

Considerations on the Release of C-14 from a Closed Final Repository for Low-Level
Radioactive Waste

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ABSTRACT

The contribution of C-14 to radiation exposure in the biosphere from a repository for low-level radioactive waste can be significant. The release pathways of C-14 and processes relevant to its release from a closed final repository for low-level radioactive waste are discussed. Because a conservative approach may lead to undue overestimation of the potential radiation exposure, a more realistic approach is outlined. At the present level of refinement, it has sufficient safety margins to federal limits for radiation exposure to demonstrate compliance with the ALARA (as low as reasonably achievable) principle and thus facilitate licence approval.

INTRODUCTION

The proof of long-term safety of a final repository for low-level radioactive waste requires an assessment of the potential radiation exposure from gaseous radionuclides. C-14 is the only radionuclide that can contribute significantly to radiation exposure as all other gaseous radionuclides can be neglected due to their short half-lives, low inventories or low radiological relevance.

There have been a number of conservative approaches for estimating the mobilisation, migration and release of C-14 via gas and groundwater pathways. The results of these approaches generally comply with German federal limits for radiation exposure.

Despite compliance with the limits for radiation exposure, these approaches provide insufficient safety margins to demonstrate compliance with the ALARA (as low as reasonably achievable) principle. Overestimation of the potential radiation exposure may therefore lead to false conclusions and ineffective measures for minimising radiation exposure.

The following paper outlines a concept for the realistic assessment of long-term radiation exposure by C-14. The concept is based on model final repository for low-level radioactive wastes in a salt mine. This concept provides additional safety margins to radiation exposure limits and can thus facilitate licence approval where compliance with the ALARA principle has to be demonstrated.

GENERAL BACKGROUND

Reference Scenario

The selected reference scenario for a model final repository in salt rock includes a hydraulic connection between the mine building, the overlying rock and the biosphere. Driven by rock convergence, gas and brine will squeeze out of the repository and penetrate into the overlying

rock. This process takes place on a geological time scale. There is no (or only a negligible) leakage of gas via the mine shafts. Radionuclides are retained in the near-field by limited dissolution and sorption.

The reference scenario includes features, events and processes such as:

- retarded exchange of fluids between the emplacement chambers due to engineered barriers
- time dependence of geochemistry in the emplacement chambers
- mobilisation of radionuclides
- retardation of radionuclides by sorption and precipitation
- gas generation and accumulation in emplacement chambers
- squeezing-out of fluids due to convergence and gas generation
- transport of radionuclides by density-driven convection of fluids
- ascent of radioactive gas
- movement of radioactive gas into the overlying rock.

The reference scenario also includes site-specific features of the overlying rock, such as:

- preferential fluid transport along fracture zones
- transport retardation and dynamic storage of contaminated fluid
- dilution of the fluid by ground and surface water with lower salt content.

Technical Measures

Host rock and technical measures (engineered barriers) determine the pathways of radionuclides to the biosphere. Potential radiation exposure depends on these factors. Once the repository site and thus the host rock are selected, technical measures are the only means to reduce the potential radiation exposure.

Technical measures included in the reference scenario are:

- barriers for fluid flow
- backfilling of drifts, galleries and shafts with permeable materials (gravel) to manage fluid flow
- backfilling with selected materials (solids, fluids) for control of geochemistry
- backfilling to stabilise rock mechanics
- backfilling to minimise the void volume
- sealing of shafts to preclude leakage of brine and gas
- some additional measures.

Geochemical modelling

The geochemistry (i.e. the concentration in the brine of major and minor salt components and prevailing solids and gases of an emplacement chamber) results from the interaction of the brine

with the waste matrix materials (cement/concrete), the waste packages (concrete, iron), the backfill materials and the degradation products of organic matter of the waste itself. The conversion of organic matter to CO₂ and CH₄, the degradation of cement and the corrosion of metals are time-dependent processes that determine the geochemistry of the brine. With realistic degradation rates of cement and conversion rates of organic matter to CO₂, CO₂ will predominantly precipitate as carbonate. As a result, a significant change of the initial pH dominated by cement and backfill in an emplacement chamber is not expected to occur.

Gas generation

Gas generation in the emplacement chambers is modelled on a discrete time grid. In each time interval the physical and the geochemical boundary conditions are assumed to be constant [2]. However, they may change from one time interval to the next. The waste packages may be leaky due to the emplacement technique and convergence. The following boundary conditions occur at different, consecutive time intervals:

- waste and waste packages have been exposed to air since emplacement (initial condition)
- oxidising conditions favour degradation of organic constituents (transient condition)
- leaky waste packages are exposed to anaerobic, cement-conditioned fluid (prevalent long-term condition)

Hydrogen, methane and carbon dioxide will be generated mainly under the long-term conditions.

INVENTORY OF C-14

The inventories of C-14 and other constituents of the waste are fixed on completion of emplacement. Additional C-14 does not build up (e.g. via decay chains or nuclear reactions) in low-level radioactive waste. The inventory is estimated conservatively to cover all uncertainties. However, the estimate should not be unnecessarily conservative.

The inventory of C-14 and its concentration may vary within several orders of magnitude between different emplacement chambers. Table 1 depicts a typical range of C-14 inventories and concentrations for a model repository in salt rock. The inhomogeneity of the C-14 concentration varies typically by a factor of 10 at most. To take the maximum concentration (as some models do) is too conservative.

Table 1: Inventory and concentration of C-14 in emplacement chambers

Emplacement chamber	C-14 inventory (10 ¹¹ Bq)	C-14 concentration (10 ⁸ Bq/Mg)
lowest	0.02	0.05
typical range	0.5 – 5	1-10
highest	10	35

The waste can be characterised in terms of organic / inorganic / metallic and non-metallic fractions. Some fractions are known from the waste documentation. Others have been estimated. The organic fraction typically accounts for 10-30 % of the waste. As an assignment of the C-14 inventory to each of these fractions is unavailable from the waste documentation, a working assumption had to be made.

It is generally assumed that the C-14 inventory is bound to organic matter. This assumption ignores that C-14 can be bound to solid phases in the form of e.g. carbonates in concrete or carbides in metals.

If C-14 were homogeneously distributed in the waste, a significant amount (70-90 %) would not be contained in organic matter and thus would not contribute to the generation of gaseous methane or carbon dioxide by organic decay. The release of C-14 would thus be significantly reduced or retarded. Hence, the assumption that the C-14 inventory is bound to organic matter rather than homogeneously distributed in the waste is conservative.

In contact with brine, carbides occurring in ashes would generate methane rather instantaneously. This methane would be removed quickly from the mine by ventilation prior to its closure via backfilling with brine and thus would not influence long-term safety. It may, however, represent a safety hazard in the closure phase. Hence, the assumption that the C-14 inventory is bound to organic matter rather than to carbides in ashes is conservative.

C-14 bound in metals would be released by corrosion, mainly in the form of elemental carbon or methane. The release of C-14 to the brine and the gas phase is retarded by the slowness of corrosion relative to organic decay. The total release would be reduced by the radioactive decay of C-14, which is relatively fast in comparison with the corrosion. Hence, the assumption that the C-14 inventory is bound to organic matter rather than in metals is conservative.

The chemical composition of organic C-14 may be different from that of the organic fraction. Nevertheless, organic matter does not completely convert under saline conditions [2]. A large fraction of C-14 will thus remain within the deposited waste and will undergo radioactive decay. This means that the release of C-14 will be significantly reduced compared with the predictions of conservative models that assume a complete conversion. For a quantitative assessment the chemical speciation of C-14 should be known.

BRINE PATHWAY

The transition of C-14 from deposited radioactive waste to the brine depends on its chemical speciation. The important processes are:

- dissolution of surface contamination
- lixiviation (leaching) from metals (this process was studied on zircaloy hulls and activated core parts of LWRs [5])
- conversion, dissolution or desorption of organic compounds
- isotope exchange of C-14 with inactive C

The rate of transition and accumulation of C-14 in the brine may be correlated with the gas generation rate by microbial processes. Only a fraction of the C-14 will transfer to the brine. The remaining C-14 will transfer to the gas phase or remain in the solid phase.

The concentration of C-14 depends primarily on the geochemistry and the composition of the brine. The concentration of inorganic C-14 is lowered by precipitation of carbonates, sorption of CO_3^{2-} on solid backfill [4], and isotope dilution when the C-14-bearing brine is transported out of the emplacement chamber [1].

The conversion of organic matter produces intermediates that may be soluble in brine. These intermediates are probably comparable to substances from standard waste dumps under anaerobic conditions and consist mainly of glucose, amino acids, fatty acids, hydroxycarbonic acids, isosaccharinic acids etc. [3]. The final products are methane and carbon dioxide. The solubility of methane in brine is low. Carbon dioxide is the main soluble component. It equilibrates rapidly with dissolved and precipitated carbonates.

Reliable equilibrium constants are known for alkali and alkaline-earth carbonates, carbonate complexes and mixed solid phases. A nearly complete data set of Pitzer constants is available. This data can be used for the geochemical modelling of brines. The main carbonate compounds that occur in a salt mine are $\text{MgCO}_3(\text{aq})$, $\text{CaCO}_3(\text{aq})$ and $\text{CO}_3^{2-}/\text{HCO}_3^-$. Solid phases such as magnesite, calcite and dolomite limit the concentration of dissolved inorganic carbon.

The typical range of concentrations expected in brine in emplacement chambers, assuming a closed system, is shown in Table 2. The dissolved fraction of inorganic carbon represents only a small amount of the total carbon inventory. The concentration of dissolved carbonates may vary. The major amount of carbonates is fixed in the solid phase.

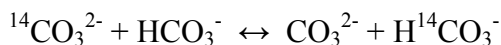
Table 2: Typical range of dissolved concentration of carbon and carbonates in brine in emplacement chambers (Inventory given as concentration)

Speciation	Concentration (10^{-5} mol/(kg H_2O))
C (inventory)	200 000 – 3 000 000
C (total dissolved inorganic C)	0.8 – 40
CO_3^{2-}	0.04 – 1
HCO_3^-	0.000001 – 3

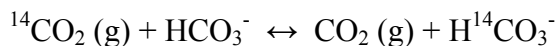
Chemical reactions such as equilibration, precipitation, sorption and gas generation are for practical purposes identical for compounds with or without C-14.

An important process is isotope exchange, which is illustrated by the following:

The isotope exchange of C-14 in carbonates takes place rapidly in brine by hydrogen exchange.



Isotopic equilibrium between the gas phase and the fluid phase is also rapidly achieved.



The isotopic equilibration of solid phase and brine may be slow, as the kinetics of dissolution and precipitation are controlled by accessible surfaces. The isotopic equilibration of other compounds such as hydrocarbons, fatty acids, or alcohols is controlled kinetically and may be slow.

The typical isotope ratio of C-14 to total carbon in the low-level waste in our example equals 10^{-8} - 10^{-9} . To a first approximation, C-14 can be assumed to be homogeneously distributed with a similar isotope ratio in all carbon species in the brine due to isotopic exchange.

When brine passes C-14 free solids, isotopic exchange may retard the transport of C-14. This lowers the C-14 concentration in the brine being transported.

In summary, the following can be said:

- 1) The transfer of C-14 to the brine is not instantaneous.
- 2) The transfer rate of C-14 to the brine is correlated with the degradation rate of organic matter.
- 3) The concentration of C-14 in the brine is determined by isotopic equilibration with carbonates in the solid phase and CO₂ in the gas phase.
- 4) Some C-14 may be bound to other compounds dissolved in brine.
- 5) Due to the composition of the brine and the relative amount of mineral phases, most C-14 will be fixed in the solid phase as carbonates.
- 6) Isotope exchange processes will equilibrate with any C-14 in the brine.
- 7) Sorption, precipitation and isotopic exchange take place when brine is transported. They retard the transport of C-14, and lower the concentration of C-14 in the brine.

GAS PATHWAY

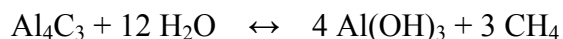
C-14 can be present in all carbon-bearing gaseous compounds. In the order of decreasing amounts, the gas phase is expected to consist of:

- 1) methane, ¹⁴CH₄
- 2) carbon dioxide, ¹⁴CO₂
- 3) hydrocarbons other than methane
- 4) other volatile compounds.

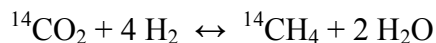
Radioactive waste repositories in mines show a continuous release of C-14 by mine ventilation. Radiation exposure is of limited concern, but the release of C-14 from deposited waste accounts for a fraction of at least 2 % within 30 years of operation in our model repository. According to some previous studies, 75 % to 90 % of the C-14 is ¹⁴CO₂. The remaining fraction is dominated by ¹⁴CH₄. The domination of ¹⁴CO₂ can be explained by microbial degradation under aerobic conditions that prevails during the operational phase.

After the closure of a repository, the release of C-14 to the gas-phase will continue by microbial degradation of organic matter, corrosion of metals containing C-14, and hydrolysis of carbides:

- 1) The hydrolysis of carbides (e.g. Al₄C₃ contained in ashes) will instantly release ¹⁴CH₄:



- 2) The release of C-14 by corrosion is determined by the progress of corrosion
- 3) In the long term, microbial degradation will become the major release mechanism of C-14 to the gas phase. However, according to some previous studies [2], the gas yield from microbial degradation will be limited.
- 4) An additional release of C-14 is possible by methanogenesis:



Hydrogen needed for this process is generated by anaerobic corrosion of metals. Methanogenesis is supported by microbial activity and catalysts. Due to the consumption

of hydrogen, the total amount of gas is reduced by a factor of 4. In the case of significant methanogenesis, this has a profound influence on the transportation of fluids. However, due to its low enthalpy, methanogenesis is not favoured over other reactions (e.g precipitation of CO₂ as carbonate).

Gaseous compounds generated from organic matter need not be released to the gas phase instantaneously. Equilibrium processes of brine, gas phase and solid phase limit the concentration of C-14 compounds, especially ¹⁴CO₂, in the gas phase. Absorbing materials such as active carbon or cement may fix ¹⁴CO₂ and other carbonaceous gases. The capacity for precipitation of carbonates may be increased by backfill. Surface absorption on solid backfill provides an additional mechanism for retention of C-14.

Furthermore, isotopic exchange will lower the C-14 concentration of the gas during transport through uncontaminated parts of the mine and the overlying rock. The release of C-14 from the mine may be additionally limited by oxidation of C-14 compounds to CO₂ with concomitant precipitation as carbonate when transported through sulphate-containing backfill and rock (e.g. gypsum overlying a salt rock formation).

The retardation of gas transport in the mine will leave more time for these processes and the radioactive decay to take place and thus lower the released fraction of C-14 to the biosphere.

The above can be summarised as follows:

The release of C-14 via the gas phase to the biosphere will be limited by following processes:

- 1) The release of C-14 to the gas phase is limited by the rate and the overall extent of degradation of organic substances to gaseous compounds.
- 2) Equilibration with other phases limits the concentration of ¹⁴CO₂ in the gas phase.
- 3) Sorption and precipitation lower the C-14 concentration of the gas phase.
- 4) Isotope exchange dilutes the C-14 concentration during transport.
- 5) A fraction of the C-14 inventory is released to the environment by mine ventilation already before closure.

These processes will significantly lower the release of C-14 to the biosphere via the gas phase.

POTENTIAL RADIATION EXPOSURE

The radiation exposure depends on site-specific scenarios. Nevertheless, the following can be shown to be valid [7]:

- 1) The long-term assessment of a potential radiation exposure by ¹⁴CO₂ yielded an insignificant dose for both pathways (brine and gas). The dose limits are easily met with a large safety margin. Therefore, the exposure by ¹⁴CO₂ need not be further discussed here.
- 2) Provided that ¹⁴CH₄ is released via the gas phase directly to the overlying rock, migrates to the biosphere and is oxidised there, a potential radiation exposure by ingestion may become relevant. The contribution of non-oxidised ¹⁴CH₄ and of ¹⁴CH₄ being oxidised prior to reaching the biosphere and causing potential radiation exposure is insignificant.

Therefore, we recommend a realistic approach for long-term safety assessments. This will demonstrate that a repository in a mine meets dose limits with large safety margins in all cases. This complies best with the ALARA (as low as reasonably achievable) principle. Conservative approaches are unable to demonstrate such compliance.

DISTRIBUTION OF C-14

The distribution of C-14 was obtained by a realistic approach that considers some processes outlined above (Other processes may be considered at a deeper level of refinement). Figure 1 depicts the speciation (CO_2 , CH_4) and quantitative distribution of C-14 between phases (solid, solution, gas).

The assumptions underlying this approach are given below:

- 1) C-14 is mainly bound to organic materials. Within these it is homogeneously distributed. Occurrences of easily purgeable C-14 in e.g. carbides or non-purgeable C-14 in inorganic compounds were not considered. They would lower the total release, but were neglected at the present level of refinement.
- 2) CO_2 is formed mostly by oxidation under aerobic conditions prior to closure and during a transient period after closure.
- 3) A realistic gas generation rate which includes methanogenesis for CH_4 and $^{14}\text{CH}_4$ is applied.
- 4) Dilution by isotopic exchange of CH_4 is slow and was therefore neglected at the present level of refinement.
- 5) Oxidation of CH_4 during transport that would result in the precipitation of C-14 is insignificant in the absence of oxidising backfill, rock or other materials. It was therefore neglected at the present level of refinement.
- 6) The equilibration of carbonates (solid, solution, gas) is assumed to be instantaneous.
- 7) C-14 in transient intermediates of chemical processes was neglected at the present level of refinement.
- 8) C-14 released prior to mine closure does not contribute to the post-closure exposure. Therefore, it lowers the total release after closure but was neglected at the present level of refinement.
- 9) C-14 occurs in all phases
- 10) C-14 in carbonates is mainly precipitated and remains fixed to the solid phase

The assessment shows that less than 1 % of C-14 is released with the brine to the biosphere. The gas phase releases 5.7 % of C-14 to the overlying rock and can thus contribute to the potential radiation exposure in the biosphere.

The following effects were not considered at the presented level of refinement:

- A fraction of C-14 is fixed in inorganic compounds (cement, concrete, metals) and decays before these can significantly degrade.
- A fraction of C-14 is released before closure of the final repository.

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