Behaviour of Carbon-14 Released from Activated Steel in Repository Conditions – a Key Issue in the Long-term Safety of Decommissioning Waste

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1. Introduction

The major part of the activity inventory in the decommissioning waste of a typical LWR is found in the activated steel components, i.e. in the reactor pressure vessel and its internals. In the long-term performance assessments, Carbon-14 often dominates the radiation exposure in the environment, especially if all the uncertainties relating to its behaviour are addressed. Hence special attention in the long-term safety case is to be given for the behaviour and speciation of C-14 released from activated metals in the repository conditions.

In activated metal waste the C-14 originates mainly in a neutron-proton reaction of N-14 in the metal. The two other reactions forming C-14, i.e. the neutron capture reaction of C-13 and neutron-alpha reaction of O-17 play a minor role only. The chemical speciation of C-14 in the lattice of steel may not be similar to the inactive C-12 in the metal, since the high energy involved in the activation reaction as well as the fact that originally the C-14 atom in the metal was a nitrogen atom, likely as a nitride probably may change its speciation.

The presentation summarizes the open questions identified in the long-term safety case for the decommissioning waste from Loviisa NPP as well as discusses the possibility to enhance the knowledge on this issue by experimental work. Although the problematics is discussed from the point of view of the final disposal of the decommissioning waste from the Loviisa NPP, the issue is relevant to other final disposal concepts as well.

2. Final disposal of the activated components from the Loviisa NPP

According to the decommissioning plan for the Loviisa NPP (Kallonen et al. 2008), the reactor pressure vessel and its internals will be disposed of as one piece. The pressure vessel will be transported to the repository, lifted with the aid of a bridge crane to a silo excavated in the repository. A cylindrical foundation made of reinforced concrete will be built in advance on the bottom of the reactor silo. The pressure vessel will be lowered into the silo in such a way that the transport radiation shield of the pressure vessel and the silo foundation will form an integrated structure. The space under the pressure vessel bottom will be filled with pumped concrete and the joint between the radiation shield and the silo foundation will be grouted. The space between the concrete structure and the bedrock will be backfilled by crushed rock (and bentonite, if necessary) up to the upper edge level of the radiation shield. The upper part of the reactor silo concrete structure will be built using prefabricated units, and the empty space remaining around it will also be backfilled with crushed rock. The pressure vessel internals will be transported inside the shielding cylinder to the repository and loaded into the pressure vessel. The pressure vessel will be filled with pumped concrete and the pressure vessel head put in its place. After fixing the head, the pressure vessel´s upper part will also be filled with pumped concrete through the flange penetrations in the head. The space between the pressure vessel and the surrounding concrete structure will be filled by pumped concrete and the concrete structure will be closed by a concrete slab. A layer of crushed rock will be set on the slab. Furthermore, a concrete slab will be cast up to the hall floor level. Figure 1 shows the reactor silo sealed in this way.

The C-14 inventory packed in the reactor pressure vessel, assuming 50 years operational time of the reactor, is estimated to be around 30 TBq / reactor unit. However, in newer reactors with a higher power, the activity inventories may be significantly higher.

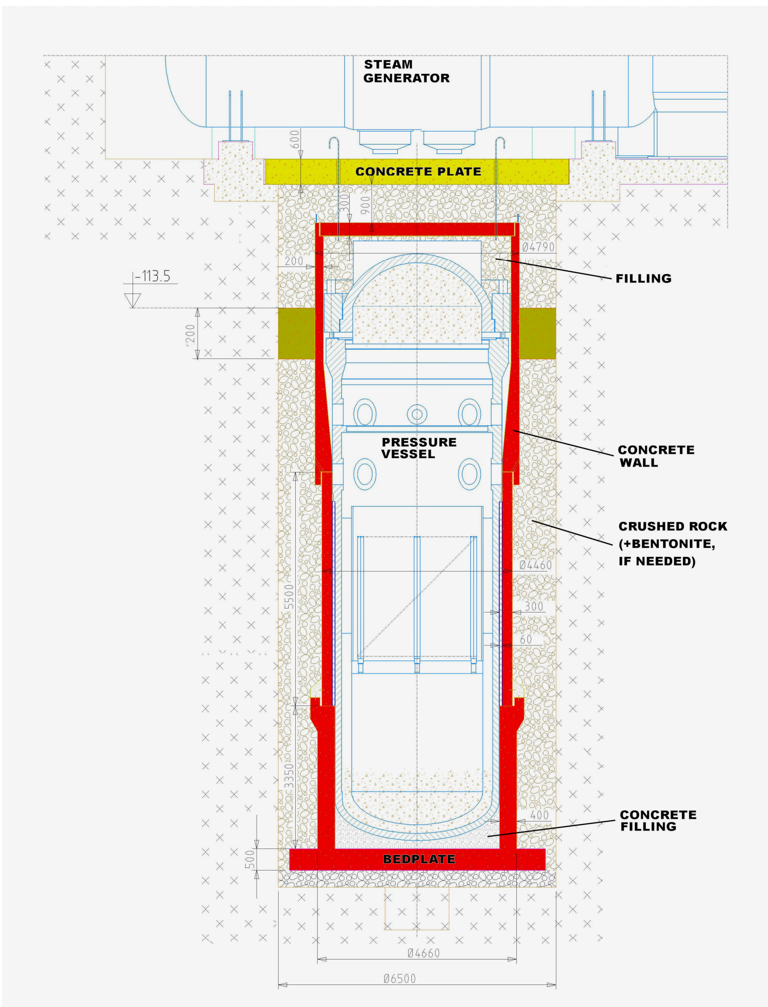

Figure 1. The sealed reactor silo (Kallonen et al. 2008).

3. Carbon behaviour in the repository

Carbon behaviour in the near-field, far-field and biosphere is a complicated issue, because carbon may form many different species having large differences in the sorption behaviour, the transfer in the biosphere and in the bioaccumulation. In some waste streams the major part of C-14 exists as carbonate, and as the dissolving calcium from concrete precipitates the carbonate, the concrete-based chemical conditions act as such as a barrier. In concrete environment the precipitation is almost complete, since the carbonate solubility is low. This would be the case also if the C-14 originating in the activated metal waste formed carbonate in the repository water. Yet the reaction mechanism and kinetics from carbide, the most probable species in metal, to carbonate is not sufficiently known, and the relating available thermodynamic data is very limited. On the other hand, there are experimental indications of both gaseous and soluble organic substances, but the applicability of those experiments to the repository conditions may be questionable. Furthermore the species may change due to some reactions either in the near- or the far-field.

The radionuclides in the activated metal components are typically considered to be released as a result of corrosion. Thus the release of C-14 from irradiated metals in the repository conditions depends on several aspects such as the surface area and the corrosion rate of the metals, the distribution of C-14 in the metal and the form in which it is released. These are affected by repository conditions such as pH, the form of oxide layer and water availability. In the alkaline reducing conditions of a cement-based final repository the corrosion rate is very low, and due to the protective oxide film at the surfaces of the metal components the corrosion may even cease. In the safety case for the final disposal of the decommissioning waste from the Loviisa NPP, the corrosion rate has been assumed to fall in the order of magnitude of 0.01 …1 µm/a depending on the prevailing conditions and steel type (carbon steel/stainless steel). Another identified mechanism to release C-14 from the metal components is diffusion from intact metal matrix, but its contribution in the repository conditions is believed to be low compared to corrosion.

In principle carbon may form any organic compounds, which have varying solubilities and other characteristics, ranging from very stable, practically insoluble compounds to soluble or even volatile compounds. It may also form carbides with metals, some which ("refractory carbides") are chemically inert, extremely hard and insoluble in water. On the other hand, salt-like carbides or the interstitial carbides of Cr, Mn, Fe, Co and Ni are much more reactive than the refractory carbides. They are rapidly hydrolysed by dilute acids and sometimes by water to H_2 and a mixture of hydrocarbons. (Greenwood & Earnshaw 1984).

In the literature only few articles on experimental results on C-14 behaviour relevant to the cementitious repository conditions are available. Experimental works by Deng et al. (1997) and Kaneko et al. (2003) are often cited in this context, but they both leave open questions regarding coverage, representativeness and relevance for the particular issue of the behaviour of C-14 released from activated metals. Even though they indicate the presence of organic, both gaseous and soluble, carbon species in the steel-water system, the relating phenomenology remains to some extent unclear. Furthermore the redox conditions in the experiments may not be representative for the repository conditions. Hence no straightforward quantitative conclusions can be drawn.

For the safety case of final disposal of the Loviisa NPP decommissioning waste, the issue was studied in a master's thesis (Kuitunen 2007), based on a literature survey. According to the thesis, *even though the formation of organic species has not been confirmed, their existence cannot be denied and this should be taken into account in the future safety assessments.* The thesis also indicated a need for further research, which was confirmed by the results of the safety assessment. The C-14 problematics and the related migration routes are demonstrated in Figure 2.

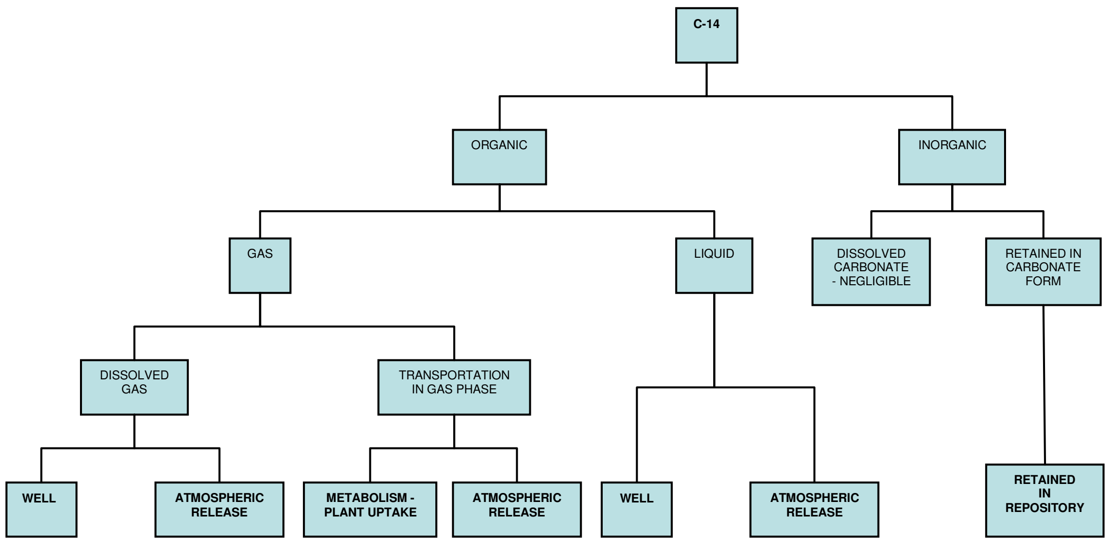

Figure 2. The different migration routes for C-14 (Kuitunen 2007).

4. Approach in the safety assessment for the Loviisa repository

In the decommissioning plan for Loviisa NPP, C-14 has been assessed in a conservative way in order not to underestimate the radiological consequences, but at the same time the need for a better knowledge on the related phenomenology was identified. In the safety assessment for the final disposal facility, all the carbon is assumed to form some mobile, organic compounds, since their existence and significance cannot be ruled out based on the present knowledge. This kind of approach certainly does not underestimate the consequences of C-14, but may overestimate them even significantly. If there are mechanisms to convert the organic carbon to carbonate or even to prevent the formation of the organic species, the C-14 bound in carbonate is released from the repository significantly less, thus resulting in a significantly lower radiation exposure in the environment

The Finnish regulations set nuclide specific constraints for the activity releases to the environment beyond a time period of several thousands of years. These constraints apply to activity releases which arise from the expected evolution scenarios and the activity releases can be averaged over 1000 years at the most. The sum of the ratios between the nuclide specific activity releases and the respective constraints shall be less than one. The release of the main radionuclides from the Loviisa reactor pressure vessel silos to the biosphere in the case of expected evolution case is presented in Figure 3. Release rates are calculated with conservative corrosion rates and parameters. The release rates are averaged over the periods of 1000 years. All the release rates remain clearly below the nuclide specific constrains (dashed lines). C-14 has the smallest margin to the constraints, about a factor of 4. The shape of its curve between 30 000 and 40 000 years reflects the modelled vanishing of the reactor pressure vessel wall and an increase in the corrosion rate due to the decrease of pH caused by dissolution of concrete. Even though the dominance of C-14 originates in the conservative assessment approach, the result indicates its significance also in the environmental consequences, and hence the need for a better understanding of its behaviour and the related phenomenology.

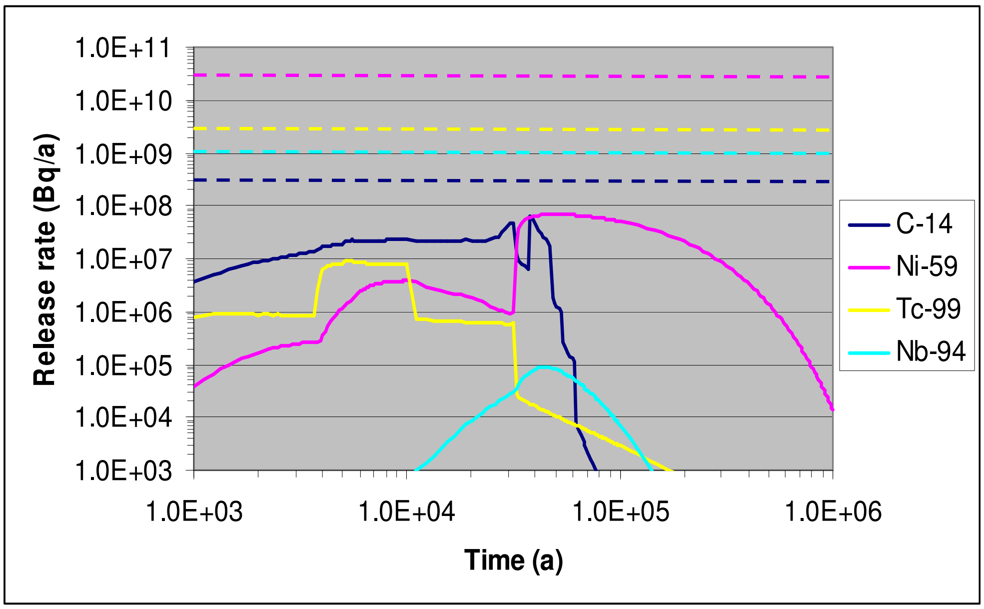

Figure 3. Activity release to environment from the RPV silos, calculated with conservative corrosion rates and parameters. The maximum represents 1000 years average. Nuclide specific constraints defined by the Radiation and Nuclear Safety Authority are presented with dashed lines. (Kallonen et al. 2008).

5. Discussion on the further research needs

Since there is no unambiguous conception on the speciation of C-14 released from metal components in repository conditions, and on the other hand, there are experimental indications of both gaseous and soluble organic substances, there is an obvious need for further experimental work to study the issue. Due to the complex phenomenology, it may be reasonable to study different phenomena separately. The understanding may be enhanced e.g. regarding the following phenomena:

- Partition of released carbon (either inactive or C-14) between organic and inorganic species

- Chemical reactions and kinetics between organic forms and carbonate in the repository conditions
- Some catalysts that may enhance the reactions
- Isotopic exchange
- Radiolysis to decompose the organic molecules as indicated by Kani (2007)
- Microorganisms, which in general have a key role in the carbon behaviour in nature
- Possible retarding mechanisms of the organic species in the repository conditions, such as sorption or diffusion in the cementitious engineered barriers.

As a peculiarity, in the experimental research of the carbon-14 issue one has to consider the related timescales. The issue is characterized by an extremely low evolution in the repository, and hence also very slow phenomena may play a role crucial for the long-term safety. On the other hand, in order to keep the experiment arrangements practical, one has to accelerate the experiment by some means, e.g. by increasing the surface-volume ratio. However, in an accelerated experiment, the phenomena should be known sufficiently to be sure of the relevance of the results.

If any experiments should be conducted with real irradiated metal samples, another challenge arises, i.e. the work with radioactive substances. The induced gamma activity in the samples makes the handling more difficult requiring special radiation protection arrangements. Hence it is reasonable to consider, to which extent the relevant phenomenology can be explored with inactive substances, and which phenomena are specific to the carbon-14 originating in the activation reaction from nitrogen-14.

6. Conclusions

Since C-14 is a major contributor to the environmental radiation exposure arising from the final disposal of typical decommissioning waste from LWRs, and since its behaviour and the related phenomenology in the repository conditions is not thoroughly known, there is an obvious need for further experimental work to research the issue. A key question in the research is the speciation of C-14 in the repository conditions after being released from metal components. Three different variants are possible, and there are some indications to be found in literature for each of them: carbonate, organic gaseous substance, and organic soluble substance. However, no quantitative conclusions on the speciation can be drawn based on the currently available data.

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