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157

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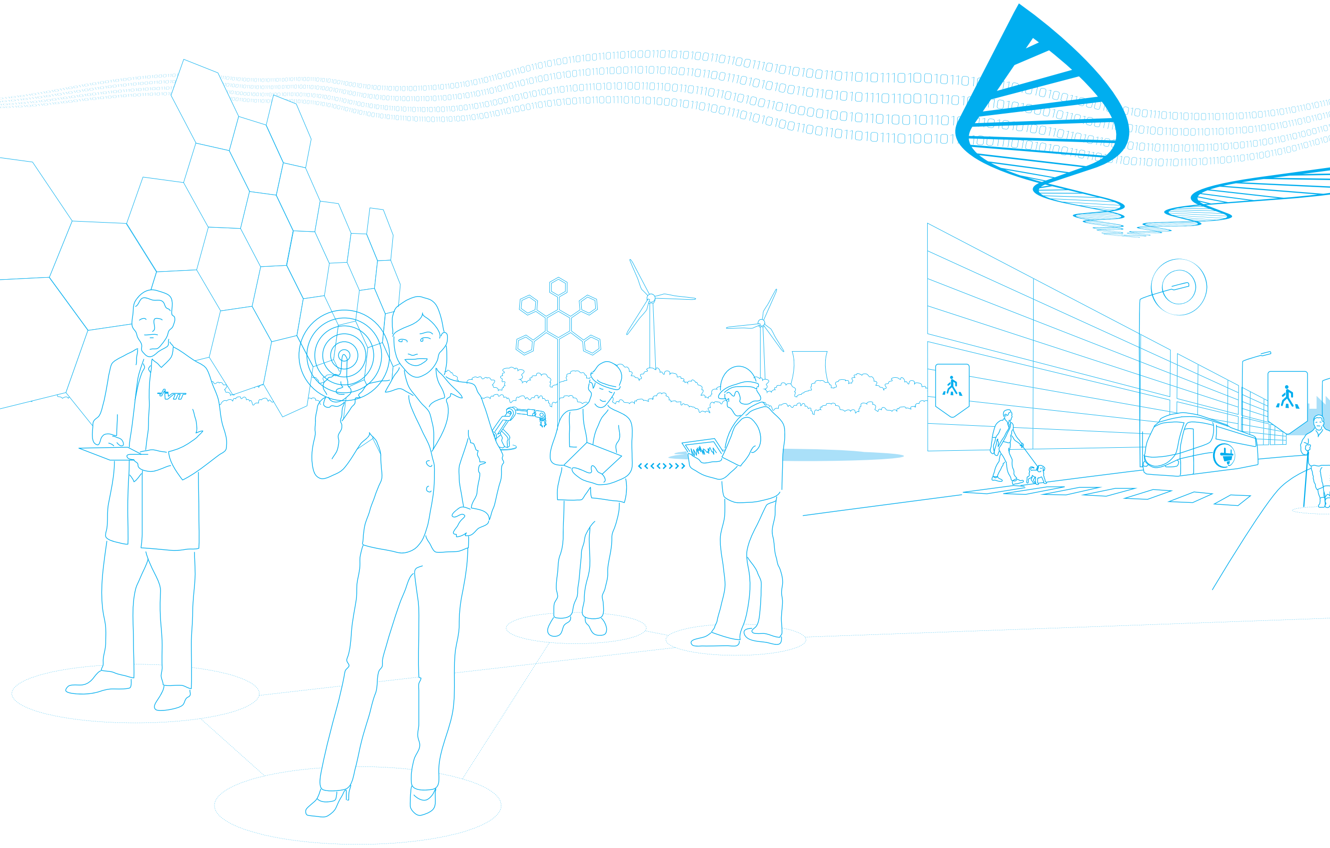
Transport and speciation

Tiina Heikola



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Leaching of ^{14}C in repository conditions
Transport and speciation

^{14}C:n liukeneminen loppusijoitusolosuhteissa. **Tiina Heikola.**
Espoo 2014. VTT Technology 157. 35 p.

Abstract

Long-term exposure of materials in a repository may result in significant alterations in material structures. The activated decommissioning wastes including the reactor pressure vessel and its internals made of stainless steel, as well as, spent fuel claddings and reactor graphite contain nitrogen as impurity. ^{14}C is generated as a result of nuclear reactions involving nitrogen (^{14}N) or ^{13}C atoms in these materials. ^{14}C is one of the most important radionuclides when considering safe disposal of nuclear waste due to its long half-life.

Both organic and inorganic carbons have been identified in leaching experiments with carbon containing steel, although clearly higher proportion is released as small organic molecules. The origin of these compounds and their reaction mechanisms is not fully understood. The specific iron-water experiments suggest that both the carbide carbon and the reduction of aqueous CO_2 could be the sources of hydrocarbons in solution.

Carbon analyses are highly sensitive to filtration which may cause incorrect results by either releasing or sorbing organic compounds. The filters should be cleaned by soaking in double distilled water (DDW) before use or at least to discard the initial filtration volumes. The best materials for DOC analysis are hydrophilic polyethersulphone and hydrophilic polypropylene membrane filters which induced least interference.

In this literature research, it has become clear that there is very little conclusive knowledge and evidence on the form and fate of ^{14}C in irradiated steel materials. A need for careful assessment of the different routes of ^{14}C production in neutron-activated materials and its chemical form and transport is required.

Keywords ^{14}C, radiocarbon, carbon speciation, decommissioning waste

^{14}C:n liukeneminen loppusijoitusolosuhteissa

Leaching of ^{14}C in repository conditions. Transport and speciation.
Tiina Heikola. Espoo 2014. VTT Technology 157. 35 s.

Tiivistelmä

Aktivoitunut metallijäte, mukaan lukien ruostumattomasta teräksestä valmistettu ydinreaktorin paineastia ja sen sisusta sekä käytetyn polttoaineen suojakuori ja reaktorin hidastinaine grafiitti, sisältävät typpeä epäpuhtautena. ^{14}C muodostuu pääasiassa säteilyn vaikutuksesta näissä metallimateriaaleissa olevista alkuaineista (^{14}N ja ^{13}C). Pitkän puoliintumisaikansa sekä sen kallioperässä kulkeutumiseen liittyvien epävarmuuksien takia ^{14}C on olennainen nuklidi tarkasteltaessa ydinjätteen loppusijoituksen turvallisuutta.

Tutkimusten perusteella ^{14}C voi metallimateriaaleista vapautuessaan esiintyä sekä orgaanisena että epäorgaanisena hiilen spesieksenä. Selvästi suuremman osan on kuitenkin havaittu esiintyvän lähinnä lyhytketjuisina orgaanisina yhdisteinä, mutta niiden alkuperä ja muodostumismekanismit eivät ole täysin selvillä. Muutamassa artikkelissa (Deng *et al.* 2007 ja Hardy & Gillham 1996) on pyritty selvittämään erityisesti rautametalli-vesisysteemeissä muodostuvien hiilivetyjen hiilen alkuperää. Sekä veteen liuenneen hiilidioksidin (CO2) pelkistyminen että metallissa olevan karbidimuotoisen hiilen uskotaan molempien olevan mahdollisia lähteitä.

Analysoitaessa hiilen määrää (TIC/TOC) vesinäytteestä näytteiden suodatus saattaa aiheuttaa ongelmia. Suodattimet saattavat joko lisätä tai vähentää näytteen todellisen hiilen pitoisuutta sitomalla tai luovuttamalla hiiltä membraanistaan. Ennen suodatusta suodattimet tulisikin pestä liottamalla niitä ionivaihdetussa vedessä tai vähintään huuhtelemalla suodattimien membraani ennen käyttöä. Selvityksen mukaan parhaat suodatinmateriaalit DOC-analyyseihin (liuennut orgaaninen hiili) ovat hydrofiiliset PEP- ja PP-membraanit.

Kirjallisuusselvityksen edetessä on käynyt selväksi, ettei kirjallisuudesta löydy yhtenevää ja yksiselitteistä tietoa 14C:n muodostumis- tai kulkeutumismekanismista aktivoituneesta metallijätteestä loppusijoitusolosuhteissa, ja lisätutkimukset aiheeseen liittyen ovat paikallaan.

Avainsanat ^{14}C, radiocarbon, carbon speciation, decommissioning waste

Contents

1. Introduction

^{14}C (radiocarbon) is a crucial isotope when considering safe disposal of nuclear waste. In the final disposal of decommissioning waste from nuclear reactors it is a major contributor to the environmental radiation exposure because of its long half-life of 5730 years and ability to move in the biosphere and geosphere (Eurajoki 2010).The release rates of some nuclides given in Figure 1 are averaged over 1000 year periods . All the other release rates remain clearly below the nuclide specific constraint (dashed lines), except in the case of ^{14}C whose margin to the constraint is the smallest. The activated decommissioning waste includes the reactor pressure vessel and its internals, as well as, spent fuel claddings and metal parts from the fuel assemblies. The pressure vessel is made of stainless steel and contains carbon (^{13}C) as an alloying element and nitrogen (^{14}N) as an impurity. These stable isotopes are involved in two of the three reactions producing ^{14}C, listed in Table 1. In stainless steel the first reaction is the major contributor, because ^{14}N has the largest neutron capture cross section of the three nuclides, and its abundance is much greater than that of the other two nuclides.

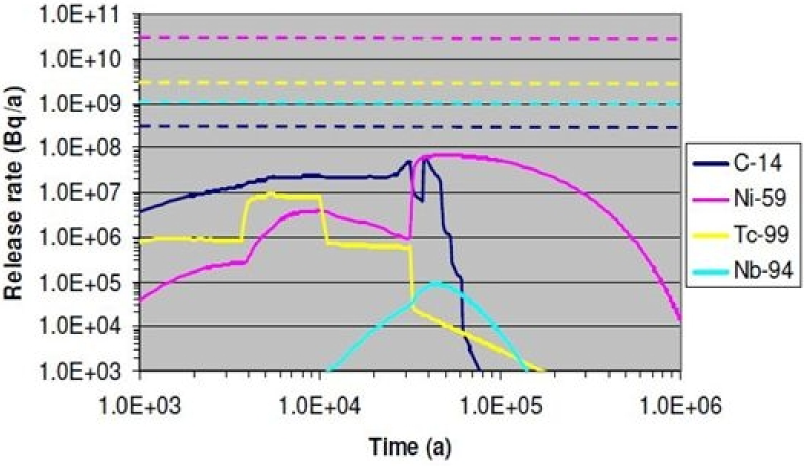


Figure 1. Release rates for the main radionuclides from the Loviisa reactor pressure vessel silos. Nuclide specific constraints defined by the Radiation and Nuclear Safety authority are presented with dashed lines. (Eurajoki 2010).

Table 1. ^{14}C reaction mechanisms and cross-sections. (Yim & Caron 2006).

Target isotope	Mechanism	Neutron cross-section area (barns)
^{14}N	$^{14}N(n,p)^{14}C$	1.81
^{13}C	$^{13}C(n,\gamma)^{14}C$	0.0009
^{17}O	$^{17}O(n,\alpha)^{14}C$	0.235

(1 barn = 10^{-24} cm^2)

A generally acknowledge fact is that there is no conclusive evidence on the form and fate of ^{14}C in irradiated materials. Both organic and inorganic carbons have been identified in leaching experiments with carbon containing steel e.g. (Kaneko *et al.* 2003). However, the origin and the reaction mechanism of these compounds are not fully understood. In addition, the versatile chemistry of carbon (organic/inorganic) has in recent years raised its importance concerning the nuclear waste disposal. ^{14}C plays an important role in the estimation of radiation exposure to the public (Johnson & Schwyn 2004).

In NDA's (The Nuclear Decommissioning Authority in U.K.) report the key processes of generation and migration of ^{14}C are presented (Figure 2) (NDA 2012). If water is in contact with nuclear waste, corrosion of metals and degradation of organic materials are the main gas generating processes.

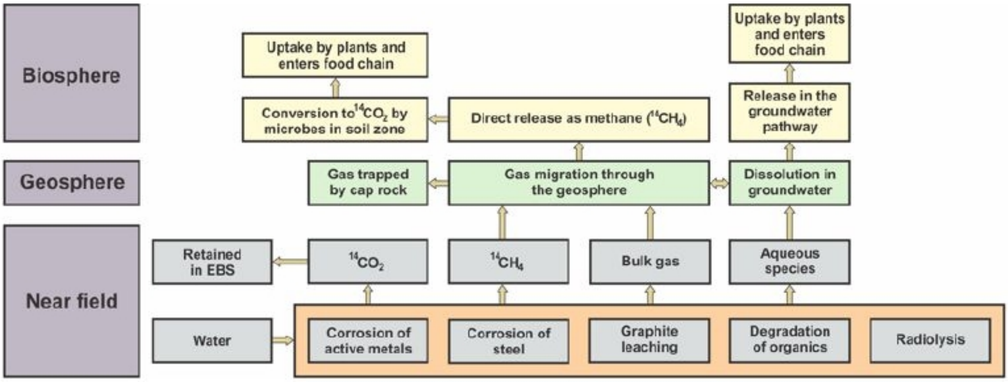


Figure 2. Diagram showing the key generation and migration processes (NDA 2012).

Some of the gas that is produced could contain ^{14}C. If in the form of carbon dioxide it is likely to be retained within the cementitious engineered barrier system through carbonation (NDA 2012). Under anaerobic conditions, the major release mechanism of ^{14}C is microbial degradation, which produces intermediates like; glucose, amino acids, hydroxycarbonic acids etc. The final products are carbon bearing gaseous compounds, such as CH_4, CO_2 and volatile hydrocarbons, and aqueous compounds like HCO_3^-/CO_3^{2-} (Bracke & Müller 2008).

Transport of inorganic carbon species is closely connected to the solid/liquid/gaseous carbonate equilibrium, while organic carbon is more related to the bio-geochemical cycle. For these reasons it is important to know in which chemical form carbon is present in the waste and in which form it will be released. It has been shown that more ^{14}C is in the spent fuel cladding than in the spent fuel matrix. From the zirconium alloy cladding ^{14}C is released to groundwater mainly in the form of organic carbon species (Tanabe *et al.* 2007). This indicates that carbon is present in the zircaloy cladding in the form of metal carbide as interaction of metal carbide with water can produce organic molecules. The mechanism however, which affects the organic/inorganic release ratio, is not yet known (Grambow 2008).

2. Materials

2.1 Steels

Steel is an alloy of iron containing no more than 2% carbon. Alloys with higher carbon content are known as cast iron. Besides carbon, other alloying elements including Mn, Cu, Mo, Ni, Cr, S, N, and Al determines the properties of the material, such as physical and chemical performance (Leffler 1998). Carbon and other alloying elements exist either as dissolved in crystal lattice or as chemical compounds in which case they form separate inclusions in the structure.

The ferrous alloys are classified in three goups:

- Iron: less than 0.008 wt % C
- Steels: 0.008 - 2.14 wt % C (usually < 1 wt %)
- Cast iron: 2.14 - 6.7 wt % (usually < 4.5 wt %).

The iron-carbon equilibrium diagram (Figure 3) is a plot of transformation of iron with respect to carbon content and temperature. It is also called iron-iron carbon phase diagram.

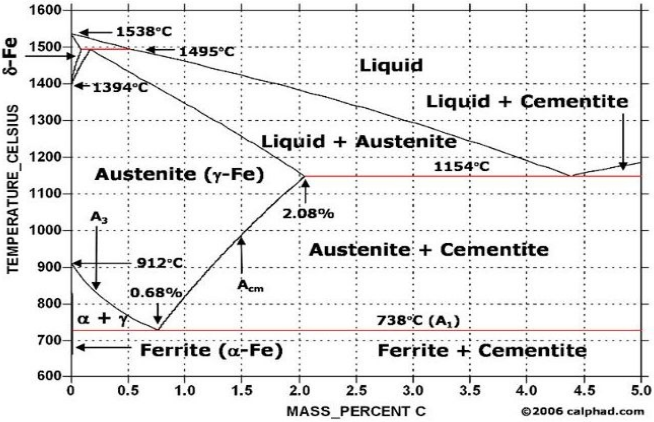


Figure 3. The Fe-C phase diagram shows phases which are present at different carbon content and temperature (http://www.calphad.com/iron-carbon.html).

Ferrite (α) is virtually pure iron. It is stable at all temperatures up to 910 °C. Carbon solubility in ferrite depends upon the temperature; the maximum being 0.02% at 723 °C. Austenite (γ) is stable at temperatures above 723°C depending upon carbon content. It can dissolve up to 2% of carbon. Cementite, iron carbide (Fe_3C), is a compound of iron and carbon, containing 6.67% carbon by weight. Addition of carbon to iron beyond this percentage would result in formation of free carbon or graphite in iron (Nevalainen 2006). Also other transition carbides exist, e.g. chromium, nickel, manganese, molybdenum and cobalt (Table 2). The atomic radius of iron is too small for typical interstitial carbide to form, and hence carbon atoms interact and carbon chains run through distorted metal lattice. Therefore, iron carbide is hydrolysed by water and dilute acids to generate hydrocarbons (Hicks 2004). Many of the existing research on ^{14}C have concentrated on reactor graphite, zircaloy cladding and fuel matrix, while only very few investigations have been made on stainless steel alloy components. In general, the release of carbon via corrosion of metals is a very slow process compared to microbially assisted corrosion.

Table 2. Carbides of some transition elements (Hicks 2004).

	Fe	**Cr**	**Ni**	**Mn**	**Mo**	**Co**
Carbide	Fe_3C	$Cr_{23}C_6$ Cr_7C_3 Cr_3C_2	Ni_3C	$Mn_{23}C_6$ Mn_3C Mn_5C_2 Mn_7C_3	Mo_2C Mo_3C_2	Co_3C Co_2C

2.1.1 Corrosion of steels

The corrosion of steels is an electrochemical process that occurs in stages and requires the simultaneous presence of moisture and oxygen. In the absence of oxygen the corrosion potential for steel in aqueous solution is determined by anodic (oxidation) and cathodic (reduction) reactions. The overall reaction for the anaerobic corrosion of iron under moderately alkaline conditions is:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \uparrow \qquad (1)$$

AEAT/ERRA-0313 report (Smart *et al.* 2004) gives a summary of the work undertaken within the Nirex Safety Assessment Research Programme related to the anaerobic corrosion of steel in a radioactive waste repository. The program had following three objectives:

a) to dermine the corrosion and hydrogen production rate for carbon steel and 316L stainless steel under anaerobic and alkaline repository environments,

b) to identify the composition of the solid corrosion products,

to investigate the ability of steels to repassivate in oxygen-free, alkaline conditions.

The carbon steel used in the studies was a type BS4360 grade 43A and the stainless steel type AISI 316 S42 (0.07% C max). The samples were in the form of thin wire and rod in order to provide a large surface to volume ratio. Various test solutions were used, including synthetic Sellafield Borehole 2 groundwater. The experimental techniques like, electrochemical, weight loss and gas volume measurements, as well as gas chromatography, were applied to determine the corrosion rates of steel. Composition of the oxide film produced on steel was analysed using X-ray diffraction and Raman spectroscopy. Guillotined electrode and abrasion techniques were used to investigate the repassivation of steel by generating completely oxide-free surface, which was then monitored by analysing the surface by SIMS (Smart *et al.* 2004).

It was concluded that in oxygen-free and alkaline conditions, stainless steel and carbon steel are likely to maintain a protective passive film for a long-time, leading to very low general corrosion rates. The long-term carbon steel general corrosion rates (< 2 500 days) were estimated to be < 0.1 µm yr^{-1}. The corrosion products on carbon steel were identified predominantly as magnetite (Fe_3O_4), but included also some ferrous hydroxides. The passive film on stainless steel composed mostly of an oxyhydroxide that was enriched in chromium. Both steel surfaces were able to repassivate rabidly in anoxic alkaline conditions by direct reaction with water, Chlorine ions were observed to reduce the repassivation, but did not prevent the formation of a passive film (Smart *et al.* 2004).

2.1.2 Nitrogen in steels

As mentioned, steels contain nitrogen (N) as impurity in the form of very fine and coherent nitride or solid solution. One essential source is the raw materials used in steel making. In Table 3 is shown the amount of nitrogen present in each of the feed materials typically used in EAF (electrical arc furnace) steel making. On the other hand, nitrogen is added to steels to improve mechanical and corrosion properties. However, high nitrogen contents in steel can lead to decrease of formability and toughness of the final material. Nitrogen acts as an interstitial element in a solid solution and forms precipitates of nitrides and carbonitrides which eventually yields more homogenous and fine-grained structure in steels (Ciésla & Ducki 2008).

The maximum solubility of nitrogen in liquid iron is approximately 450 ppm and less than 10 ppm at ambient temperature, as is shown in Figure 4. The presence of other elements, like sulphur and oxygen, affects the solubility, as well as the composition of the alloy, crystal structure and temperature.

Table 3. Nitrogen content of feed materials. (www.keytometals.com)

Feed material	**Nitrogen content**
Scrap	30–120 ppm
HBI / DRI *	20–30 ppm
Liquid iron from the BF *	60 ppm
Cold pig iron	20–30 ppm
Hot heel	10 ppm
Coke	5000–10000 ppm
Oxygen	30–200 ppm
Carbon carrier gas (air)	78%
Bottom stirring gas (N_2)	> 99,9%
Bottom stirring gas (Ar)	< 30 ppm
Cao	400 ppm

** HBI = Hot-briquetted iron, DRI = Direct-reduced iron, BF = Blast Furnace*

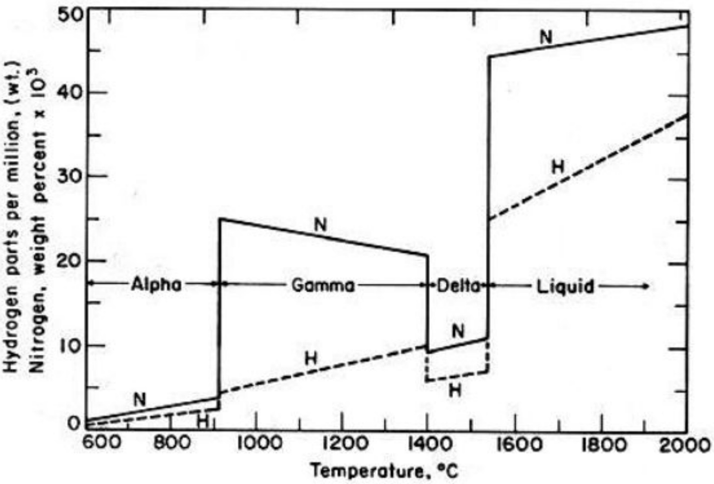


Figure 4. Solubility of nitrogen in iron for temperatures of 600–2000°C. (www.keytometals.com)

Steels are classified according to their grades. Number of standards organisations has been developed to classify various steel by their composition and properties. SAE International is one of the standards organisations which have been involved together with American Iron and Steel Institute (AISI) in standardising a numbering system for steel grades. Today both SAE and AISI systems are rather identical and are used in parallel with each other to identify the steel grades. Other existing systems include e.g. British Standards, International Organization for Standardization ISO/TS 4949:2003, European standards (EN), Japanese Industrial Standards (JIS) standard and Chinese standard (GB) (Féron 2012).

Carbon steels and low alloy steel (LAC) are commonly used in nuclear industry as structural materials. Exposure to the neutron flux leads to hardening and embrittlement of the pressure vessel steel. Parameters controlling the alteration are: exposure temperature, steel chemistry and irradiation dose. Type 304 and 316 and especially the type 316L steels, which is an extra low carbon grade of 316, are the main stainless steels used in nuclear facilities including nuclear power reactors BWR and PWR (Table 4). The lower carbon content in 316L minimizes deleterious carbide precipitation as a result of welding. The internal surface of the pressure vessels are also clad with 308/309 stainless steel weld overlays. Use of these materials is due to their excellent resistant to uniform corrosion and to their good mechanical properties (Féron 2012).The materials close to core of nuclear reactor are subjected to high-energy neutron fluxes. Neutron irradiation causes atom displacements creating vacancies and interstitial (defects). In addition to that, also changes in the elemental composition are caused by nuclear reactions. Nitrogen in steel transforms into ^{14}C as a result of ^{14}N (n,p)^{14}C reaction, but the problem is that there is no clear knowledge of the form of ^{14}C in steel structure.

Carbon steels are also candidate materials for overpacks of nuclear waste for geological disposal in several countries (e.g. France, Switzerland, Japan). They will corrode at a significant but predictable and low corrosion rate: the challenge is to predict their behaviour over thousands of years which require an increase in fundamental knowledge of corrosion processes in geological environment (Féron 2012).

Table 4. Chemical composition (wt.%) of types 316 and 316L stainless. (Data sheet: http:// www. aksteel.com)

SAE/AISI designation	Cr	Ni	C	Mn	Si	P	S	N	Mo
316	16–18	10–14	0.08	2.0	0.75	0.045	0.03	0.10	2.0–3.0
316L	16–18	10–14	0.03	2.0	0.75	0.045	0.03	0.10	2.0–3.0

2.2 Graphite

Graphite used for nuclear reactors is often referred to as nuclear graphite. Special grades of synthetic graphite are used as a moderator or reflector within nuclear reactors. About 60% of the ^{14}C generated in graphite moderators is produced by interaction with the nitrogen impurities and 40% by interaction with carbon-13 according to (NDA 2012). On the other hand, additional nitrogen contamination of the graphite can arise from the adsorption of nitrogen from coolant gases onto graphite surfaces. ^{14}C atoms in the graphite lattice formed from nitrogen-14 impurities or from carbon-13 are released very slowly (if at all). Therefore, graphite itself would be expected to be unreactive under repository conditions. However, ^{14}C trapped within closed porosity on the surface is more reactive than the bulk graphite (Marshall *et al.* 2011). Uncertainties rise also from the fact that the initial content of impurities (e.g. nitrogen) is not known. As Narkunas *et al.* (2011) noticed in their research, the data of nitrogen impurities for the studied material was not available. In the absence of a mechanistic understanding of ^{14}C release from irradiated graphite, simple empirical approaches are used in the models. This is usually resulting from the difficulty to apply suitable qualitative and quantitative methods to determine nitrogen and other light element impurities in the material. In general, characterisation of radioactive graphite waste is complicated. Number of variable has to be taken into account, such as operational lifetimes, reactor assembly, fuel, coolant composition and shutdown periods (NDA 2012). (Narkunas *et al.* 2011) used the ORIGEN-S code from the SCALE 5 codes system to model the graphite activation and the composition of radionuclides in Ignalina NPP Unit 1 reactor on the basis of modelled neutron fluxes and reactor operation history. The modelling results showed that the location of maximal ^{14}C activity coincides with that of the maximal thermal neutron flux and confirms that the generation of ^{14}C is determined by thermal neutron flux. In addition, the activity of ^{14}C generated from activation of the nitrogen impurity was considerably lower than that from carbon activation and did not influence the total ^{14}C activity when the concentration of nitrogen impurity was lower than 1×10^{-4}% mass. At higher contents of nitrogen impurity, the generation of ^{14}C from the activation of nitrogen increased and $^{14}N(n,p)^{14}C$ became predominant.

Marshall *et al.* (2011) concentrated on the long-term release of ^{14}C from irradiated graphite as well as on the speciation of gaseous carbon using a modified sampling apparatus capable of separating carbon monoxide and volatile hydrocarbons. The experiment measured the release of ^{14}C from a solid block of BEPO graphite. The ^{14}C inventory of the block was 2.1 MBq. At the end of the experiment, a total of 112 Bq of gaseous ^{14}C (87.5 Bq CO and 24.8 Bq organically bound) was generated and 2.1 kBq of ^{14}C was found in the aqueous phase. The rate of ^{14}C release decreased with time and was found to correspond fairly well with the first-order function (Figure 5). The authors assume that it is possible that the trend observed represents the behaviour of a small labile fraction of the ^{14}C inventory (e.g. absorbed species on the graphite surface) and the ^{14}C bound more strongly or held in the graphite lattice may be released at much slower rates. For measurements ^{14}C was trapped with a series of columns containing silica gel and soda lime which collect water and carbon dioxide. The apparatus used comprised two gas sampling units set up in series with the reaction vessel containing the graphite sample (Figure 6). The apparatus allowed the ^{14}C associated with CO to be collected separately from that in organic species. The graphite to be analysed was submerged in high pH solution representing near-field cementitious pore water. The solution of sodium hydroxide at initial pH value of 13 was used, in order to avoid the possible precipitation of calcium carbonate in the system which might limit the concentration of ^{14}C-carbonate in the solution.

A considerable amount of work on the release of ^{14}C from irradiated graphite and metal wastes has been undertaken in Japan (Table 5). Recent studies from the Tokai (Magnox) reactors have included separation of the organic ^{14}C species in solution from ^{14}C-carbonate. The organic components were separated into fractions by High Performance Liquid Chromatography (HPLC) and analysed for ^{14}C. Also the sorption potential of the ^{14}C species was determined. Results showed similar elution times for the leached organic species as is typical to small organic molecules (methanol, formate, acetate, etc), but these species were found to be more strongly sorbing and as a result, the leached organic ^{14}C species were not confirmed (NDA 2012).

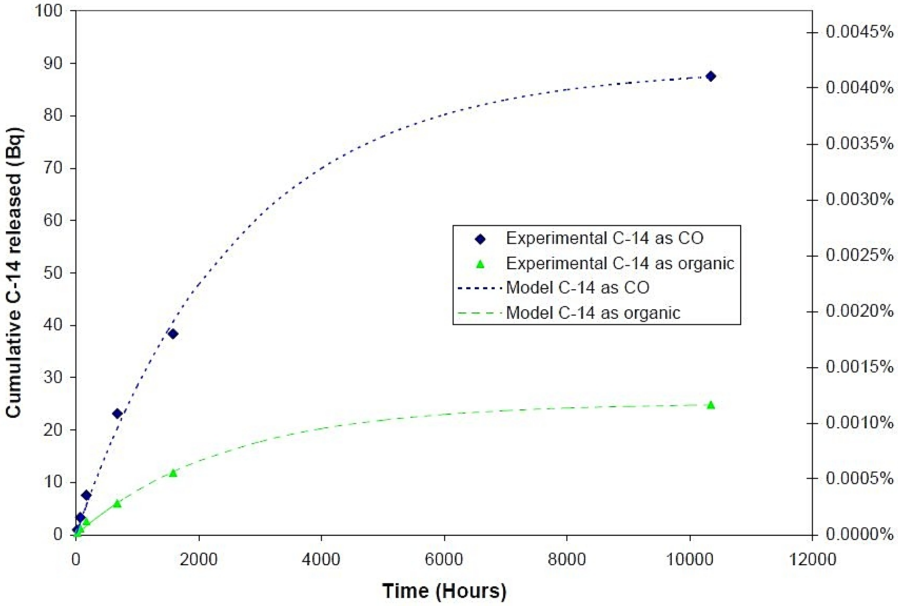


Figure 5. Cumulative ^{14}C release (inorganic/organic) from BEP0 graphite under alkaline (pH 13) conditions into the gaseous phase (Marshall *et al.* 2011).

The European project ‘Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste (CARBOWASTE)’ which was launched in 2008 concentrated, among other things, on the disposal of irradiated graphite materials. Since 2010, Germans have had their own complementary project ‘Disposal of irradiated Graphite (CarboDIPS)’ which is specialized in requirements in German waste repository (von Lensa *et al.*).

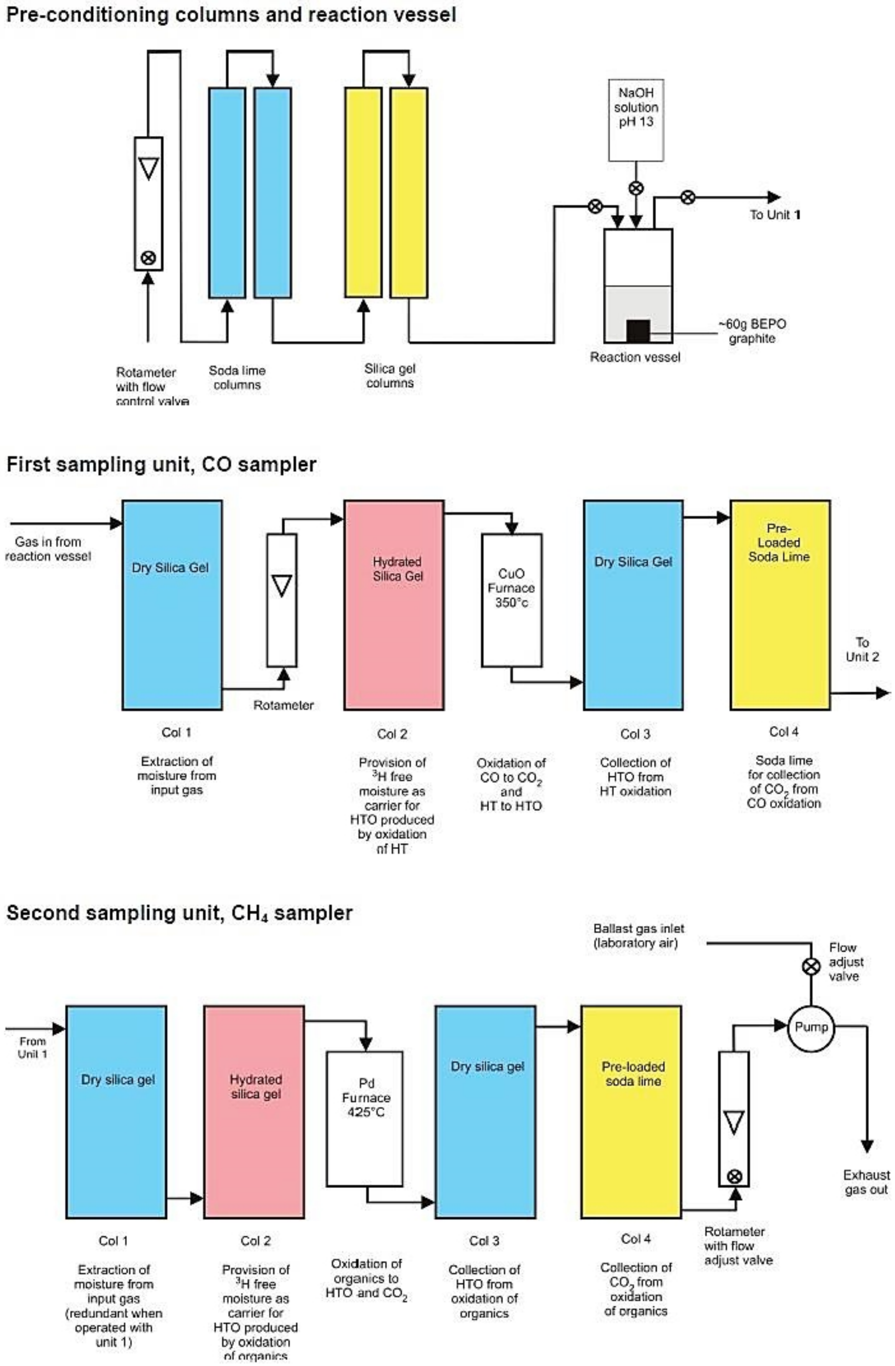


Figure 6. Schematic diagram of the experimental set-up by Marshall *et al.* (2011).

Table 5. Summary of experiments on ^{14}C releases from irradiated metals and graphite in Japan (NDA 2012).

Study	Material			Abstract
1	Activated	Zircaloy	PWR Zry-4 Base metal, Oxide film	Organic ^{14}C. Not detected in gas phase. In analysis, organic ^{14}C was oxidized by $KMnO_4$. Most of organic ^{14}C was neutral species (organic ^{14}C passes through anion exchange paper).
2			BWR Zry-2 STEP I Base metal, Oxide film	Detected in gas and liquid phases. Amount of ^{14}C leaching out from Zircaloy with oxide film was more than that from Zircaloy metal. The same amounts of inorganic and organic ^{14}C were detected by the leaching test of 30 months. In the leaching test conducted by a stepwise sampling method, decreases of ^{14}C in summarising samples were observed. Formate, formaldehyde and acetate were isolated by HPLC.
3			BWR Zry-2 STEP III Base metal	More than 40% of ^{14}C was organic carbon. Detected in gas phase, however not detected in gas phase of leaching sample for 12 months. Leaching test continuing.
4		Stainless steel	BWR Upper grid	Not measured in gas phase. 66~75% of ^{14}C in liquid phase was organic carbon, oxidized by $KMnO_4$. ^{14}C chromatograph was measured by HPLC + LSC, some peaks were obtained and associated with formate, formaldehyde, acetate, methanol.
5			BWR Shroud	25% of ^{14}C in gas phase, 38% of organic ^{14}C and 37% of inorganic ^{14}C in the liquid phase were detected. Organic carbon in liquid phase was separated by anion exchange resin to obtain neutral and anion species. Of organic ^{14}C, neutral species were 18%, anion species were 82%.
6		Graphite	Moderator Reflector	Not measured in gas phase. 80% of ^{14}C in liquid phase was organic carbon. In analysis, organic ^{14}C was oxidized by $KMnO_4$. ^{14}C chromatograph was measured by HPLC + LSC to obtain peaks at the same positions as for formate, acetate, and methanol. The K_d value of OPC for total ^{14}C was 69 cm3 g-1. The K_d values of organic carbon to be assigned to the peaks of the ^{14}C chromatograph were more than 30 cm^3/g, and were not consistent with that of ^{14}C bearing compounds for OPC. It was suggested that organic carbon leaching out from the graphite is not formate, acetate or methanol.
7	Non-activated		Fe3, ZrC, Zr, carbon steel	Not measured in gas phase. ^{14}C detected in liquid phase was inorganic and organic carbon. Ratio of organic was more than

BWR=Boiling water reactor; HPLC = High performance liquid chromatography; K_d = Sorption distribution ratio (cm^3/g); LSC = Liquid scintillation counting; OPC = Ordinary Portland cement.

2.3 Zircaloy

Zirconium alloys (also called Zircaloy) are solid solutions of zirconium or other metals. They are widely used in nuclear reactors as fuel cladding of fuel rods and as reactor structural elements because of their low neutron cross section and corrosion resistance. During reactor operation, the Zr alloys are exposed to irradiation. For example, CANDU fuel cladding receives neutron fluxes of around 1025 neutrons/m^2 which leads to the formation of neutron activation products, such as ^{14}C, ^{59}Ni, ^{63}Ni and ^{93}Zr in fuel cladding, and ^{94}Nb and ^{93}Zr in pressure tubes (Shoesmith & Zagidulin 2011). These radionuclides may be released from the Zr alloys as a result of corrosion. Shoesmith & Zagidulin (2011) reviewed the corrosion mechanisms and rates for zirconium alloys under repository conditions. In the case that the waste container containing the Zr cladding fails, the corrosion and radionuclide release will depend on the properties of the groundwater, its composition, redox potential and pH. It was concluded though that the redox conditions within a failed container would remain reducing and hence leaves passive corrosion as the only long-term corrosion mechanism with a rate less than 1 nm/year (Shoesmith & Zagidulin 2011).

Majority of the Zircaloy related studies have concentrated on the corrosion behaviour of the fuel cladding and cladding acting as a barrier against radionuclide release. According to Fraker (1989) corrosion of Zircaloys in water is increased with temperature as well as with carbon and nitrogen impurity contents. Smith & Baldwin (1993) investigated the release of ^{14}C species from irradiated Zircaloy-4 cladding samples from spent fuel with 28 MWd/kgHm burn-up. Two types of experiments in both argon and air atmosphere were conducted with a specially designed apparatus (Figure 7) for measurement of kinetic thermal release rates of ^{14}C species. The first type of experiment involved short stepped-temperature release tests and the other more extensive series of constant-temperature release tests. The results showed that only a fraction of the total ^{14}C inventory (10%) was readily available for release at the particular temperatures, indicating that ^{14}C was released only from part of the cladding samples, i.e. the oxide film on the surface. The obtained data gave reason to consider both surface desorption and bulk diffusion to be possible in rate controlling at different times. At later times, the release rate curves appeared to follow the classical diffusion curves indicating that diffusion becomes the dominant rate-controlling step and desorption less important. Speciation of the diffused carbon compounds was not identified, but only fully oxidized carbon species were found in the traps.

Tanabe *et al.* (2007) have studied the release properties of ^{14}C from simulated hull specimens from PWR and BWR to evaluate the ^{14}C inventories in Zircaloy metal and Zircaloy oxide. Two types of test, short- and long-term tests, were performed. The irradiated Zircaloy tube samples were analysed according to the chart in Figure 8. The results showed that most of the ^{14}C released from the hull was in the organic form in the liquid phase. Due to the low concentration of leached ^{14}C, the chemical species could not be identified. In Figure 9 is presented the results of the long-term leaching test. ^{14}C was detected only in the liquid phase and the leaching rate seemed to decrease with time. Based on these results Tanabe *et al.* (2007) were able to estimate that minimum period of 20 000 years or longer would be required for all the ^{14}C to be released from the Zircaloy metal and 400 years from oxide film.

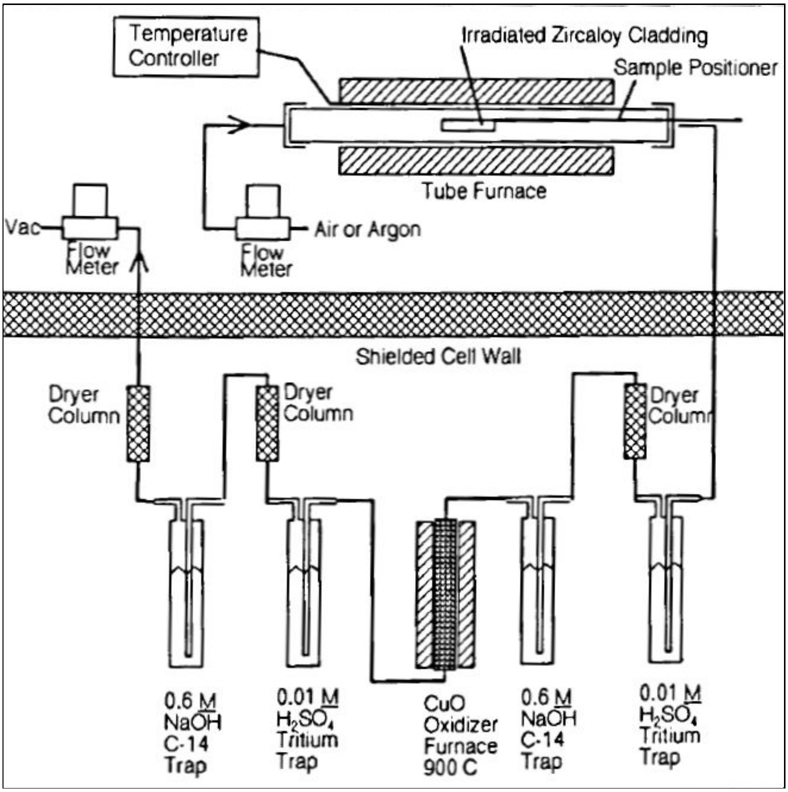


Figure 7. Schematic draft of the experimental apparatus by (Smith & Baldwin 1993).

Tanabe *et al.* (2007) have also conducted preliminary leaching tests with inactive materials, Fe_3C and ZrC at two different pHs (8.0 and 12.0). The tests were conducted under reducing atmosphere (in a glove-box) at room temperature with liquid-to-solid ratio 1 mL/g. The content of organic carbon was measured and species identified with HPLC and GC-MS. The organic species detected were low-molecular weight alcohols, carboxylic acids and aldehydes. The identified organic carbon species from Fe_3C and ZrC experiments are shown in Table 6. Carboxylic acids and formaldehyde were detected in all the test samples, while alcohols, both methyl and ethyl alcohols, were only formed in the higher pH solutions with one exceptions; no methyl alcohol in the case of Fe_3C. Another exception was ZrC test at pH 8 as ethyl alcohol was detected.

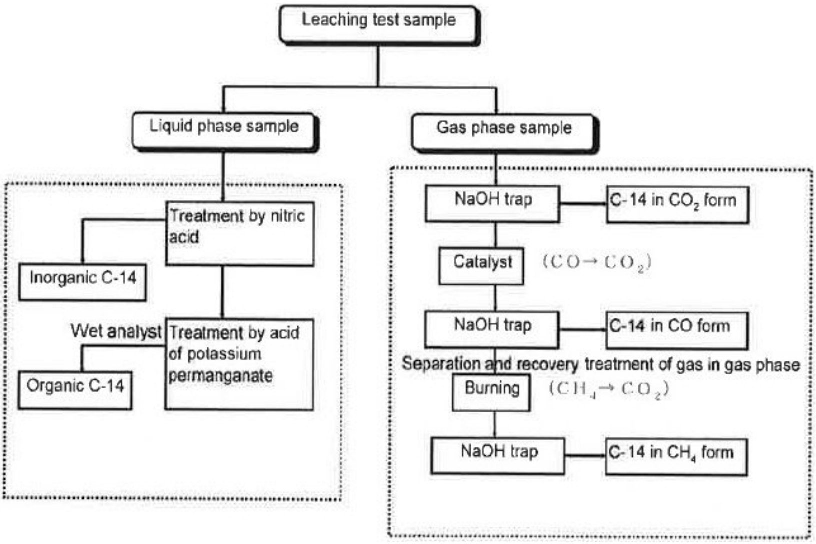


Figure 8. Sampling procedure for the leaching test samples (Tanabe *et al.* 2007).

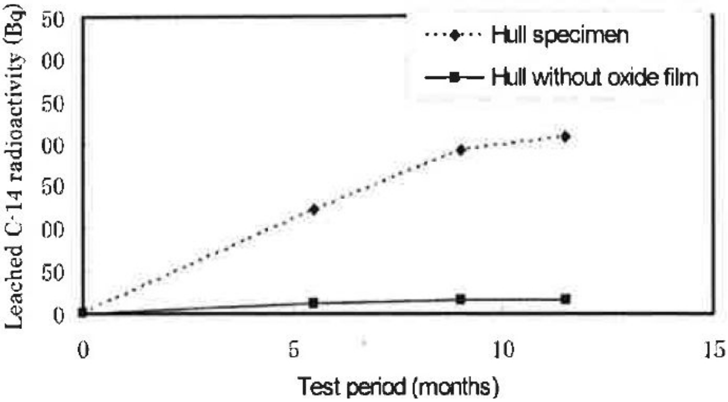


Figure 9. The results of the leaching test of PWR hull (Tanabe *et al.* 2007).

Table 6. Results of the identification of organic carbon in the Fe_3C and ZrC leaching test *(*Tanabe 2007*)*.

Metal	pH	CH_3OH	C_2H_5OH	HCHO	HCOOH	CH_3COOH
Fe_3C	8.0	–	–	○	○	○
	12.5	–	○	○	○	○
ZrC	8.0	–	○	○	○	○
	12.5	○	○	○	○	○

2.4 Spent fuel

^{14}C in spent fuel is produced primarily by the $^{14}N(n,p)^{14}C$ and $^{17}O(n, \alpha)^{14}C$ reactions, with the former being the dominant path. As a result, the final inventories depend not only on the integrated flux, but also on impurity contents that are influenced by the manufacturing process and specifications. Maximum permissible N levels in UO_2 pellets range from 50 to 100 ppm, depending on the fuel and reactor type. The main uncertainties in the concentrations of ^{14}C and in fuel and structural materials arise from uncertainties in the concentrations of the precursor nuclides (principally ^{14}N) in the unirradiated materials (Johnson *et al.* 2008). Hicks (2004) reported that about 80% of the ^{14}C produced in PWR fuels is derived from ^{14}N and 20% is derived from ^{17}O. Most ^{14}C produced in the fuel is retained in the spent fuel, although some is lost from the external surface by dissolution in the water pools or exchanged with ventilation air.

Based on the measurements and calculations (Van Konynenburg 1992) estimated the ^{14}C inventory of PWR spent fuel with 33 000 MWd/MTU burnup to be 37 GBq per metric ton of initial uranium. However, there are large uncertainties concerning the actual values and the calculated average inventories are the best values at present. The chemical forms of ^{14}C are uncertain, but it is expected to exist partially as elemental carbon and carbide in the UO_2 (Van Konynenburg 1992).

Neal *et al*. (1987) have studied the radionuclide release behaviour of spent fuel at repository-relevant hydrothermal conditions. The investigated spent fuel was from pressurized water reactor H.B. Robinson Unit 2. The characterized fuel was reacted with simulated Hanford groundwater (GR-4) in Dickson-type pressure vessels at 200 °C for periods of up to 9 months. The initial solution to solid mass ratio, dissolved oxygen and methane contents of the groundwater and spent fuel particles size were varied among the experiments in order to test the effects of these parameters. The solution samples were extracted and cooled to room temperature, analysed for pH and then filtered through 400 nm polycarbonate and 1.8 nm membrane filters in order to distinguish colloidal-sized particles from dissolved species. The results indicated that ^{14}C existed as dissolved species and was readily released in to solution in gaseous form (CO_2).

3. EXPERIMENTS – analytical methods and protocols

3.1 Determination of ^{14}C

As mentioned earlier ^{14}C is a weak beta-emitter which has non-discreet decay energies. Its separation from other beta-emitting radionuclides is the first step before measuring the activity using liquid scintillation. Highly radioactive state of samples imposes the need to work with shielded facilities, which is time consuming and besides, ^{14}C is often trapped in matrices that are difficult to work with (Berg & Fonnesbeck 2001). Different analytical methods are required for a variety of sample types. In general, the sample preparation methods depend on the nature and physical state of the sample, but in all cases ^{14}C in the sample is converted into CO_2 and then absorbed e.g., into NaOH solution for Liquid Scintillation counting. The scintillation spectrometry is one of the most employed techniques for measurement of ^{14}C (IAEA 2004).

Ion, gas and liquid chromatography (IC, GC, LC) as well as liquid-liquid extraction method can be used to separate the organic carbon species in gas or liquid phase. Combining these with more sensitive analytical instruments like, mass spectrometry (MS) or fourier transform infrared spectroscopy (FTIR), complex mixtures of relatively low molecular weight compounds can be identified and quantified. With an accelerator mass spectrometry (AMS) isotopes like ^{14}C can be separated from an abundant neighbour mass of ^{12}C, and atomic isobars like ^{14}N from ^{14}C.

3.2 Iron-water systems

One of the questions is the origin of the organic carbon in the iron-water systems. Possible sources for these compounds are: 1) carbon impurities in the metallic iron, 2) aqueous CO_2 and 3) other unidentified organic compounds dissolved in the source water (Hardy & Gillham 1996). Experiments on inactive steel suggest that carbon may be released from stainless steel primarily as water soluble organic species, but there is also some evidence for the release of volatile species including methane (NDA 2012). According to (NDA 2012), there is uncertainty concerning speciation of ^{14}C derived from neutron activation compared with bulk carbon in steels, which leads to uncertainty concerning also the speciation (e.g. CH_4, CO_2, CO, C_2H_2) of ^{14}C releases from irradiated materials compared with ^{14}C and ^{13}C.

Various batch experiments have been conducted in order to investigate the origin of produced hydrocarbons (e.g. Hardy & Gillham 1996, Deng *et al.* 1997). The results from these two experiments are rather conflicting. Deng *et al.* (1997) suggest that carbide carbon in iron seems to be the most likely source of hydrocarbons as nearly 100% of carbide carbon present in the iron structure was observed to convert into hydrocarbons. An excess of hydrocarbons were analysed compared to the carbon available in the initial aqueous CO_2 indicating that the dissolved CO_2 could not be the major source of hydrocarbons formed. Contrary to Deng *et al.* (1997), Hardy & Gillham (1996) conclude that hydrocarbons were formed by the reduction of aqueous CO_2 by iron. They base their hypothesis on the observation that hydrocarbons were also detected in the experiments conducted with electrolytic iron, which has low carbon content, and the remaining possibility was that hydrocarbons were formed by the reduction of aqueous CO_2. Either way, this matter needs to be explored in order to really understand the formation of organic carbon species in such systems.

3.3 Chemical forms and migration

In EPAs (United States Environmental Protection Agency) Gruhlke *et al.* (1986) examined the quantities and concentrations of ^{14}C in low level radioactive waste burial sites. They categorise wastes in three classes: a) nuclear fuel cycle, b) institutional wastes, and c) industrial wastes. The activated metal waste falls in the first category. It is assumed that these wastes make approximately seven percent of the total ^{14}C budget and are rather immobile compared to other waste form.

^{14}C is acknowledged as special radionuclide in the long-term performance assessments of the waste inventory due to transport in both the gas and aqueous phases. Under repository conditions the transport is controlled by the movement of groundwater. Also the geochemical factors, like precipitation, sorption, matrix diffusion and isotope exchange affect the migration of radiocarbon. Precipitation depends commonly on the presence of other ions and pH of the solution. The mobility of ^{14}C is typically represented by the sorption or partition coefficient K_d, which is a parameter used to estimate the migration potential of compounds. Processes between the soil and groundwater define the migration of ^{14}C at this interface. Most of the K_d values for ^{14}C are for the inorganic species of carbon, but some are also for the organic species (Yim & Caron 2006, Sheppard & Thibault 1990). Compared to e.g. uranium, neptunium and technetium which can be regarded as trace contaminant species it has been recognised that solubility and sorption data for carbon species is more complex. It requires the consideration of isotopic exchange with stable carbon (^{12}C, ^{13}C) species of both inorganic and organic form (Small *et al.* 2009).Organic carbon species comprise a very wide range of compounds with carbon-carbon or carbon-hydrogen bonds and the average oxidation state is less than +4. In the case of ^{14}C it is more appropriate to considered it being in either inorganic or organic form rather than its oxidation states. The organic fraction typically accounts for 10–30% of the deposited radioactive waste (Bracke & Müller 2008). For inorganic ^{14}C the primary retention mechanism is precipitation to carbonates (principally $CaCO_3$) under the alkaline conditions in repository environment. Whereas, soluble organic compounds including ionic species, such as carboxylates and more soluble non polar compounds (e.g. alkanes), may be retained by adsorbed to mineral and other material surfaces (Small *et al.* 2009).

The chemical form of ^{14}C in spent fuel and activated metal materials is one of the main issues as it is crucial for its retardation properties. Soluble organic forms may include dissolved methane and C2-C6 alkanes and alkenes, as well as alcohols, aldehydes and carboxylic acids (Small *et al.* 2009). A few studies about the chemical forms and migration behaviour of ^{14}C have been conducted (Yamaguchi *et al.* 1999, Kaneko *et al.* 2003, Sasoh 2004a). Yamaguchi *et al.* (1999) conducted two types of experiments with three types of hull specimen: 1) Short-term test with higher SA/V (surface area to volume of leaching solution) 40 cm^2/L, and 2) Long-term test with lower SA/V 10 cm^2/L. The first leaching test focused on chemical speciation of leached ^{14}C. These experiments were already discussed briefly in section 2.3. along with Zirconium metals. Based on the results of the leaching test and model calculation, ^{14}C was not released immediately by corrosion but was incorporated into the corrosion film and released by diffusion. Yamaguchi *et al.* (1999) evaluated that a minimum period of 20 000 years or longer is required for all ^{14}C to be released from the hull. In the short-term test most ^{14}C was in organic form in the liquid phase. However, the concentration of the leached ^{14}C was too small to identify the chemical species. Similarly in the long-term leaching test ^{14}C was detected in the liquid phase not in the gas phase and most of it was in organic form. Kaneko *et al.* (2003) found both organic and inorganic carbon species in the solution after leaching experiment with ZrC and Fe_3C, both powder mixtures of carbon and zirconium and of carbon and iron. The concentration of total carbon (both organic and inorganic) in the solution was noticed to increase with pH and time but becoming constant after approximately five months. Also Sasoh (2004a,b) have studied the chemical forms of ^{14}C released from activated metals as well as the chemical behaviour of organic ^{14}C under alkaline conditions. Zirconium and carbon steel powders were immersed in alkaline solutions (pH adjusted to 8 and 12.5). The experiments were conducted in a glove box under anaerobic conditions. The concentrations of total carbon, organic carbon and inorganic carbon were measured in both liquid and gas phase. The ratio of the organic carbon compounds to the total carbon content in the liquid phase varied from 55% to 90% and the main compounds were formic acid and acetic acid. In the gas phase the carbon content was very low. It was assumed that organic carbon in the liquid phase is formed through hydrolysis reaction of carbide carbon with water. In the case of atomic carbon, the organic species were assumed to result from the reduction of carbon with oxidizing metal. In the repository conditions (alkaline and reducing) the organic carbon might be oxidized to inorganic compounds depending on pH of the solution (Sasoh 2004b). Figure 10 shows the Eh-pH diagram for C and Zr and the conditions in the repository environment.

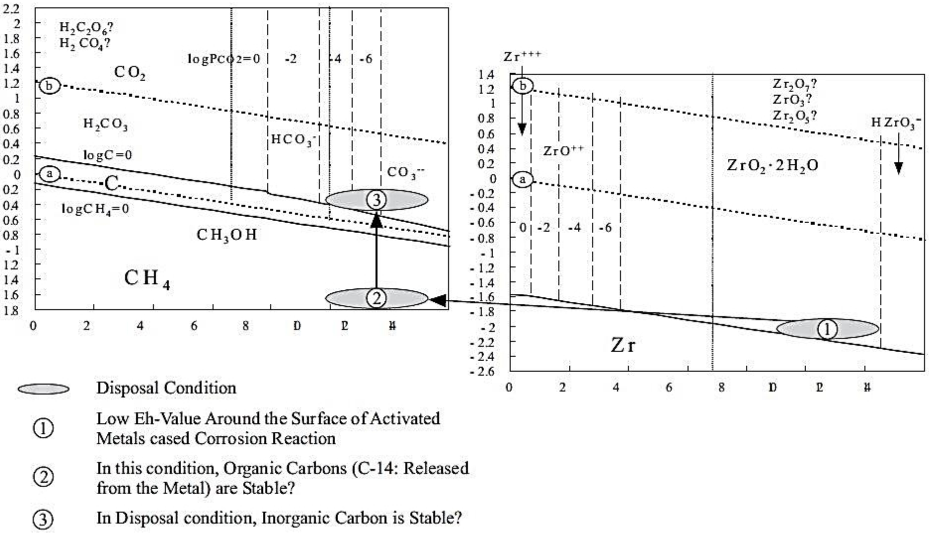
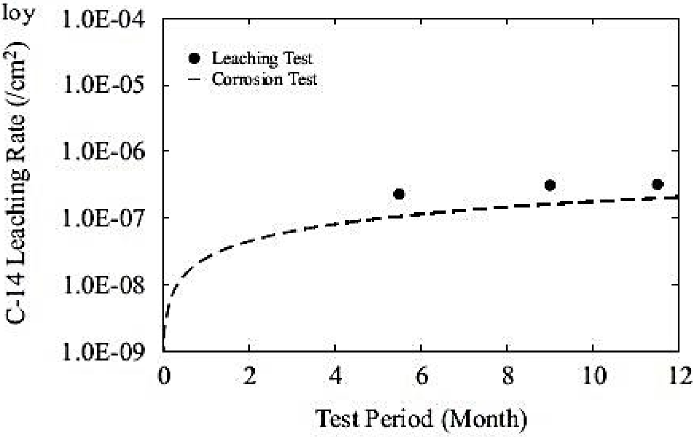


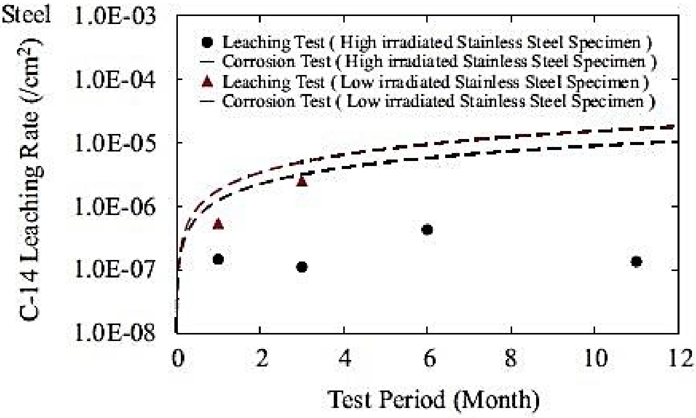
Figure 10. Eh-pH diagram for C and Zr and conditions in the repository environment (Sasoh 2004b).

Kogawa (2004) determined the leaching and corrosion rate of metal specimens in order to provide data for modelling the migration mechanism of ^{14}C. Two types of tests were performed, a) corrosion test for inactive metals, and b) leaching test for activated metals. The corrosion test were conducted under anaerobic alkaline conditions in simulates disposal environment for zirconium and nickel alloys and stainless steel. A polarisation resistance measurement technique was applied to obtain the corrosion parameters. Results showed that the corrosion rates decreased quickly after and became stable over experimental time scale (Figure 11). The corrosion products on the surface of stainless steel and nickel alloy samples were identified as chromium by XPS (X-ray photoelectron spectroscopy) which hinders corrosion. In leaching test, the activated metal samples (zirconium alloy, stainless steel and nickel alloy) were immersed in the test solutions of simulated groundwater for a particular period of time (1–11.5 months) in anaerobic alkaline conditions. The amount of ^{14}C in the test solution after experiment was analysed for inorganic and organic carbon. Most of the released ^{14}C existed in organic form, but the speciation was not examined. The leaching rate of ^{14}C in the high irradiated stainless steel was observed to be lower compared to that of the low irradiated steel. The conclusion given by Kogawa (2004) was that the lower leaching rate was due to the oxide film formed on the surface of the material which functions as passive film.

(a) Zirconium Alloy



(b) Stainless Steel



(c) Nickel Alloy

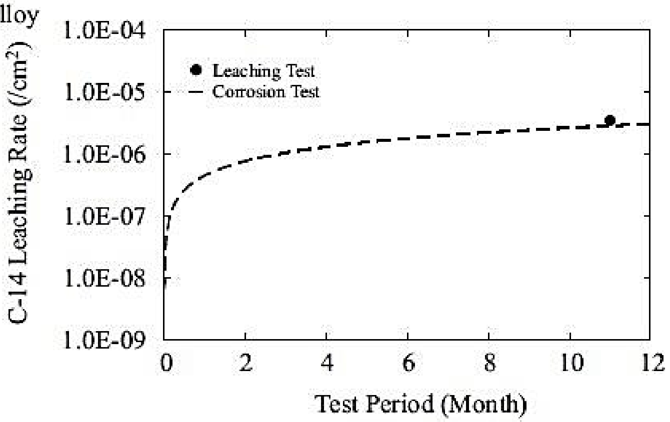


Figure 11. Comparison of the ^{14}C leaching rates from corrosion test and leaching test (Kogawa 2004*)*.

3.4 Carbon analysis

In highly sensitive analysis, filtration is usually an essential procedure in sample preparation. However, filtration can cause contamination by releasing organic compounds, which may interfere in organic analysis. Therefore, care must be taken when processing samples. There are a few studies on the effect of the filtration on water samples. Filtration of samples with relatively low concentrations of dissolved organic carbon (DOC) must be performed with extra caution. Khan & Subramania-Pillai (2007) investigated 19 different filters, including 16 membrane filters and 3 glass fibre filters and found interferences in DOC analysis in 14 out of 19 filters tested. Table 7 presents the results from Khan's investigation. The results suggest that the filters which showed interference in organic analysis should be cleaned by soaking in double distilled water (DDW) before use. The recommended cleaning method for the filters which leached only minor amounts of carbon was to discard the initial filtration volumes. According to Khan & Subramania-Pillai (2007) Gelman FP-Vericel and Gelman HT-Tuffryn filters should be avoided for dissolved organic analyses because of their high organic contamination and cleaning difficulty, whereas Gelman Nylaflo does not introduce any artefacts to organic analysis and can be used even without any pretreatment. However, the results of this study are based only on DDW, and in real water samples the interference might not be the same. Also the quality of the filters can vary from lot to lot, and each batch should be tested separately before use.

Also Norrman (1993) and Karanfil *et al.* (2003) have evaluated different filter membrane materials from major manufacturers for dissolved organic carbon. Their results agreed well with Khan & Subramania-Pillai (2007). Hydrophilic polyethersulphone filters (Osmonics Micron PES and Gelman Supor) and a hydrophilic polypropylene filter (Gelman GH Polypro) were found to be the best options among the filters tested. Karanfil *et al.* (2003) gave even more detailed recommendations about cleaning. According to them filters should be rinsed with a minimum of 30 mL DDW/cm^2 filter surface area prior to use, and during the sample filtration discarding the initial volume. They also remind that before choosing the appropriate filter, it is essential to conduct filtered blank experiments to demonstrate that there is no gain or loss of DOC during the filtration. Similar conclusions were obtained by Norrman (1993). Glass fibre filters such as GF/F filters can sorb DOC and the best suitable filters were those made of polysulphone, which caused no increase in DOC concentration above the initial DDW level. In addition Norrman (1993) leached the filters in a breaker with 1 M HCl for several hours followed by thorough washing with deionised water (MQ). After the filtration the samples were transferred in plastic vials (polypropylene) and acified with 100 µl of 0.75M HCl and stored until used in analysis (within 6 h). Yoro *et al.* (1999) who have studied dissolved organic carbon contamination from filters and storage bottles in seawater samples also concluded that without appropriate initial treatment, polycarbonate, aluminium oxide and polytetrafluoroethylene filters can induce significant DOC contamination. They also found out that only after intensive cleaning with 1% HCl and MQ water, the PFA-Teflon, glass, polyethylene and polycarbonate bottles are suitable material for 10 day-storage for seawater samples.

Table 7. Summary of the results from filter leaching test (DDW = double distilles water) (Khan & Subramania-Pillai 2007).

Filter type	**Interference in the analysis of**				**Suggested cleaning method**
	DOC[1]	*COD*[2]	*BOD*[3]	*BDOC*[4]	
Gelman Versapor	Yes		N[a]	N[a]	Soak in 100 mL DDW for 24 hours
Gelman GN-6	Yes			Yes	Soak in 100 mL DDW for 24 hours
Gelman FP-Vericel	Yes	Yes	Yes	Yes	Soak in 100 mL DDW for 10 days
Gleman HT-Tuffryn	Yes	Yes	Yes	Yes	Soak in 100 mL DDW for 72 hours
Gelman Nylaflo			*N*[a]	*N*[a]	*Requires no pretreatment, however filter at least 100 mL of DDW before use for analysis*
Millipore Nylon	Yes			Yes	Filter at least 150 mL of DDW before use for analysis
Osmotic Magna Nylon	Yes			I[b]	Filter at least 100 mL of DDW before use for analysis
Whatman Nylon	Yes			Yes	Soak in 100 mL DDW for 24 hours
Gelman Supor 200	Yes		N[a]	N[a]	Soak in 100 mL DDW for 48 hours
Gelman Supor 450			*N*[a]	*N*[a]	*Requires no pretreatment, however filter at least 100 mL of DDW before use for analysis*
Gelman SUpor 800			N[a]	N[a]	Requires no pretreatment, however filter at least 100 mL of DDW before use for analysis
Whatman (WCN)	Yes			Yes	Soak in 100 mL DDW for 48 hours
Whatman Nucleopore			N[a]	N[a]	Requires no pretreatment, however filter at least 100 mL of DDW before use for analysis
Gelman GH Polypro	Yes		Yes	Yes	Soak in 100 mL DDW for 48 hours
Cellulose acetate (0.20 µm)	Yes			Yes	Soak in 100 mL DDW for 24 hours
Cellulose acetate (0.45 µm)	Yes			Yes	Filter at least 150 mL of DDW before use for analysis
Whatman GF/F	Yes		N[a]	N[a]	Filter at least 150 mL of DDW before use for analysis
Gelman A/E	Yes			Yes	Soak in 100 mL DDW for 24 hours
Whatman 934-AH			N[a]	N[a]	Requires no pretreatment, however filter at least 100 mL of DDW before use for analysis

[1] *Dissolved Organic Carbon,*
[2] *Chemical Oxygen Demand,*
[3] *Biochemical oxygen demand,*
[4] *biogegradable dissolved organic carbon*

[a] *N = not tested*
[b] *I = inconclusive*

4. Summary

The safety of nuclear-waste management relies mainly on the immobilization of radioactive constituents and long-term isolation from the biosphere (Bairi *et al.* 2010). Long-term exposure of materials in a repository may result in significant alterations in their structure. Due to this, various forms of degradation can be expected such as corrosion of metals. The activated decommissioning wastes including the reactor pressure vessel and its internals made of stainless steel, as well as, spent fuel claddings and graphite used as a moderator or reflector in a reactor contain nitrogen as impurity. ^{14}C is generated as a result of nuclear reactions involving nitrogen (^{14}N) or ^{13}C atoms in these materials. The fate of ^{14}C depends on the form in which ^{14}C is present. It is assumed that if nitrogen is originally present as nitrides the resulting ^{14}C may be present as carbide (Hicks *et al.* 2004). At the same time carbon may also be present in elemental form in steel and remain in solid form after corrosion, but as carbide it is hydrolysed with water to produce hydrocarbons. Clearly higher proportion of ^{14}C from activated metals is released in organic form compared to inorganic form, which affects also the transport characteristics. The small organic molecules (short-chain carboxylic acids, alcohols and aldehydes) exhibit significant sorption capacity. In inorganic form as CO_2, ^{14}C is likely to be retarded in alkaline systems due to precipitation of calcite, whereas reduced to methane (CH_4) may lead to more rapid transport (Johnson & Schwyn 2004).

Considerably larger proportion of ^{14}C was observed to be released in gaseous phase from irradiated graphite compared to aqueous phase in a long-term experiment (Marshall *et al.* 2011). According to Japanese research small organic molecules were released in leaching studies of moderator and reflector graphite samples from the Tokai (Magnox) reactors, but could not be identified (NDA 2012). Compared with the reactive metals, steels and Zircaloy have very low corrosion rates under alkaline, anaerobic disposal conditions which make them difficult to measure (NDA 2012). In Zircaloy, ^{14}C is assumed to be present as stable zirconium carbide which may be released in organic form in the liquid phase (Hicks 2004). As in the case of graphite, the organic species detected were low-molecular weight alcohols, carboxylic acids and aldehydes. There are large uncertainties concerning the average inventories of ^{14}C in the spent fuel. The main errors arise from uncertainties in the concentrations of the precursor nuclides. The chemical form of ^{14}C in the UO_2 is assumed to be an elemental carbon and carbide. The leaching experiments indicated that ^{14}C was readily released in to solution as gaseous form (CO_2) (Neal *et al.* 1987).Experiments on inactive steel have suggested that carbon may be released from stainless steel as water soluble organic species, but there is also some evidence for the release as volatile compound (NDA 2012). The specific iron-water experiments suggest that both the carbide carbon and the reduction of aqueous CO_2 could be the sources of hydrocarbons in solution (Hardy & Gillham 1996, Deng et al. 1997).

One concern in highly sensitive carbon analysis is filtration which may cause incorrect results by either releasing or sorbing organic compounds. This is especially important issue to be considered in the case of non-radioactive ^{12}C experiments. The majority of the investigated filters were found to introduce contaminants to DOC analysis (Khan & Subramania-Pillai 2007). The results suggested that the filters should be cleaned by soaking in double distilled water (DDW) before use or at least to discard the initial filtration volumes. The best materials for DOC analysis were found to be hydrophilic polyethersulphone and hydrophilic polypropylene which induced least interference.

Object of this literature survey was to examine the present status of ^{14}C research in nuclear waste management field, particularly the leaching of ^{14}C under repository conditions. It has become clear that there is very little conclusive knowledge and evidence on the form and fate of carbon-14 in irradiated steel materials. A need for careful assessment of the different routes of ^{14}C production in neutron-activated materials and its chemical form and transport is required.

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Title	**Leaching of ^{14}C in repository conditions** **Transport and speciation**
Author	Tiina Heikola
Abstract	Long-term exposure of materials in a repository may result in significant alterations in material structures. The activated decommissioning wastes including the reactor pressure vessel and its internals made of stainless steel, as well as, spent fuel claddings and reactor graphite contain nitrogen as impurity. ^{14}C is generated as a result of nuclear reactions involving nitrogen (^{14}N) or ^{13}C atoms in these materials. ^{14}C is one of the most important radionuclides when considering safe disposal of nuclear waste due to its long half-life. Both organic and inorganic carbons have been identified in leaching experiments with carbon containing steel, although clearly higher proportion is released as small organic molecules. The origin of these compounds and their reaction mechanisms is not fully understood. The specific iron-water experiments suggest that both the carbide carbon and the reduction of aqueous CO_2 could be the sources of hydrocarbons in solution. Carbon analyses are highly sensitive to filtration which may cause incorrect results by either releasing or sorbing organic compounds. The filters should be cleaned by soaking in double distilled water (DDW) before use or at least to discard the initial filtration volumes. The best materials for DOC analysis are hydrophilic polyethersulphone and hydrophilic polypropylene membrane filters which induced least interference. In this literature research, it has become clear that there is very little conclusive knowledge and evidence on the form and fate of ^{14}C in irradiated steel materials. A need for careful assessment of the different routes of ^{14}C production in neutron-activated materials and its chemical form and transport is required.
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Nimeke	**^{14}C:n liukeneminen loppusijoitusolosuhteissa**
Tekijä	Tiina Heikola
Tiivistelmä	Aktivoitunut metallijäte, mukaan lukien ruostumattomasta teräksestä valmistettu ydinreaktorin paineastia ja sen sisusta sekä käytetyn polttoaineen suojakuori ja reaktorin hidastinaine grafiitti, sisältävät typpeä epäpuhtautena. ^{14}C muodostuu pääasiassa säteilyn vaikutuksesta näissä metallimateriaaleissa olevista alkuaineista (^{14}N ja ^{13}C). Pitkän puoliintumisaikansa sekä sen kallioperässä kulkeutumiseen liittyvien epävarmuuksien takia ^{14}C on olennainen nuklidi tarkasteltaessa ydinjätteen loppusijoituksen turvallisuutta. Tutkimusten perusteella ^{14}C voi metallimateriaaleista vapautuessaan esiintyä sekä orgaanisena että epäorgaanisena hiilen spesieksenä. Selvästi suuremman osan on kuitenkin havaittu esiintyvän lähinnä lyhytketjuisina orgaanisina yhdisteinä, mutta niiden alkuperä ja muodostumismekanismit eivät ole täysin selvillä. Muutamassa artikkelissa (Deng *et al.* 2007 ja Hardy & Gillham 1996) on pyritty selvittämään erityisesti rautametalli-vesisysteemeissä muodostuvien hiilivetyjen hiilen alkuperää. Sekä veteen liuenneen hiilidioksidin (CO_2) pelkistyminen että metallissa olevan karbidimuotoisen hiilen uskotaan molempien olevan mahdollisia lähteitä. Analysoitaessa hiilen määrää (TIC/TOC) vesinäytteestä näytteiden suodatus saattaa aiheuttaa ongelmia. Suodattimet saattavat joko lisätä tai vähentää näytteen todellisen hiilen pitoisuutta sitomalla tai luovuttamalla hiiltä membraanistaan. Ennen suodatusta suodattimet tulisikin pestä liottamalla niitä ionivaihdetussa vedessä tai vähintään huuhtelemalla suodattimien membraani ennen käyttöä. Selvityksen mukaan parhaat suodatinmateriaalit DOC-analyyseihin (liuennut orgaaninen hiili) ovat hydrofiiliset PEP- ja PP-membraanit. Kirjallisuusselvityksen edetessä on käynyt selväksi, ettei kirjallisuudesta löydy yhtenevää ja yksiselitteistä tietoa ^{14}C:n muodostumis- tai kulkeutumismekanismista aktivoituneesta metallijätteestä loppusijoitusolosuhteissa, ja lisätutkimukset aiheeseen liittyen ovat paikallaan.
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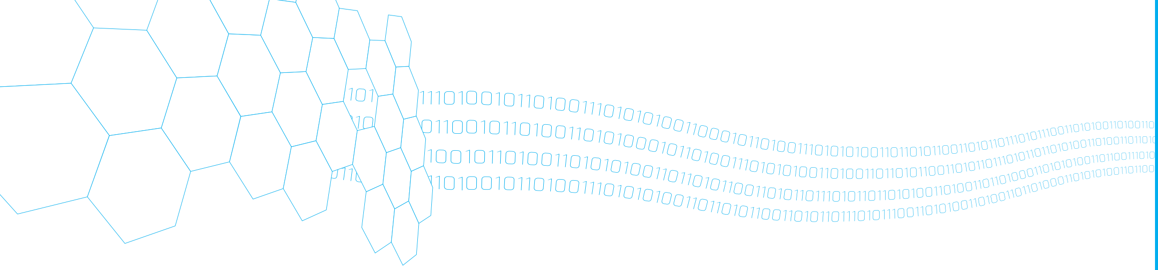

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