar, in the repository and the time will be many orders of magnitude larger than in the experiments. This would favour the development of suitable microorganisms.

It is concluded in Pedersen et al. (2004) that: "As a whole, the assimilation investigations strongly suggest that some or all of the microbes in the studied Maqarin waters were viable and responded to introduced carbon sources by assimilation. The assimilations all occurred under hyper-alkaline conditions, suggesting that microbial activity is possible under these extreme conditions, such as in the Maqarin alkaline waters."

Hydrogen is known to be produced in natural environments by serpentization reactions. Minerals that contain ferrous iron silicates e.g. Fe_2SiO_2 can react with water to form magnetite, quartz and hydrogen. The hydrogen can be released as gas at high pressures. An overview can be found in Sleep et al. (2013). Serpentization reactions and hydrogen release have been observed in many locations including subduction zones, mid-ocean ridges, and ophiolites. Serpentinization can provide the energy and hydrogen to support chemosynthetic microbial communities including methanogens even in hyper-alkaline conditions (pH=12.5) at very large depths (> 3,000 m), Schrenk et al. (2013). In different locations and sampling times gas bubbles have been found to contain mixtures of up to 99% by volume hydrogen and up to 93% methane (0.6 and 0.87 mM dissolved H_2 and CH_4 respectively) from the more than 10 locations where sampling was made and analysis were reported. The variations are large between locations. Microorganisms have been found in the sampled locations.

Brazelton et al. (2013) investigated water samples from Tablelands Ophiolite ultra-basic serpentinite springs located within Gros Morne National Park, Newfoundland, Canada (N49º27'59", W57º57'29"). Five springs in Winter House Canyon, and waters from three other locations were sampled for this study at three time points: June 2010, August 2010, and June 2011. In the springs pH was between 11.5 an 12.63, H_2 between 0.07 and 1.18 mg/l and CH_4 between 0.01 and 0.32 mg/l. Microbial population cell density varied between $0.53 \cdot 10^5$ and $4 \cdot 10^5$ cells/ml. Reaction rates per cell were not reported.

The combination of highest reaction rates and cell densities in Maqarin were high enough to be "very rapid" in the context of methane generation in SFR if they were applicable to methane production from hydrogen reaction with a carbon source. However, the reactions in Maqarin were not those of methane production from hydrogen and the pH was not consistently around 12.5. The largest observed cell population in the Ophiolite ultra-basic serpentinite springs in Canada was about a factor five smaller than in Maqarin but the pH was much nearer the conditions expected in SFR and it was probably hydrogen that was the source of the methane observed.

Although one cannot claim from the above observations that there is definite evidence of rapid microbially catalysed methane production we must conclude that with present knowledge the assumption of sufficiently high microbial activity to "rapidly" convert the hydrogen to methane in SFR is not ruled out and not unreasonable.

The authors of the present report are not sufficiently knowledgeable about the different aspects of microbial reactions and how they can be influenced by different factors to venture to speculate how it could be limited by the conditions in SFR. It would be valuable to engage microbiologist to give expert input in this matter.