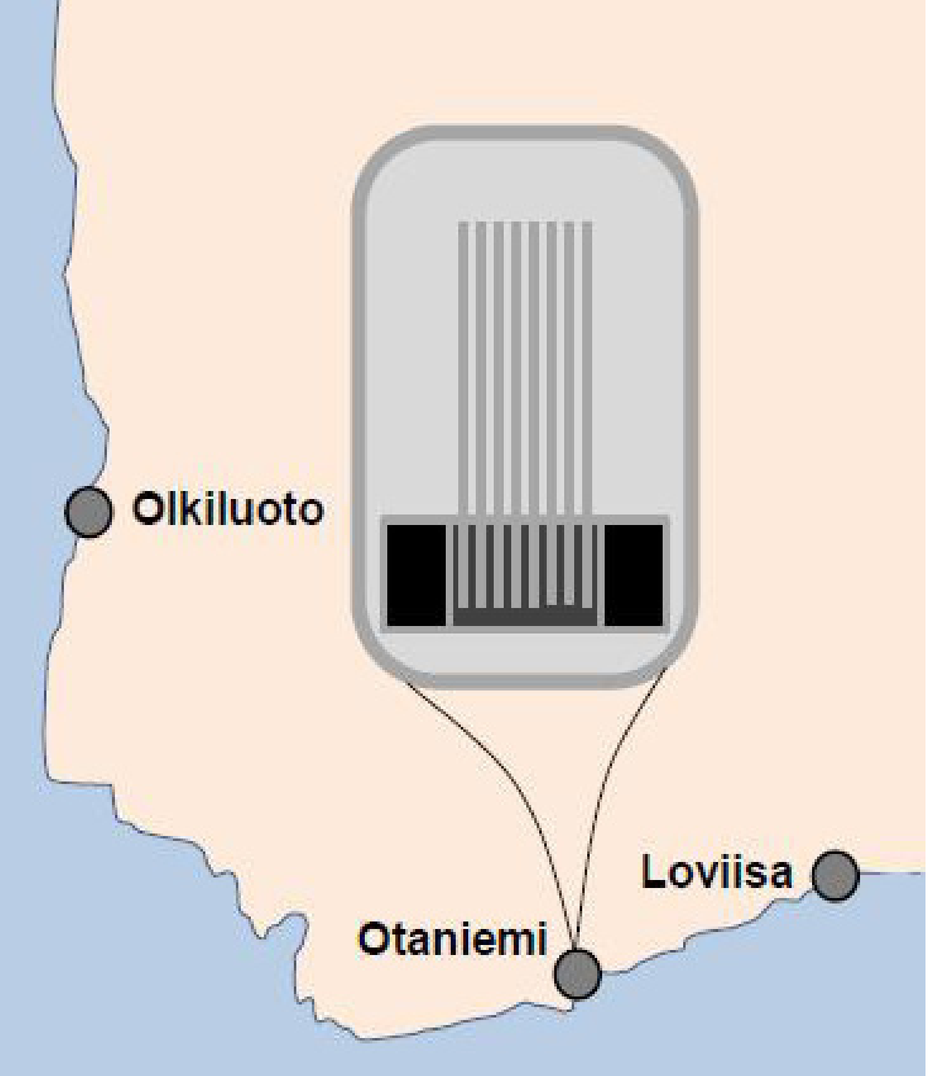

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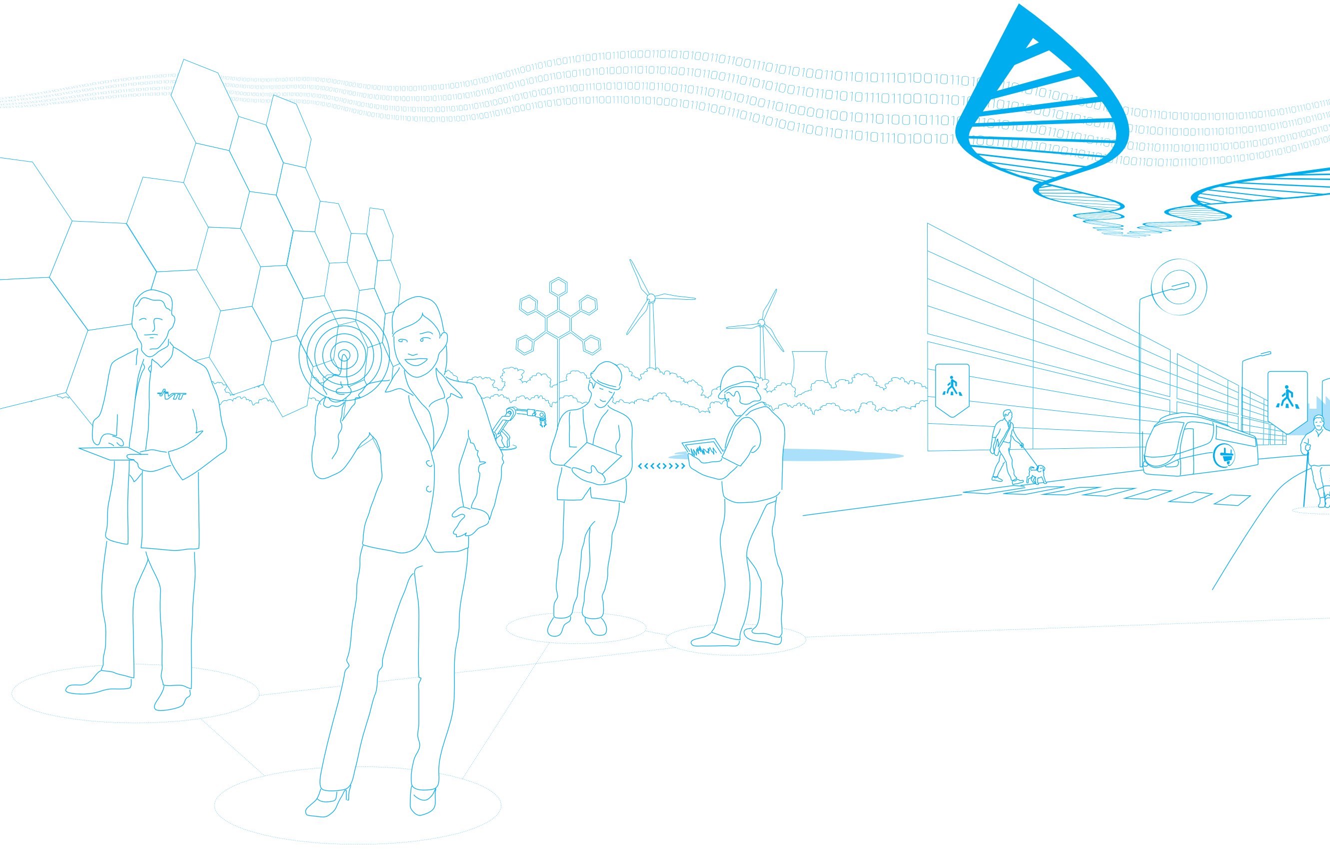
Chemical aspects on the final disposal of irradiated graphite and aluminium

A literature survey

Torbjörn Carlsson | Petri Kotiluoto | Olli Vilkamo |
Tommi Kekki | Iiro Auterinen | Kari Rasilainen


VTT

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Chemical aspects on the final disposal of irradiated graphite and aluminium
A literature survey

Kemiallisia näkökohtia säteilytetyn grafiitin ja alumiinin loppusijoituksesta. Kirjallisuusselvitys.
Torbjörn Carlsson, Petri Kotiluoto, Olli Vilkamo, Tommi Kekki, Iiro Auterinen & Kari Rasilainen. Espoo 2014. VTT Technology 156. 57 p. + app. 1 p.

Abstract

The Finnish FiR 1 TRIGA Mark II reactor is facing shut-down after more than 50 years of operation. The decommissioning of the reactor is planned to start during fall 2015. The management and final disposal of the decommissioning waste require knowledge about, among other things, the possible waste-related chemical reactions and the effects of such reactions on long-term safety.

The above warrants the rationale for the literature survey, which was conducted to collect information on:

i) The chemical behaviour of irradiated aluminium and graphite in FiR 1 decommissioning waste under expected final repository conditions.

ii) The international practices concerning the management and final disposal of irradiated aluminium and graphite.

iii) The experimental techniques for determining the chemical form (organic or inorganic) of the ^{14}C released from graphite waste.

The report describes initially the FiR 1 TRIGA reactor, its associated decommissioning waste and foreseen final disposal conditions. The main part of the report focuses on the chemical behaviour of aluminium and graphite under such conditions. In addition, a few examples are provided concerning available methods for managing irradiated graphitic waste and for measuring the contents of organic and inorganic ^{14}C in irradiated graphite. Finally, the report proposes outlines for some experiments to be conducted at VTT in order to determine the release rates of organic and inorganic ^{14}C from the FiR 1 decommissioning waste.

Keywords FiR 1 TRIGA reactor, decommissioning waste, final disposal, graphite, aluminium

Kemiallisia näkökohtia säteilytetyn grafiitin ja alumiinin loppusijoituksesta
Kirjallisuusselvitys

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Tiivistelmä

Suomen FiR 1 TRIGA Mark II -reaktori on ollut käytössä yli 50 vuotta ja on nyt päätetty sulkea. Reaktorin käytöstäpoisto on tarkoitus aloittaa syksyllä 2015.

Purkujätteen huolto ja loppusijoitus edellyttävät luotettavia tutkimustietoja, muun muassa mahdollisista jätteisiin liittyvistä kemiallisista reaktioista ja tällaisten reaktioiden vaikutuksesta loppusijoituksen pitkäaikaisturvallisuuteen.

Tämä kirjallisuustutkimus koostuu pääosin seuraavista aiheista:

i) alumiinin ja grafiitin mahdolliset kemialliset reaktiot loppusijoitusolosuhteissa

ii) säteilytetyn alumiinin ja grafiitin käsittelyn ja loppusijoituksen raportoidut kansainväliset käytännöt

iii) ^{14}C:n kemiallisen muodon (orgaaninen tai epäorgaaninen) määrittäminen säteilytetylle grafiitille.

Raportissa kuvataan aluksi FiR 1 TRIGA -reaktoria, sen purkujätettä ja purkujätteiden odotettavissa olevia loppusijoitusolosuhteita. Suurin osa raportista kohdistuu alumiinin ja grafiitin kemialliseen käyttäytymiseen loppusijoitusolosuhteissa. Raportti antaa esimerkkejä säteilytetyn grafiitin käsittelystä ja loppusijoituksesta ulkomailla ja kuvaa raportoituja kokeellisia menetelmiä, joilla voidaan määrittää orgaanisen ja epäorgaanisen kemiallisen muodon pitoisuuksia säteilytetyn grafiitin ^{14}C:sta. Lopuksi pohditaan alustavasti kokeellista tutkimusta, jolla voitaisiin määrittää orgaanisen ja epäorgaanisen ^{14}C:n vapautuminen FiR 1 -purkujätteestä.

Avainsanat FiR 1 TRIGA reactor, decommissioning waste, final disposal, graphite, aluminium

Preface

The literature survey aims to study good practices reported in open literature concerning chemical aspects of the final disposal of irradiated graphite and aluminium.

The starting point of the report is VTT's decision to shut down its research reactor Triga Mark II. Therefore, this report aims to bring reported scientific views to the planning of the decommissioning of the reactor.

The research prospects presented in the report are preliminary ideas for possible use in the forthcoming decommissioning planning.

List of acronyms and concepts

AGOT	AGOT is a brand of reactor graphite manufactured in the past by U.S. National Carbon Company
BNCT	boron neutron capture therapy
Graphite	graphite refers in this report to nuclear graphite, or reactor graphite; a synthetic material manufactured from filler coke and pitch, see Appendix A
HLW	high-level waste
IAEA	International Atomic Energy Agency
I-graphite	irradiated graphite
ILW	intermediate-level waste
KAJ	final repository for intermediate-level waste
KPA	interim storage facility for spent fuel
LILW	low- and intermediate-level waste
LLW	low-level waste
MAJ	final repository for low-level waste
NPP	nuclear power plant
VLJ	repository for operational waste
SFR	the Swedish repository for short-lived low- and intermediate-level waste

Contents

Appendix A: Nuclear graphite

1. Introduction

1.1 Background

The decommissioning waste from the FiR 1 research reactor contains, among other things, metallic aluminium and irradiated graphite. These components are not present in the main waste stream of nuclear power reactors in Finland and therefore require special consideration in the performance assessment of waste repositories.

In addition, there is about 1 350 kg of Al-rich FLUENTAL™ moderator[1] close to the reactor core. There is presently no decision on how to treat the FLUENTAL™. The main options are either to sell the material abroad or to include it in the decommissioning waste.

The presence of aluminium in decommissioning waste can be problematic, because under final repository conditions aluminium can react with steel items that have been in the nuclear power plants.

In the case of graphite, ^{14}C requires consideration in the long-term safety analyses. In FiR 1, ^{14}C is mainly created by the irradiation of N_2, which is present in the air-filled pores in the graphite. During release and transport of ^{14}C from the graphite, there is a possibility that ^{14}C is present in a soluble organic form. The graphite used in nuclear reactors is a synthetic product, the production of which is briefly described in Appendix A.

Graphite is used as a moderator in, for example, RBMK-, Magnox and AGR-reactors, and activated graphite has been produced in large amounts. The amount of ILW graphite in the UK was, for example, 81 000 tonnes by April 2010 (NDA 2011).

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[1] The Boron Neutron Capture Therapy (BNCT) at VTT utilized the FiR 1 TRIGA reactor as a source for the neutron beam. The fast fission neutrons from the reactor needed to be slowed down to the epithermal energy range (0.5 eV–10 keV) prior to reaching the patient. The epithermal neutrons were produced in a block of FLUENTAL™ set between the the reactor and the patient. FLUENTAL™ is a patented material that has been developed and produced by VTT (Auterinen & Salmenhaara 2008, Savolainen et al. 2013). The composition of FLUENTAL™ is AlF_3 (69 w-%), metallic aluminium (30 w-%) and LiF (1 w-%). The manufacturing process is based on a hot isostatic pressing technique, which results in a FLUENTAL™ product consisting of solid blocks with a density of 3 000 kg/m^3.

The decommissioning of the FiR 1 reactor leaves VTT with two options; to sell it abroad or to dispose of it together with the other decommissioning waste. At present, both options are considered and the final decision will be made at a later stage.

According to present plans at VTT (Vuori & Kotiluoto 2013), the decommissioning waste from the FiR 1 reactor might be placed in the repository for low- and medium-level waste owned by the Finnish nuclear power companies. This plan has been discussed between Fortum, TVO and VTT. The planning work revealed a need to improve the knowledge among the Finnish experts concerning final disposal aspects of decommissioning waste that contains aluminium and graphite. In the first step, knowledge was improved by performing a literature survey to collect experiences from other decommissioning and waste management studies conducted abroad. In the second step, experimental work may also be carried out in the future in order to complement the knowledge gained from the literature study.

This study does not deal with the treatment options including exemption and the technical barriers which are needed in a disposal system. Another topic will also be tackled separately, which is the real safety case for the relatively small amounts of aluminium and graphite for final disposal from the FiR 1 research reactor in the final disposal system for operational, service and decommissioning waste of the nuclear power plants.

1.2 Literature survey

The objective of the literature survey was twofold. Firstly, to collect information on international experiences from the management of aluminium and graphite in decommissioning waste. Secondly, to learn about the state-of-the-art concerning the behaviour of aluminium and graphite under repository conditions, with special emphasis on:

- The interaction between aluminium and steel under disposal conditions
- The corrosion of aluminium under disposal conditions
- The compound form of the ^{14}C in graphite (inorganic / organic)
- The ^{14}C release and distribution of graphite (also including the combined form)
- Plan for the further studies.

2. The FiR 1 TRIGA Mark II reactor

The Finnish FiR 1 reactor is a TRIGA Mark II open tank reactor with a graphite reflector (Auterinen & Salmenhaara 2008). The core consists of about 80 TRIGA fuel elements, four control rods, some graphite elements and irradiation positions. The reactor was put into operation in 1962. In order to achieve greater neutron flux, the power of the reactor was raised from 100 kW to 250 kW in 1967. Originally, the FiR 1 reactor included a thermal column, created by graphite blocks. In 1996, an epithermal neutron beam was constructed based on a new neutron moderator material, FLUENTAL™, developed at VTT (Auterinen 2007 and references therein).

The FLUENTAL™ replaced the graphite of the original thermal column, and the reactor building was renovated and turned into a BNCT facility. Clinical trials for various brain tumours were performed from 1996 to 2012. The FLUENTAL™ was originally developed for reactor-based BNCT, but it is also an excellent moderator for accelerator-based neutron sources for BNCT (Salehi et al. 2012). A comprehensive description of the FiR 1 reactor, the FLUENTAL™ moderator, etc., is found in Auterinen (2007). The FiR 1 reactor will be shut down for economic reasons and subsequently dismantled during 2015 (Vuori & Kotiluoto 2013).

The reactor core is schematically described in Figure 2.1. The reflector consists of circular graphite blocks, which are covered by watertight aluminium cladding. Next to the reflector are a fission chamber and three ionization chambers, which are used for measuring the reactor power. Some of the main characteristics of the reactor are presented in Table 2.1. The graphite used in the FiR 1 contains a network of interconnected air-filled pores. The irradiation of the air in these pores leads to the production of ^{14}C, mainly via the $^{14}N(n,p)\,^{14}C$ reaction (see below). Preliminary β activity measurements on irradiated graphite blocks removed from the original thermal column indicate that the ^{14}C is evenly distributed throughout the whole graphite blocks (Kekki & Kotiluoto 2012). Most of the graphite consists of reactor grade graphite with a porosity of ~30% (Kekki 2013). Based on the General Atomics FiR 1 TRIGA mechanical maintenance and operating manual, the original thermal column graphite is AGOT brand. It is not explicitly stated in the manual whether the reflector graphite is the same brand. AGOT is a pitch-bonded graphite, known to be a very good insulator, but no longer commercially available (Woodcraft et al. 2003). The porosity of the AGOT in the FiR 1 reactor has not been determined to date. According to general information supplied by the manufacturer, AGOT typically has a porosity of 24% (National Carbon Company 1955).

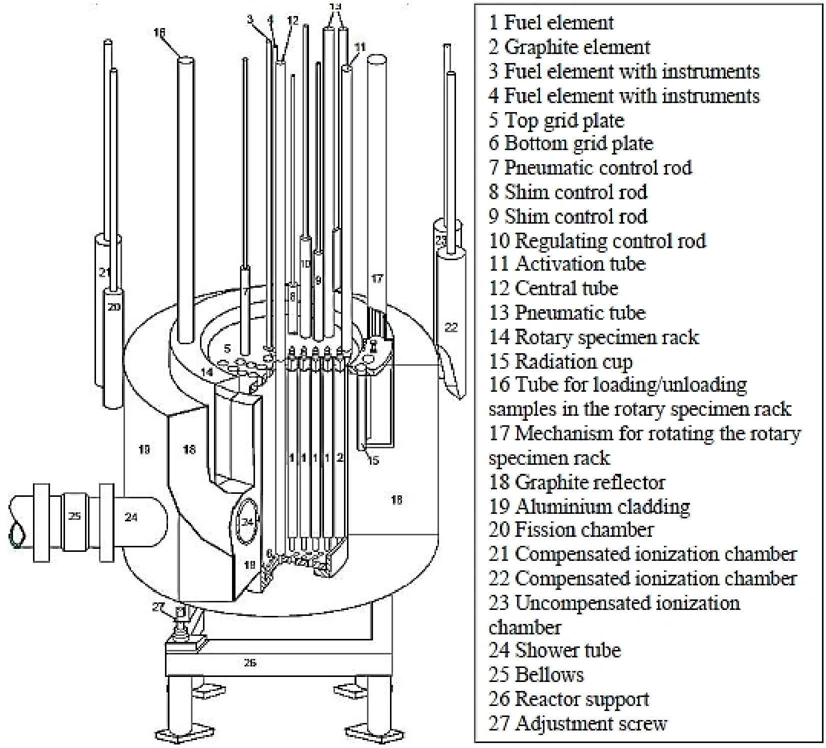

Figure 2.1. The FiR 1 reactor core (Vuori & Kotiluoto 2013).

Nitrogen in the graphite pores is converted to ^{14}C, and for this reason reliable porosity values are needed for inventory calculations. The inventory of VTT's graphite has been estimated both by modelling and by measuring the ^{14}C content by a carbon analyser (Junitek Oxidizer). Samples obtained from the combustion and CO_2 absorption system were analysed by liquid scintillation counter.

The difference between the calculated and measured results was large (Viitanen 2012). There are probably two reasons for this. First, the modelling was performed without quantitative knowledge about the impurity content in the graphite. Second, the modelling was done without considering the air content in the graphite pores, which underestimated the amount of nitrogen present.

This report focuses only on the graphite and the metallic aluminium directly associated with the reactor. A special form of irradiated aluminium is found in the FLUENTAL™ neutron moderator, which is located next to the reactor. The aluminium content comprises a mixture of 30% metallic Al (by weight), 69% AlF_3, and 1% LiF (e.g., Savolainen et al. 2013, Auterinen & Hiismäki 1994). The dimensions and the relative position of the FLUENTAL™ moderator are shown in Figure 2.2.

Tables 2.2–2.4 present estimated amounts of different waste types due to the FiR 1 decommissioning. Further information concerning the FiR 1 decommissioning waste is found in Vuori & Kotiluoto (2013).

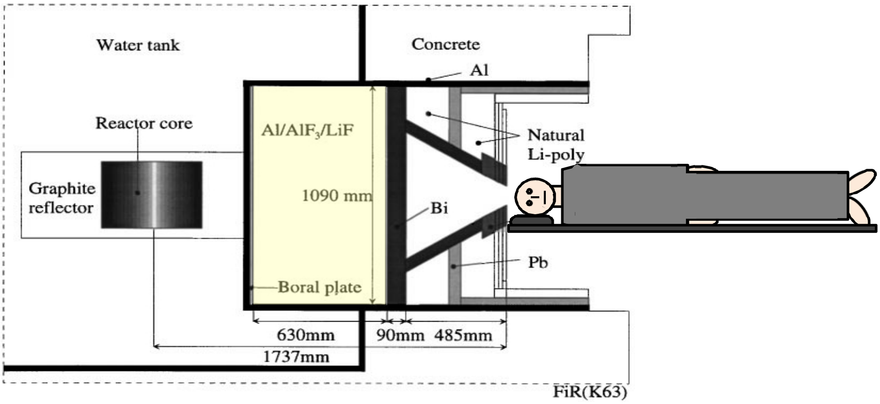

Figure 2.2. The Finnish BNCT beam facility layout with the Al/AlF$_3$/LiF FLUENTAL™ moderator block (indicated by the yellow area). The approximate position of a patient is schematically indicated (modified from Tanner et al. 1999).

Table 2.1. Some characteristics of the FiR 1 reactor (Auterinen & Salmenhaara 2008).

Maximum steady-state thermal power	250 kW
Maximum pulse power (duration ~30 ms)	250 MW
Maximum excess reactivity	4 $
Maximum thermal flux	$1 \cdot 10^{13}$ n/cm^{2}s
Uranium-zirconium hydride	8 or 12 weight-%, rest Zr with 1 weight-% H
Uranium enrichment	20 weight-% ^{235}U of the U
Core loading	2.7 kg ^{235}U (13.5 U)
Fuel element cladding	0.76 mm aluminium or 0.5 mm stainless steel
Dimensions of the active configuration	355 mm x 435 mm
Control rods	Four boron carbide control rods

Table 2.2. Estimated amounts of FiR 1 decommissioning waste and total activity (Vuori & Kotiluoto 2013).

	m (kg)	**A (Bq)**
Activated parts		
- **Steel**	3 556.4	$2.36 \cdot 10^{13}$
- **Al**	3 932.9	$6.39 \cdot 10^{11}$
- **concrete**	10 900	$8.27 \cdot 10^{10}$
- **graphite**	5 125.4	$4.60 \cdot 10^{10}$
Contaminated parts		
- **steel**	2 072.7	$2.76 \cdot 10^{8}$
- **Al**	365.5	$9.4 \cdot 10^{7}$
Mixed decommissioning waste and ion exchange resin	2 000	$4.30 \cdot 10^{7}$
Sum	27 960	$2.44 \cdot 10^{13}$

Table 2.3. Estimated nuclide inventory in activated aluminium (Vuori & Kotiluoto 2013).

Nuclide	$t_{1/2}$	**A (Bq)**	**Fraction of total activity**
Sc-46	83.9 d	1.11×10^{8}	1.74×10^{-4}
Mn-54	312.5 d	4.43×10^{9}	6.93×10^{-3}
Fe-55	2.6 a	3.15×10^{11}	0.493
Co-60	5.263 a	1.55×10^{8}	2.42×10^{-4}
Ni-63	100 a	4.90×10^{7}	7.67×10^{-5}
Zn-65	243.8 d	3.19×10^{11}	0.500
Total		6.39×10^{11}	1.00

Table 2.4. Estimated amounts of activated graphite and total activities (Vuori & Kotiluoto 2013).

	m (kg)	**A (Bq)**
Reflector	600	4.52×10^{10}
Graphite element	4.9	7.15×10^{8}
In storage	4 520	8.36×10^{7}
Pulse rod	0.5	4.32×10^{7}
Total	5 125.4	4.60×10^{10}

3. Final disposal conditions

The waste management plan is based on immediate dismantling after the final shutdown of the FiR 1 reactor. The decommissioning waste is preliminarily planned to be disposed of in a Finnish repository located in the bedrock. The final decisions concerning where and how the waste will be disposed of are, however, still open. Salmenhaara (2008) presents plans for disposal at the Loviisa NPP, according to which the decommissioning waste is planned to be placed at a depth of 110 m in the repository to be constructed next to the Loviisa nuclear power plant. Similar indications are also given by STUK (2008):

> "Low and intermediate level waste generated from the operation of the research reactor FiR 1 is stored at the reactor facility until decommissioning. Disposal of the operational and decommissioning waste from FiR 1 in the disposal facility at Loviisa site is under discussion. The additional wastes arising from the FiR 1 decommissioning were taken into account in the safety assessment by Fortum. However, no formal agreement or decision has yet been made between VTT and the utility."

Kustonen (2010) on the other hand, notes that the FiR 1 decommissioning waste will be disposed of in one of the waste repositories at either Olkiluoto or Loviisa. The disposal alternatives are still held open, both in a document presenting management plans for the FiR 1 decommissioning waste (Vuori & Kotiluoto 2013) and in a recent environmental impact assessment (Pöyry 2013).

The possibility of disposing of the FiR 1 decommissioning waste at the Olkiluoto NPP includes two options: the HLW repository and the LILW VLJ repository. The planned HLW repository is based on the well-known KBS-3 concept. Details concerning its two alternative designs – KBS-3V and KBS-3H – are presented elsewhere, see e.g. Posiva (2013) and references therein. The fuel from FiR 1 will possibly be stored in the HLW repository, while LILW like irradiated graphite and aluminium possibly is to be stored in the VLJ repository. Figure 3.1 shows the layout of the VLJ repository with its planned extensions.

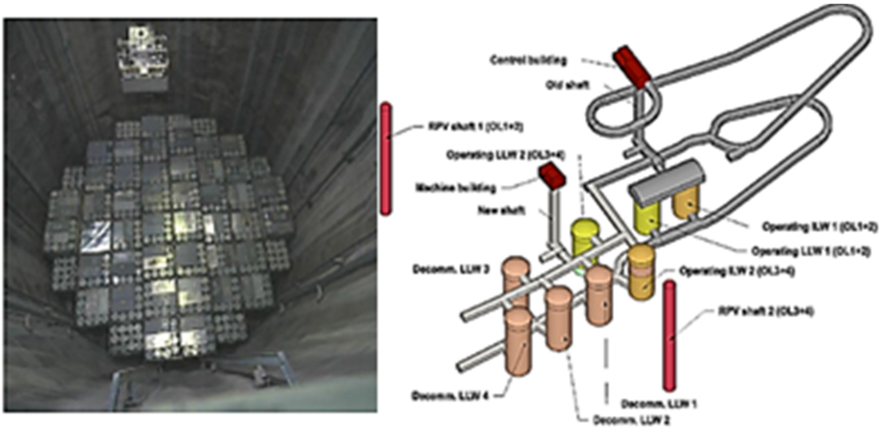

Figure 3.1. The Olkiluolto low- and intermediate-level waste repository. Left: LLW drums in the disposal silo (STUK 2008), right: cross-sectional view of the repository lay-out with planned extensions (Nykyri et al. 2008, Posiva 2013).

The Olkiluoto VLJ repository consists of two silos at a depth of 60 to 95 m in tonalite bedrock, one for solid LLW and the other for bituminized ILW (e.g. STUK 2008). The silo for solid LLW is a shotcreted rock silo, while the silo for bituminized waste consists of a thick-walled concrete silo inside a rock silo where concrete boxes containing drums of bituminized waste will be emplaced. The LILW from the Olkiluoto 3 reactor will be disposed of in the same repository. The repository will be extended in the future, to be able to receive all the waste from Olkiluoto 1, 2 and 3 units during the planned 60 years of operation of the units (Figure 3.1). The VLJ repository will also be used in the future for disposal of decommissioning waste once the nuclear power plants are closed down, as pointed out by e.g., Äikäs & Anttila (2008). In a safety assessment for the Government's radioactive waste, the pH of the silo water was assumed to be high (12.5–13.0) due to the large amount of crushed concrete present in the KAJ silo. In the MAJ silo the pH might not reach such high values, because the amount of concrete is smaller and also the water exchange rate is faster (Nummi 2012, Nummi et al. 2012).

According to STUK (2008), the wastes are segregated, treated, conditioned, packaged, monitored and stored, as appropriate, before they are transferred to their disposal facilities. At Olkiluoto, wet LILW is immobilized in bitumen before transfer to the disposal facility. Sludge, radioactive concentrates and spent ion exchange resins from liquid waste treatment in Okiluoto 3 are planned to be dried in drums. Solid LLW is, after conditioning, transferred to the disposal facility. Activated metal waste consists of irradiated components and devices that have been removed from the inside of the reactor vessel. So far, this kind of highly activated waste has not been conditioned but is stored at the NPP and is expected to be conditioned and disposed of together with decommissioning waste of a similar type.

Aalto & Valkiainen (1999) mention that drums with waste are packed in concrete casks, containing 12 or 16 drums. The casks are piled layer upon layer in the VLJ concrete silo. The silo will be filled after closure with local surface water from a river nearby. The pH of the water in contact with the concrete structure of the silo will become alkaline and reach a pH value of about 12. Vuorinen (2012) estimates that groundwater in a final repository for nuclear waste may reach a pH that is about 10–12.5 in an environment that contains cementitious material.

Kekki & Tiitta (2000) distinguish between five combinations of ‘waste category’ and ‘package’ in the VLJ final repository, see Table 3.1. Kekki & Tiitta give further details concerning the packages and disposal of LILW at Olkiluoto in Finland and also, *inter alia*, a brief overview of the corresponding handling of waste in some other EU countries. The differences between the waste handling and practical handling seem to be quite small.

Table 3.1. Waste categories and associated package in the VLJ final repository (Kekki & Tiitta and reference therein).

Waste category	Package
Intermediate, bituminized waste	200 L steel drum
Low-active maintenance waste etc.	200 L steel drum or 200 L steel drum compacted to 100 L
Mixed maintenance waste and scrap	1.3 m^3/1.4 m^3 steel box
Mixed maintenance waste and scrap	5.2 m^3 concrete box
Mixed maintenance waste and scrap	Stored without packing

Eurajoki & Kelokaski (2006) made an assessment of the long-term safety of the decommissioning waste from VTT’s FiR 1 reactor in case the waste is disposed of in the Loviisa repository. The study does not include graphite and aluminium, since the available data regarding these elements were incomplete at the time of the assessment. However, Eurajoki & Kelokaski provide a thorough description of the foreseen chemical conditions at the Loviisa repository: The repository caverns will be sealed with massive concrete structures, plugs, which reduce the water flow in and between the tunnels. Blasted and crushed rock is also used as filling materials. The engineered barrier system, consisting of waste packages, sealing of the repository, etc., create conditions which effectively limit the release of radioactive substances from the repository. The large amount of concrete in the repository creates long-standing alkaline conditions where the corrosion of steel and dissolution of minerals is slow. Details concerning the Loviisa final disposal concept, the safety case for the Loviisa LILW repository, as well as results from radiation dose calculations, are found in Eurajoki & Kelokaski (2006).

4. Basic Al corrosion chemistry

The content of metallic aluminium in the FiR 1 decommissioning waste is about 4 300 kg, which consists mainly of ‘activated’ Al and to a minor extent of ‘contaminated’ Al (see Table 2.2). The aluminium will be stored under alkaline conditions together with cementitious and other material. This chapter covers some chemical aspects relevant to the storage of aluminium under such conditions.

4.1 Basic Al corrosion/dissolution chemistry

Metal corrosion, i.e. the gradual destruction of a metal by reaction(s) with chemicals in its environment, occurs in aquatic solutions or in places where metal is exposed to humid conditions. State-of-the-art compilations of the literature dealing with the corrosion of aluminium and aluminium alloys have been performed by the IAEA organization (IAEA 1998, 2003, 2009).

The study by the IAEA (1998) presents results from a state-of-the-art literature survey on the corrosion of aluminium alloys, which contains, i.a., a section on aluminium corrosion with focus on wet storage. Two subsequent publications, IAEA (2003) and (2009), also discuss this matter. Briefly, the above IAEA reports give the same picture of Al corrosion. Several types of Al corrosion are covered briefly; general corrosion, galvanic corrosion, crevice corrosions, stress corrosion cracking, and pitting corrosion. However, this report only discusses the first two types of corrosion, since these are the only ones that are relevant for the present purposes. It should be noted that corrosion science is a fast-growing field, and the picture of corrosion given in the above reviews has recently been somewhat modified (see below).

4.2 General Al corrosion

The solubility of aluminium in an aqueous environment is closely connected to the pH value of the water phase. This is demonstrated in Figure 4.1, which shows the solubility of aluminium oxides vs. pH in pure water. Figure 4.2 provides an alternative way to overview the stability by plotting the electrochemical potential, E, vs. pH in a Pourbaix diagram. It is often claimed that (e.g. IAEA 2009) aluminium alloys are generally resistant to corrosion in aqueous solutions with pH in the approximate range from 4 to 8. The main exceptions are those environments containing aggressive species, mainly chloride ions. In these cases, the oxide film could be attacked and lose its protective effect, leading to subsequent metal corrosion.

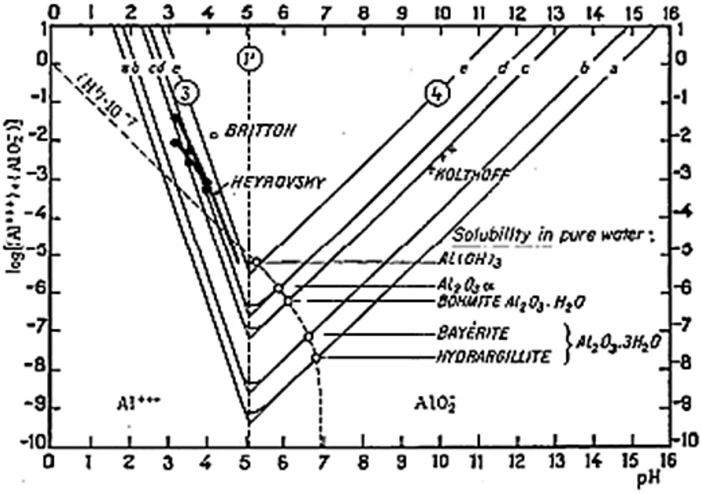

Figure 4.1. Solubility of aluminium oxides in water at 25°C (Pourbaix 1974).

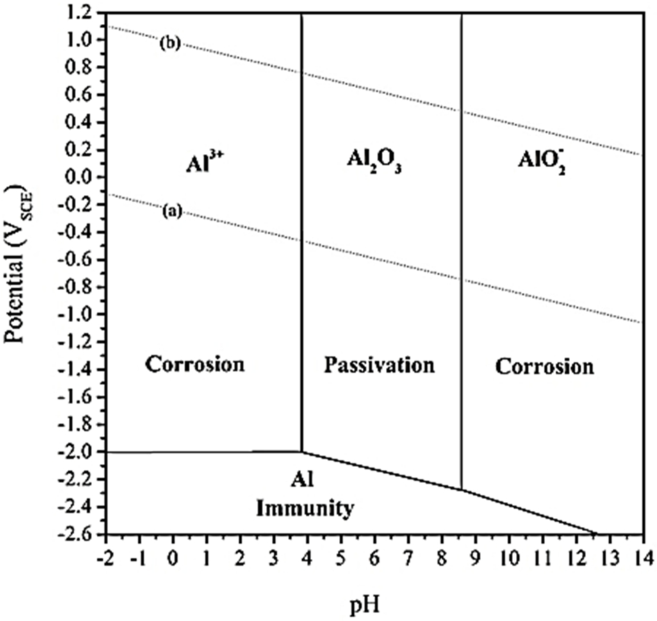

Figure 4.2. E-pH diagram for pure Al at 25˚C in aqueous solution. The lines (a) and (b) correspond to water stability and its decomposed product (Sukiman et al. 2012).

The main types of aluminium corrosion concerning the nuclear fuel performance, especially during long-term interim wet storage in water basins, are (IAEA 2009) localized corrosion (including pitting, crevice, galvanic and inter-granular corrosion). The generalized corrosion is expected where the chemical conditions correspond to acid or alkaline extremes.

In the case of galvanic corrosion, the IAEA (2009) states that "galvanic contact of aluminium with other metals will produce an increase in the electrode potential through intensification of cathodic reactions. This will tend to increment all the electrochemical corrosion processes. In the presence of corrosive species, such as chloride ions, the electrode potential can become higher than the pitting potential Ep and pitting corrosion will occur. Other forms of corrosion, as crevice corrosion, will also be enhanced. In highly pure water, instead, only some increment in the oxidation rate should be expected, which will depend on the temperature and should only affect the vicinity of the electrical contact region."[2]

Sukiman et al. (2012) give an overview of the durability and corrosion of aluminium and its alloys. They state that there is a general consensus for Al and its alloys such that they are resistant towards corrosion in mildly aggressive aqueous environments. The protective oxide layer represents the thermodynamic stability of Al alloys in a corrosive environment – acting as a physical barrier as well as being capable of repairing itself in oxidizing environments if damaged. The corrosion behaviour of Al can be explained and predicted by using thermodynamic principles, as is done in Pourbaix analysis. This results in a Pourbaix diagram showing potential vs. pH based on electrochemical reactions of the species involved, see Figure 4.2.

Pourbaix diagrams give the impression that corrosion prediction is a straightforward process. However, Sukiman et al. (2012) point out that, in actual engineering applications, there are several variables that were not considered by Pourbaix, like (i) the presence of alloying elements in most engineering metals, (ii) the presence of substances in the electrolyte such as chloride (albeit this has been addressed in more modern computations), (iii) the operating temperature of the alloy, (iv) the mode of corrosion, and (v) the rate of reaction. Taking these factors into account is nominally done on a case by case (i.e. alloy by alloy) basis.

Gimenez et al. (1981) point out that the theoretical Pourbaix diagram for the aluminium-water system does not take into account pitting corrosion, the usual form of corrosion for aluminium in chloride-containing environments. To obtain a practical representation of aluminium corrosion usable in sea water, pitting potentials, protection potentials, and uniform attack potentials were measured on aluminium specimens. Figure 4.3 shows the results from such measurements with AA5086 specimens in 3% NaCl solutions buffered within the 4 to 9 pH range. Gimenez et al. extended the plots both to more acidic and more alkaline environments. The potentials limit passivity, pitting corrosion, and uniform corrosion areas in the potential-pH diagram. The results are interpreted on the basis of local pH evolutions

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[2] The excerpt is reproduced with written permission by the IAEA (on 14th January 2014).

during polarization of the specimens. This experimental diagram has been extended both to more acidic and more alkaline environments. Figure 4.3 indicates areas where localized corrosion is highly possible, although the region is supposed to be a passive one (Gimenez et al. 1981). It is also seen that localized attack is possible across the whole range of pH depending on the specific potential. Sukiman et al. therefore stress that one should not rely solely on the Pourbaix diagram as a direct index to actual corrosion rates. Gimenez et al. express the same thing somewhat more bluntly by saying that the theoretical diagram in Figure 4.2 is “practically useless”.

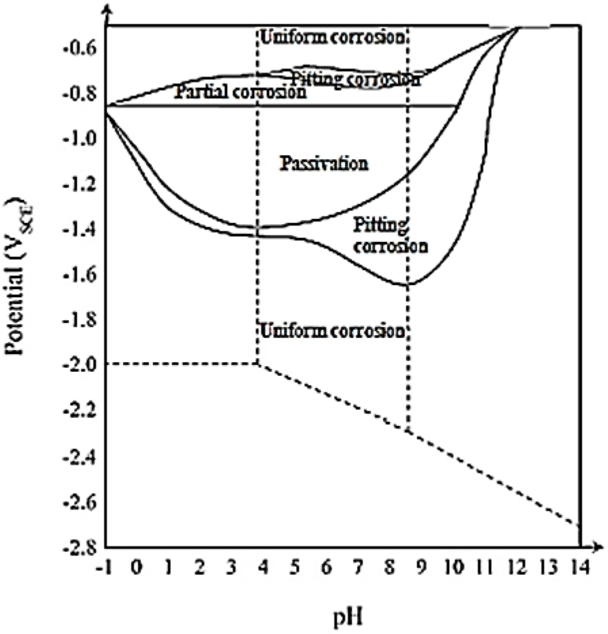

Figure 4.3. Experimental E-pH diagram of the AA5086 aluminium alloy in 0.5 M NaCl solution with extrapolation of pH less than 4 and more than 9. The experiments were performed at 20°C. Dotted lines show the thermodynamic graph (Gimenez et al. 1981).

Generally speaking, Pourbaix diagrams show where certain phases are stable and unstable in an aqueous electrochemical system. However, conventional Pourbaix diagrams suffer from a number of limitations (McCafferty 2010): (i) thermodynamic equilibrium is assumed, although the actual conditions may be far from equilibrium; (ii) kinetics is not considered, i.e. corrosion rates are disregarded; (iii) only single elemental metals are considered and not alloys; (iv) passivation is ascribed to all oxides or hydroxides, regardless of their actual protective properties; (v) localized corrosion by chloride ions is not considered, and (vi) the diagrams apply mostly to the temperature of 25˚C.

Attempts to improve conventional Pourbaix diagrams by including kinetic considerations have been made. Minguzzi et al. (2012), e.g., notice that, as with all predictions made on thermodynamic data, the ability to predict reactivity and the actual stability of phases is related to the kinetics of reactions that depend on pH, temperature and applied potential, and especially when one considers multi-electron transfer reactions, the predictive strength of E-pH diagrams is limited. One way to improve the E-pH diagrams is offered by adding either a third axis or using a colour code, in which case the rate of the investigated reaction is expressed in terms of the current density. A similar approach was used by Zhou et al. (2010) who studied pure Al metal with staircase potentiometric-electrochemical impedance spectroscopy. Zhou et al. produced a kinetic stability diagram for Al using the reciprocal of polarization resistance as a measure of reaction rate, see Figure 4.4. One of the conclusions that Zhou et al. drew from Figure 4.4 was that there are regions of high potential where pure aluminium may be in a thermodynamically stable region, but still not usable due to dissolution processes.

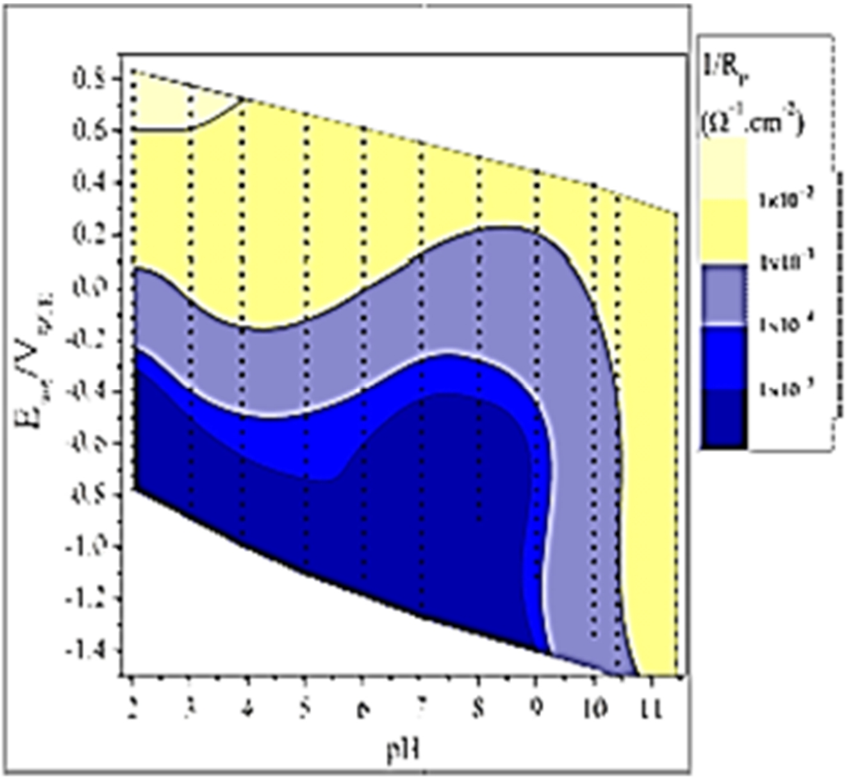

Figure 4.4. Kinetic stability diagram for a polycrystalline Al specimen showing relative reaction rates (expressed as the reciprocal of the polarization resistance) for the E-pH space. Legend: light yellow; fastest reaction, darkest blue: slowest reaction (Zhou et al. 2010).

The corrosion of aluminium becomes more complex when more materials are present. The corrosion between, e.g., flawed areas of the protective aluminium oxide layer, will proceed in the presence of chloride ions according to (Sherif et al. 2011 and refs. therein):

$$Al = Al^{3+} + 3e^{-} \tag{1}$$

$$Al^{3+} + 4Cl^{-} = AlCl_4^{-} \tag{2}$$

The last reaction does not necessarily have to be perfectly correct. For example, Tomcsányi et al. (1989) mention that an oxychloride complex, $Al(OH)_2Cl_2^{-}$, may form instead of the $AlCl_4^{-}$ complex. However, irrespective of the differences in details, both alternatives, in principle, give the same picture of the aluminium chloride interaction: the metal dissolves under complex formation.

Godfrey (2007) discusses metallic material present in decommissioning wastes which will have to be treated for disposal. Godfrey focuses on the situation in the UK where there is a need to treat steels, aluminium, Magnox (a magnesium aluminium alloy) and uranium metals. In the UK, the preferred process for treatment of these wastes is to encapsulate them in a matrix based on ordinary Portland cement, typically blended with blast furnace slag or pulverized fuel ash. As water is present in the cement matrix, even after hydration has occurred, corrosion reactions can take place. This has several significant consequences, like:

- possible generation of hydrogen gas from corrosion reaction;
- possible generation of expansive corrosion products, which may eventually cause degradation of the encapsulation matrix, and
- possible generation of methane and other hydrocarbons formed from the reaction between carbides present in the metallic wastes and waste present in the cement matrix.

Aluminium often forms a protective oxide layer when it is contact with oxygen. As long as the layer is stable, it protects aluminium or aluminium alloys from corrosion. However, Al can corrode, e.g., in an alkaline cement environment although the metal initially contains a layer of protective Al_2O_3 (Godfrey 2007):

$$Al_2O_3 + 2OH^{-} + 7H_2O \rightarrow 2[Al(OH)_4 \bullet 2H_2O]^{-} \tag{3}$$

The aluminium metal can continue to react with the alkaline solution in a following step and thereby produce both hydrogen gas and further amounts of soluble Al-complexes:

$$2Al + 2OH^{-} + 10H_2O \rightarrow 2[Al(OH)_4 \bullet 2H_2O]- + 3H_2 \tag{4}$$

Studies in the UK show that the corrosion properties of metals in cement based matrices depend to a high degree on parameters like:

- storage temperature;
- chemical and physical properties of the encapsulation matrix;
- the exact composition of the waste, e.g., different alloys and purity of the
- metal;
- shape/surface area of the waste encapsulated;
- surface condition of the waste – clean surfaces or presence of protective
- layers, and
- galvanic coupling.

Therefore, only general overviews of corrosion properties of the metals is possible, as data such as corrosion rates and gas generation rates will depend to a large extent on the actual conditions and environment the encapsulated waste will experience.

Waste disposal studies started in the UK during the early 1980s. Aluminium and uranium corrosion in cement has been studied to support the disposal of decommissioning/historic wastes. Less detailed work has been carried out for steel, as it is much less reactive in cement than the other metals assessed and hence is of much lower concern (Goodfrey 2007).

4.3 Galvanic Al corrosion

Generally speaking, galvanic corrosion can take place when two metals of different 'nobility' are in contact with each other in, mostly, an aqueous environment. The relative 'nobility' of a metal is expressed by the galvanic series. The corrosion rate is favoured by the presence of electrolyte. Galvanic corrosion between two metals can formally be described in the following general way:

$$mA + nB^{m+} = nB + mA^{n+} \tag{5}$$

where A and B are two metals with the valency +n and +m, respectively, and A is supposed to be less noble than B according to the galvanic series for metals. The reaction requires the presence of water (or some other liquid) to take place and proceeds faster in the presence of electrolyte.

According to present plans (Vuori & Kotiluoto 2013), activated aluminium is to be packed in five containers consisting of either steel or concrete with a wall thickness of 10 and 24 cm, respectively, and inner dimensions of 1.3 x 1.3 x 1.9 m. The containers will probably also be used in the final disposal of the aluminium. The plausible galvanic corrosion between aluminium and other metals in the FiR 1 waste under foreseen repository conditions is then the galvanic corrosion between aluminium and steel. The above formal reaction then takes the form

$$Al + Fe^{3+} = Fe + Al^{3+} \tag{6}$$

It should be noted that B in the general reaction can also denote graphite or some other electron conductor with a higher potential than aluminium. Higher corrosion rates could then occur due to galvanic coupling via metal-to-graphite contact (Wise 1999, Ek & Mayer 2004).

Ek & Mayer (2004) investigated some of the effects of placing FiR 1 decommissioning waste in Loviisa's final repository. It is noticed that aluminium content in the FiR 1 waste is considerably higher than that in the waste from the Loviisa NPP. Ek & Mayer notice that the combination of (i) groundwater with a high chloride concentration, (ii) high amounts of steel, and (iii) aluminium may lead to a situation where the protective function of the aluminium oxide layer is lost and, consequently, galvanic corrosion will start. However, no exact information is given about the conditions under which the galvanic corrosion might occur. Ek & Mayer state that aluminium metal dissolves under acidic and alkaline conditions, in agreement with the general picture given in, for example, Figure 4.2 above. The pH will remain at an elevated level until all the Portlandite cement $Ca(OH)_2$ in the concrete is dissolved into the water. Only after the Portlandite has been dissolved, will the pH gradually decline and other minerals start to dissolve efficiently. Therefore, a concrete environment forms an effective chemical barrier even after it has lost its mechanical integrity (Atkinson & Marsh 1989). Aluminium metal and aluminium oxide do not dissolve readily in pure water, but compounds like $AlCl_3$•H2O and $Al_2(SO_4)_3$ do. These can have harmful effects on, e.g. fish in lakes with high aluminium concentrations and on humans who use water from wells in contact with repositories containing aluminium waste. Ek & Mayer conclude that the aluminium in the FiR 1 decommissioning waste cannot be disposed of in the Loviisa disposal site without careful safety assessment regarding aluminium dissolution behaviour, or by development of a packing technique which ensures that Al is dissolved at an acceptably slow rate.

The durability of concrete and the temporal development of pH in radioactive waste repositories have been studied in accelerated leach tests by, e.g. Atkinson et al. (1985) and Atkinson & Marsh (1989). Figure 4.5 demonstrates an example of the temporal evolution of pH for sulphate resisting Portland cement leached by a simulated groundwater. Briefly, the engineering lifetime of the cementitious material was estimated to be around 10^3 years, while the alkaline chemical conditions were found to remain much longer. The average pH in the given example was estimated to remain above 10.5 for more than 10^5 years (Figure 4.5). Similar temporal pH developments were more recently presented by JAEA (2007) for fresh reducing high-pH groundwater in contact with fractured cement. The results agree also with those by Höglund (2001) who modelled the long-term concrete degradation processes in the Swedish SFR repository. The modelling study indicated that alkaline conditions will be maintained in the concrete for, at least, a period of 10 000 years.

NEA (2012) stresses however, that it is important to obtain specific information on the properties of the individual cements, including both backfill and encapsulation cements, as well as their behaviour in specific disposal environments.

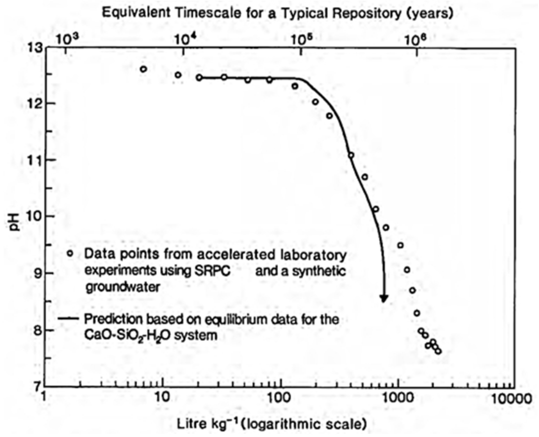

Figure 4.5. Time dependence of pH as cement hydrates dissolve in, and react with, groundwater (Atkinson & Marsh 1989).

4.4 Heat generation

The storage of metallic aluminium under alkaline conditions will lead to corrosion under the simultaneous production of heat. The corrosion products are hydrogen gas and dissolved aluminium as was seen in the above reaction (4). Zhang et al. (2009) describe the aluminium corrosion in a slightly different manner:

$$Al + 3H_2O + OH^- = 3/2\ H_2 + Al(OH)_4^- \qquad (7)$$

The reaction is highly exothermic (heat producing) and its possible heat effects in a repository require some consideration. Moreno et al. (2001) calculated the heat production caused by corroding aluminium waste in the Swedish repository for short-lived low- and intermediate-level waste (SFR). It was assumed that the aluminium would be completely degraded in a few years and that the heat generated by the aluminium corrosion therefore could be quite high. The calculations indicated that the temperature elevation due to heat-generating processes (including also some less important contributions from radiolysis) does not exceed 5˚C in any part of the repository, although locally, the temperature increase could probably be significantly higher. Details concerning the calculations and the underlying assumptions are found in Moreno et al. (2001).

4.5 Gas generation

The storage of metallic aluminium under repository conditions has been presented in a study on gas generation in a deep repository, SFL, designed for the disposal of long-lived low- and intermediate-level waste (Skagius et al. 1999). It was noted that, after closure and saturation of the SFL 3-5 repository, gas can be generated. According to Skagius et al., the main types of gas-forming processes are

- corrosion of steel and other metals in the waste and engineered barriers,
- microbial degradation of organic materials in the repository, and
- radiolytic decomposition of water caused by decaying radionuclides in the waste.

The FiR 1 waste contains steel and aluminium. The respective corrosion reactions for these elements are (Skagius et al. 1999, Moreno et al. 2001):

$$3\ Fe(s) + 4\ H_2O \rightarrow Fe_3O_4(s) + 4\ H_2(g) \qquad (8)$$

and

$$2\ Al(s) + 2\ OH^- + 4\ H_2O \rightarrow 2\ AlO(OH)_2- + 3\ H_2(g) \qquad (9)$$

or alternatively

$$2\ Al(s) + 2\ OH^- + 2\ H_2O \rightarrow 2\ AlO_2^- + 3\ H_2(g) \qquad (10)$$

Both metals thus produce hydrogen gas. The corrosion rates of the metals differ, however, considerably: being about 10^{-3} m/year for aluminium but only about 10^{-6} m/year for steel (Lindgren & Pers 1994). The values are not exact; Savage & Stenhouse (2002), for example, point out that “gas generation rates will depend on corrosion rates and surface areas of the corresponding metals undergoing corrosion. Some uncertainty exists regarding the rates of corrosion/degradation of different materials under repository conditions, which should, therefore, be reflected in a possible range of (bounding) corrosion rates for each type of material considered.” Wiborgh (1995) mention that results from literature compilations indicate that the corrosion rate of steel in anaerobic environments is usually within the range of 10^{-7} to 10^{-5} m/year, while in the case of aluminium in alkaline environment, the corrosion rate can be in the range of 10^{-3} to 10^{-2} m/year. The gas formation calculations by Skagius et al. (1999) were carried out using assumed corrosion rates of 10^{-6} and 10^{-3} m/year for steel and aluminium, respectively. The same assumed values were also used in a Swiss study for calculating the gas formation in a final repository for low- and intermediate level waste (NAGRA 1993). The corrosion rate values chosen by Skagius et al. are supported by relevant experimental data indicating corrosion rates of <0.1 µm/year and ~1 mm/year for steel and aluminium, respectively (Savage & Stenhouse 2002 and references therein).

As indicated by Equations (8) to (10), the metal corrosion produces a considerable amount of hydrogen gas. The gas formation rate due to the corrosion of, e.g. plates, where corrosion at the end is ignored can be expressed as (Skagius et al. 1999):

$$G = A \cdot r \ \cdot \rho \cdot 1/M_V \ \cdot X \cdot V_0 \qquad (11)$$

where G is the gas generation rate (m^3/year) at STP (i.e. the standard temperature of 0°C and the standard pressure of 1 atm), A is the surface area (m^2), r is the corrosion rate (m/yr), ρ is the density of the metal (kg/m^3), M_V is the weight per mole of metal (kg/mol), X is the stoichiometric coefficient (kmol H_2/kmol metal) and V_0 is the molar volume of ideal gas at 0˚C and 1 atm, i.e. 22.4136 m^3 (STP)/kmol gas. Skagius et al. used the following values in calculations of gas formation rates caused by steel corrosion: metal density: 7 800 kg/m^3, molar mass: 55.847 kg/kmol, and a stoichiometric coefficient X (in eqn. 11) equal to 4/3 kmol H_2/kmol Fe. The corresponding values for gas formation caused by aluminium corrosion were 2 700 kg/m^3, 26.9815 kg/kmol, and 3/2 kmol H_2/kmol Al. Skagius et al. do not explicitly mention any temperature value in connection to their calculations, but they inform that the results were derived for the same repository design, repository location and waste type description as applied in a pre-study of SFL 3-5 (Wiborg 1995). Wiborgh used data that were assumed to be representative for typical Swedish bedrock. The temperature at repository depth was assumed to be approximately 10°C. The groundwater in the surrounding bedrock was assumed to be reducing and to have a pH of about 8. It was also assumed that both saline and non-saline groundwater could be found at the repository depth.

The gas generation study by Skagius et al. (1999) focussed on gas produced by both steel and aluminium in the SFL repository. Due to the fast corrosion of aluminium in the waste, they calculated estimated a gas formation rate of 350 m^3/year at repository depth. It was assumed that the aluminium was completely corroded away after five years and that the subsequent gas formation then dropped to 6.5 m^3/year, which corresponds to the gas formation rate for corroding steel. The numbers indicate that the gas production due to Al corrosion might be considerable.

Skagius et al. (1999) concluded from their calculations that the corrosion causes a build-up of gas pressure and that it is reasonable to assume that even if the waste packages are initially gas-tight, the internal gas pressure will cause cracks through which the gas may escape. This may occur within the first few decades after repository closure. The same conclusions can be drawn for the concrete structure even though the time for the pressure build-up is longer. Cracking of the structures is to be expected within the first 200 years of gas generation.

4.6 Disposal of Al waste

The conditions in the Swedish SFR repository are in many ways (chemically, geologically, etc.) quite similar to those in the corresponding Finnish facilities. The FiR 1 decommissioning waste contains steel, aluminium and graphite and these materials are also present in the SFR. Table 4.1 shows the quantities of the various wastes and gives an indication concerning the package options used.

The SFR repository consists of the silo and the storage tunnels BMA, 1BTF, 2BTF and BLA (e.g. SKB 2010, Bergström et al. 2011). The dominant metal in the waste is steel, but the waste also contains other metals such as aluminium and zinc. Table 4.1 contains data selected from several tables in Moreno et al. in order to provide an approximate overview of the content of iron and aluminium (+ zinc) waste metal content in SFR. The contents of aluminium and zinc are combined in the original report by Moreno et al. (2001), which also provides more detailed information about the waste content.

Table 4.1. Major contents of metal waste in SFR (compiled from Moreno et al. 2001).

Part of SFR	**Waste category (Number of packages)**	**Fe (tonnes)**	**Al+Zn (tonnes)**
Silo	Steel drum with cement conditioned waste	90	2.2
Silo	Other packages[1]	3 559	0
BMA	Concrete mould with cement conditioned waste	1 193	3.3
BMA	Steel mould/drum with cement conditioned waste	985	10.8
BMA	Steel mould/drum with bitumen conditioned waste + other	861	0
1BTF	Concrete mould with cement conditioned waste	63	0.01
1BTF	Steel drum in steel drum with ashes (6 479)	194	42
1BTF	Steel box with unconditioned graphite (96)	14	0.5
1BTF	Concrete tank with unsolidified resins (186)	121	0
1BTF	Odd waste (415)	2 905	0
2BTF	Concrete tank with unsolidified resins (800)	518	*
BLA	ISO-container with unsolidified trash (514)	3 290	51
BLA	Steel drums in ISO-container with bituminised resins (27)	75	*
BLA	Steel drum with unsolidified trash in steel drum in a container (73)	412	13
BLA	Odd waste (64)	851	*

[1] Steel moulds and steel drums with cement conditioned waste, etc.
* No value was given.

The disposal aspects for low- and intermediate-level decommissioning waste were considered in an international IAEA project 2002–2006 (IAEA 2007a, b). Fourteen countries (Argentina, Canada, China, Germany, Hungary, India, Republic of Korea, Lithuania, Russian Federation, Slovakia, Sweden, the United Kingdom, Ukraine, and the USA) participated in the project. A few results concerning metallic aluminium waste will be given here. In Argentina, the disposal aspects of waste from total dismantling of research reactors were considered (Harriague et al. 1999). The oldest reactor, RA-1, was reported to generate decommissioning waste estimated to consist of 71.5 metric tonnes, most of it concrete (57 tonnes), the rest being steels, lead and reflector graphite (4.8 tonnes). Disposal of metallic waste was planned to be as follows:

(i) In the case of piping, tubes and tanks, either of stainless steel or carbon steel, they were to be cut by conventional means and packed and cemented in drums for transport and disposal at the LLW repository. Due to the small volumes involved, compaction did not seem relevant.

(ii) Due to their relatively small size, pumps and valves would be packed without cutting. Either cementation and/or backfilling with concrete waste rubble were planned to be used.

(iii) The conditioning of aluminium waste was analyzed, due to its potential for gas generation. It was stated that the RA-1 aluminium waste was of little importance, in the order of 350 kg, although decommissioning of the other research reactors would add to it.

Harriague et al. (1999) concluded concerning metallic aluminium that it should not pose particular disposal problems as, i.e., gas generation.

In the UK there is a large amount of metallic material present in decommissioning waste which will have to be treated for disposal. Godfrey (2007) notes that in particular, the UK needs to treat steels, aluminium and Magnox (a magnesium aluminium alloy). Briefly, the waste is stored inside cementitious material. The presence of water in the cement matrix, even after hydration has occurred, means that corrosion can take place, which, i.a., may lead to (i) generation of hydrogen gas, (ii) degradation of encapsulation matrix due to the formation of expansive corrosion products, and/or (iii) generation of methane and other hydrogen carbons formed from the reaction between carbides present in the metallic wastes and water present in the cement matrix.

The high pH in the cement pore solution influences metals in different ways. It may passivate or reduce the corrosion rate of, e.g., steel, but on the other hand it increases the corrosion rate of aluminium. The safety aspects are stressed; it is necessary to ensure that the potentially explosive hydrogen gas is safely dispersed and also that the build-up of gas pressures is not high enough to cause fracturing of the cement matrix. Fracturing is undesirable as it may ultimately increase the rate at which nuclides can be leached from the matrix after disposal.

According to Godfrey (2007), the research in the UK on the corrosion reactions of metals encapsulated in a cement matrix has been carried out for more than 20 years. The preferred process for treatment of these wastes consists of encapsulation of the metal in ordinary Portland cement, typically blended with blast furnace slag or pulverized fuel ash.

The hydrogen production due to, e.g., aluminium corrosion, can be reduced by decreasing the area exposed to corroding, e.g. by melting the metal. This method was utilized at the Paul Scherrer Institute (PSI) in the handling of two aluminium reactor tanks as well as a number of other aluminium components (Lauridsen 2001). Remelting of the aluminium parts reduced the surface area by a factor of 20. A number of remotely operated or automatic tools were developed in order to accomplish the cutting and melting of the aluminium components with a minimum personnel dose.

Finally, Ek & Mayer (2004) stress that the disposal of the aluminium in the FiR 1 decommissioning waste in the Olkiluoto or Loviisa repositories cannot be done without either making safety analyses which show there is no risk to safety, or by using methods (packaging etc.) that control the release of aluminium to the environment. Ek & Mayer demonstrate that, i.a., dissolved Al in the repository might reach chemical concentrations that exceed the limits given by health authorities.

4.7 Reactions between Al and C

The FiR 1 reflector consists of graphite that is covered by water-proof aluminium metal. It is unlikely that the eventual deposition of intact reflector blocks in a repository of the type discussed in this report would lead to any significant reactions between aluminium and graphite. The reason for this is simply that the temperature in the repository is too low for the reactions to occur. It is known, for example, that aluminium and graphite can react to form aluminium carbide:

$$4\ Al + 3\ C = Al_4C_3 \qquad (12)$$

However, the reaction occurs at high temperatures; aluminium carbide is normally prepared in an electric arc furnace. The need for a high temperature to form Al_4C_3 has been demonstrated, for example, in the preparation of thin Al films prepared by ultra-high vacuum deposition of Al onto a graphite surface (Hua et al. 2001). Hua et al. needed a temperature of about 770K just to see some indication of a reaction between Al and C, and not until the temperature reached 970K could Al_4C_3 be observed. Ballóková et al. (2011) noticed that reaction 12 occurs in mixtures of powdered aluminium and graphite heated at 550˚C for three hours. The cited references suffice to indicate that the formation of carbide is not expected for the expected disposal conditions.

In case aluminium carbide would, after all, form in contact with an aqueous solution, the expected products are hydroxide and methane gas. Berry (1948) gives the following reaction for the hydrolysis of aluminium carbide in contact with water:

$$Al_4C_3 + 12\ H_2O = 4\ Al(OH)_3 + 3\ CH_4 \qquad (13)$$

According to Berry, the reaction rate is slow in cold water but fairly rapid at elevated temperatures.

In contrast to the two previous reactions, galvanic corrosion of aluminium is an example of a much faster reaction. Equation (6) described galvanic corrosion of aluminium when in contact with iron metal. However, metallic aluminium may also corrode when in contact with graphite. IAEA (2006) explains this by pointing out that graphite can react electrochemically with other materials, by acting like a “noble metal”. In this way, graphite can accelerate the corrosion of other metals by galvanic coupling. Graphite is even more electronegative than stainless steel (and aluminium), such that direct contact between, for example, graphite and a stainless steel container may cause loss of integrity.

5. Basic graphite chemistry

5.1 Background

The FiR 1 decommissioning waste contains ^{14}C in irradiated steel and graphite components. Both these materials have the potential of releasing ^{14}C into the environment, but it is presently not known to what extent the carbon is organic and inorganic. Vuorinen (2012) studied, i.a., the release of ^{14}C from activated metal and found that the surveyed literature focussed mainly on the determination of ^{14}C concentrations and not on the speciation of ^{14}C under possible repository conditions. Vuorinen also found that the surveyed literature provides little data on possible mechanisms that might lead to the release of ^{14}C in organic form. Vines & Lever (2013) point out that it is possible for ^{14}C to be released in organic form as a gas, e.g. methane. If the gas migrates to the biosphere, the calculated dose may exceed the regulatory risk guidance levels. There is thus a need for ^{14}C to be isolated and contained within the repository system. Vines & Lever mention that carbon dioxide is likely to be retained within cementitious barrier systems due to carbonation.

Kustonen (2010) provides an overview of topics related to the final disposal of radioactive graphite waste in deep crystalline bedrock. The introductory parts of the report describe i.a. the effects of radiation on graphite, the properties of irradiated graphite, and methods used to reduce its volume. Such methods are needed, especially in the UK, France and Russia, which together host the major part of the world’s accumulated 250 000 tonnes of irradiated graphite. Kustonen notes that the question of how to finally dispose of this amount of graphite waste has not yet been solved. In the case of the FiR 1 reactor, the mass of irradiated graphite waste is about 5 tonnes (see Table 2.2). This amount is small in comparison to, e.g., the content of graphite in gas-cooled graphite reactors, which contain thousands of tonnes of graphite (e.g. Bushuev et al. 1992).

Kustonen (2010) stresses that graphite practically does not react with metals or water, although some interaction between concrete and graphite might be possible. At high temperature and pressure there is a possibility for graphite to oxidise, but such conditions are not relevant for the present discussion. The report by Kustonen neither presents the actual temperatures and pressures at which graphite oxidation occurs, nor does it give any references dealing with this matter.

Kustonen's conclusion is that graphite is practically inert. Other references have pointed out that also the formation of metal carbides, which is theoretically possible, is unlikely, due to the high temperature needed for their formation (Marsden et al. 2002). Kustonen's findings concerning the management of graphite waste are found below.

Ek & Mayer (2004) stress in their study of issues related to the disposal of decommissioning waste in the Loviisa repository that graphite differs considerably from the 'normal' waste from the power plant. Therefore, the properties of graphite should be investigated with special care. The following text covers some aspects of graphite and its properties, which may be relevant to the management of the FiR 1 decommissioning waste. The chapter also provides examples of disposal strategies that have been implemented or possibly will be in the future.

5.2 Carbon speciation

The chemical form of ^{14}C can have an impact on, e.g., the dose release rate from failed waste packages in a repository. Johnson & Schwyn (2004) mention as an example the difference between carbon in the form of inorganic CO_2(g) and carbon in the form of organic CH_4(g). The expected transport properties of these species through the repository differ considerably. In the former case, ^{14}C may be effectively retarded in alkaline systems due to calcite precipitation, while in the latter case ^{14}C may be more quickly transported.

Magnusson (2002) points out that it is necessary to know the content of organic and inorganic ^{14}C in order to be able to model and predict the future release and migration of air- and water-borne ^{14}C. However, the literature provides quite few data concerning ^{14}C on this matter. Magnusson et al. (2004) notice:

> "Very little is known about the chemical form of ^{14}C within the graphite and only a few references in the literature can be found on this topic. According to Marsden et al. (2002), some ^{14}C atoms formed in the graphite may be chemically compounded with hydrogen, nitrogen or oxygen atoms. It is also known from experience in a Canadian CANDU plant (heavy-water-moderated) that irradiation of nitrogen annulus gas produced ^{14}C, which was chemically combined with nitrogen, oxygen and hydrogen, and that the originally formed ^{14}C atoms were rapidly converted into simple hydrocarbons or carbon-nitrogen compounds (Greening 1989). The compounds were found as deposits on stainless steel components of the pressure tubes. According to Marsden et al. (2002), ^{14}C in the form of metal carbides is unlikely to be found in the graphite, due to the high temperatures needed for the formation."

Eurajoki (2010) discusses the behaviour of ^{14}C released from activated steel in repository conditions, but part of the discussion is relevant also to the release of ^{14}C from graphite. It is noted that "the 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 ^{14}C exists as carbonate, the concrete-based chemical conditions act as such a barrier. In concrete environment the precipitation is almost complete, since the carbonate solubility is low."

Eurajoki notes that the literature only contains a few articles on experimental results on ^{14}C behaviour relevant to the cementitious repository conditions. A key question in the research is the speciation of ^{14}C in the repository conditions after being released. Three 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. Eurajoki (2010) states that no quantitative conclusions on speciation can be drawn from the data available.

Marsden et al. (2002) conducted a literature survey to determine, i.a., what published data exist concerning the form of ^{14}C associated with graphite and to indicate, where possible, the potential for its release under alkaline conditions in repository storage. It was found that the majority of ^{14}C present within irradiated graphite wastes is produced by the ^{14}N reaction, with the ^{13}C reaction being the next contributor. The report refers in some cases to Magnox reactors and AGRs, but many of its findings are relevant also for FiR 1 waste. ^{14}C is generally present where the nitrogen gas has adsorbed onto surfaces and pores. It is generally bound into the structure and not easily removed. In some cases it may be compounded with hydrogen, nitrogen or oxygen atoms. Under saturated alkaline conditions, like those experienced during storage and disposal, limited leach rate data for ^{14}C are available in the literature. The data suggest that ^{14}C leach rates are low (of the order of $1 \cdot 10^{-5}$ and $1 \cdot 10^{-6}$ cm/d). Limited data available in literature suggest that graphite might react with oxygen dissolved in the water, leading to the formation of carbon dioxide. However, no leaching mechanisms from carbonaceous deposits in which carbon might be compounded with hydrogen or oxygen were reported in the literature reviewed by Marsden et al. (2002).

Isobe et al. (2008) performed leaching studies on moderator and reflector graphite samples from the Tokai (Magnox) reactors in Japan. The studies involved the separation of organic ^{14}C in solution from ^{14}C carbonate. About 0.1% of the total ^{14}C inventory was released during three years. 80% of the ^{14}C in the liquid phase was organic carbon. Attempts to identify the organic leached species were made HPLC and LSC. The analysis results did not give any clear answers about the nature of the organic compounds, but Isobe et al. suggested that they probably were not acetate, formate or methanol.

Magnusson (2002) and Magnusson et al. (2004, 2005) present results from measurements of the distribution of organic and inorganic ^{14}C in a graphite reflector, which had been used in Sweden's first nuclear research reactor. The reactor was decommissioned in the early 1980's and the graphite reflector was ready for disposal in the early 2000's. The classification of the reactor required knowledge about the distribution between organic and inorganic ^{14}C and therefore samples of gram-size were taken from different parts of the reflector.

To perform measurements of the content of ^{14}C – organic as well as inorganic - in these samples, a combustion and CO_2 absorption system was built (Figure 5.1). Samples obtained from the combustion and CO_2 absorption system were analyzed by a liquid scintillation counter.

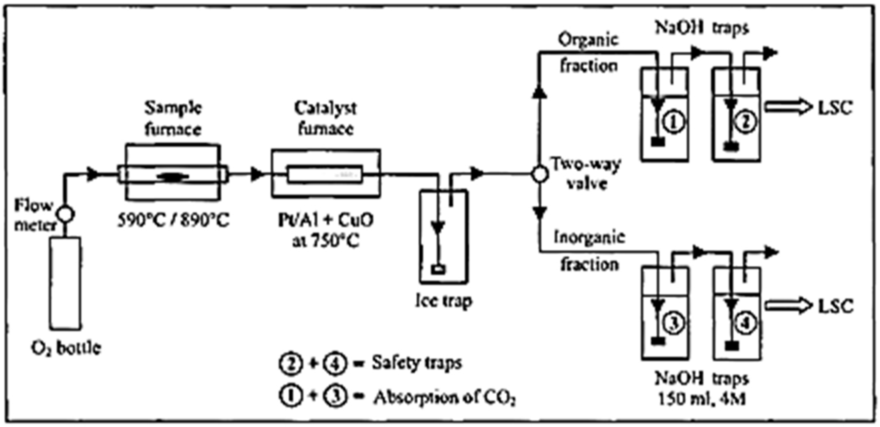

Figure 5.1. Outline of combustion and CO_2 absorption system used in measurement of organic and inorganic in graphite (Magnusson et al. 2004).

The analysis of samples from the reflector graphite clearly showed the presence of both organic and inorganic ^{14}C. The mean values for the organic and inorganic ^{14}C were 519 and 1 033 Bq/g, respectively. For the total amount of graphite, 52 tonnes, this corresponds to 27 GBq and 54 GBq, respectively.

5.3 Graphite conditioning and storage

The management of the world’s 250 000 tonnes of irradiated graphite is still in its infancy. The IAEA (2010) notes: “In most of the countries with radioactive graphite to manage, little progress has been made to date in respect of the disposal of this material. Only in France has there been specific thinking about a decided graphite waste-disposal facility (within ANDRA): other major producers of graphite waste (UK and the other countries of the former Soviet Union) are either thinking in terms of repository disposal or have no developed plans.”[3] According to Fachinger et al. (2013) the most common reference waste management option of irradiated graphite is a wet or dry retrieval of the graphite blocks from the reactor core and the grouting of these blocks in a container without further conditioning. A drawback with this method is that it produces large waste package volumes.

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[3] The excerpt is reproduced with written permission by the IAEA (on 14th January 2014).

In principle, there are several management options for graphite waste (Podruzhina 2005): i) disposal on the deep ocean bed, ii) shallow land burial, iii) incineration, and iv) deep geological disposal (inland site and coastal site). The following will however focus on what has bearing towards the FiR 1 decommissioning waste and the disposal alternatives.

Bergström et al. (2011) collected brief descriptions of LILW repositories worldwide in order to compare certain features to the Swedish LILW repository (SFR). The report included, i.a., descriptions of many facilities, waste and barriers. Graphite is not a central topic in the report, but Bergström et al. mention that repositories for disposal of long-lived low and intermediate waste are planned to be built in France and Japan. They will be of intermediate depth (many tens of metres) and are intended to accept irradiated graphite from the decommissioning of gas-cooled reactors in operation in these countries. Graphite is found in the 1BTF-tunnel in SFR (Moreno et al. 2001), where it comprises 1% of the waste. Other waste components in the 1BTD-tunnel are ion-exchange resins (27%), ashes (20%), sludge (0.5%), trash (<0.2%), and steel (52%). Most of the resins in 1BTF are unsolidified (85%), but there are also unconditioned resins. The ashes, the sludge and the trash are conditioned with cement, while steel waste and graphite are unconditioned.

The accumulated amount of irradiated graphite (including both ILW and LLW) in the UK by April 2010 was ~ 96 000 tonnes (NDA 2011). The proposed packaging strategy for graphite wastes (except for waste from the Windscale Advanced Gas-cooled Reactor, WAGR), according to Wise (1999), is to encapsulate the graphite in Nirex standard packages manufactured from 316S11 stainless steel. In a number of instances the packaging of graphite will be associated with mild steel box furniture. WAGR graphite will be encapsulated in concrete boxes, while the graphite will be held in mild steel boxes within the box.

In Switzerland, the dismantling of the research reactor DIORITE at the Paul Scherrer Institute (PSI) led to a need to condition about 40 tonnes of activated reactor graphite. However, as noticed by Wällisch (2007): “Since there was no practical path to dispose of the graphite, either in Europe or overseas, an in-house solution had to be developed.”

Briefly, the graphite management method developed at PSI involves the following steps (Beer 2009):

i) Loading decommissioning waste (steel, cast iron and barite/coleman concrete) into standardized concrete containers with an overall volume of 2.75 m^3. Loading of the waste in the most efficient way utilizes about 50% of the volume. The void volume is subsequently filled with activated reactor graphite as seen in the following steps.

ii) Crushing the graphite to less than 5 mm.

iii) Mixing the graphite with grout to get artificial sand.

iv) Spraying an aqueous solution on the graphite during grinding to avoid dust formation.

v) Developing a dedicated concrete mixer to produce graphite concrete.

vi) Filling the graphite concrete into the void volumes in the containers containing decommissioning waste.

According to Beer (2009), the graphite consisted of chemically inert reflector graphite with segments weighing up to 50 kg. The graphite was of AGOT type and was provided by Union Carbide. The main radionuclides in the graphite were ^{3}H, ^{14}C, ^{60}Co, ^{152}Eu and ^{154}Eu. The possibility of meeting problems with the Wigner energy stored in the graphite was analyzed but found to be insignificant.

The Swiss method fulfils the requirements of the Swiss Federal Nuclear Safety Inspectorate. The graphite grout exhibits a high compressive strength and high resistance against leaching for ^{137}Cs, ^{60}Co, ^{152}Eu, ^{3}H and ^{14}C in pure water and gypsum water. In total, 41.4 tonnes of graphite were conditioned. Both Wällisch (2007) and Beer (2009) point out the economic aspects of the method; it reduces the volume of the waste and thus saves a lot of costs. The PSI graphite conditioning method was patented worldwide in 2005.

Bruynooghe & Bièth (2009) provide a resumé from a three-day seminar on graphite management that was organized to discuss dismantling programmes for graphite moderated reactors and the characterization, treatment, packaging, and long-term storage of irradiated graphite. The results from characterization of graphite in the Bugey 1 reactor suggested that sampling of graphite waste for characterization should involve at least 40 core samples drilled from each graphite stack and cover its whole height and radius. Another conclusion was that extrapolation from one reactor to another is not recommended since the radiological and mechanical properties of graphite are very reactor-dependent.

Bruynooghe & Bièth (2009) also mention the use of an efficient method for reducing large volumes of graphite, Molten Salt Oxidation (MSO), and illustrate it with an example where MSO was applied to radioactive graphite (HLL-LL) from Russia’s two AMB reactors. The estimated reduction of the graphite volume was from 4 600 m^{3} to just 5 m^{3}, which led to significant savings.

The aim of the multi-national European CARBOWASTE project (2008–2013) was to develop best practices in the retrieval, treatment, and disposal of irradiated graphite, addressing both existing legacy waste as well as waste from graphite-based nuclear fuel from a new generation of nuclear reactors (Banford et al. 2008). The major challenge was related to the presence of long-lived isotopes such as ^{14}C and ^{36}Cl and shorter ones like ^{60}Co. Banford et al. point out that the wide range of activities and quantities of graphite means that the recovery, treatment and end-point may vary from country to country and potentially from site to site. It is further stated that the selection of appropriate treatment options requires an understanding of the precise location of the radionuclides in the graphite. In the case of carbon, studies at Forschungszentrum Jülich (Podruzhina 2005, von Lensa et al. 2011, Vulpius et al. 2013a, 2013b) indicate that the release of ^{14}C from irradiated graphite is coupled to different parts of the ^{14}C content; one part is more easily removed than the other. von Lensa et al. (2011) tentatively suggest that the more easily removed part consists of ^{14}C atoms created by neutron activation of nitrogen atoms that are chemisorbed on graphite surfaces, while the less easily removed part consists of ^{14}C atoms created by the activation of ^{13}C. The latter ^{14}C atoms are mainly integrated into the lattice of the graphite or as interstitial atoms between the graphene layers. Figure 5.2 shows the result of experimental studies of the fractional release of ^{14}C vs. total C released from samples from the thermal column of the Jülich MTR FRJ-1 (Merlin). The experiments were made in inert atmosphere or in water steam at 870–1 200˚C on graphite samples that were either massive of powdered. The results strongly depend on the method used; the ratio of the fractional release of ^{14}C to the fractional release of total C ranges roughly between 2 and somewhat over 20.

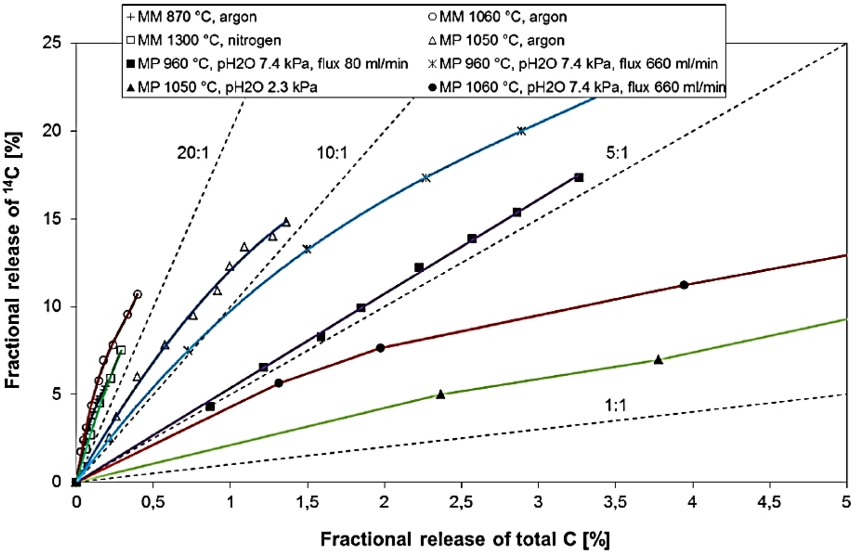

Figure 5.2. Fractional release of ^{14}C vs. total carbon release of i-graphite from the FRJ-1 MTR (MERLIN) thermal column (MM-massive sample; MP-powdered sample) (von Lensa et al. 2011).

von Lensa et al. conclude that for disposal purposes, it will be decisive that the mobile fraction of ^{14}C is preferentially removed or fixed, whereas the stable part will presumably not be released under disposal conditions.

Serco (2011) notes, that the release and migration of ^{14}C from irradiated graphite has been identified as a key issue for geological disposal of higher-activity wastes in the UK. ^{14}C has a sufficiently long half-life for its release as gas to be of relevance in a post-closure safety case. Some gaseous species containing ^{14}C, like ^{14}CH4 and ^{14}CO, could migrate with bulk gas and subsequently reach the biosphere as gaseous species or dissolved in groundwater. The production of ^{14}C is thought to take place in the same way as suggested by von Lensa et al. (2011), i.e. most of the ^{14}C is created by the neutron irradiation of nitrogen and only a minor part by the irradiation of ^{13}C. Serco mentions that the amounts of various forms of ^{14}C will depend on the reactor type, its operational history and on the location of the graphite within the reactor. The mechanisms by which the ^{14}C may be released from irradiated graphite under repository conditions are uncertain.

The report by Serco describes a long-term (~14 months) experiment focusing, i.a., on the ^{14}C release from graphite that was submerged in an alkaline solution simulating the porewater that would surround the graphite under near-field conditions. The graphite was taken from a core in the British Experimental Pile O (BEPO) reactor, which was closed in 1968 and Stage 1 decommissioned in 1969. The reactor used a graphite moderator and was cooled by air drawn through the system. The total amount of decommissioned graphite is 863 tonnes (UKAEA 2013). The experiments by Serco were, due to experimental reasons, performed under aerobic conditions, although the expected conditions in the near-field are anaerobic and reducing. The objective of the study was to examine release rates over a longer time-scale (~14 months) and to determine if the rates change with time. In addition, the speciation of ^{14}C was partially determined, by separating CO from organic components in the gas phase.

Briefly and somewhat simplified, the experiments were performed by passing CO_2-free air over (not bubbling through) a NaOH solution containing a solid piece of BEPO graphite (Figure 5.3). The outlet air was subsequently analyzed in a first step with regard to its content of ^{14}CO, and in a second step with regard to its content of ^{14}C in organic matter, like CH_4 and other volatile organic components. The solution was analyzed at the conclusion of the 14-month leaching period to determine the amount of ^{14}C released from the graphite but retained in the aqueous phase.

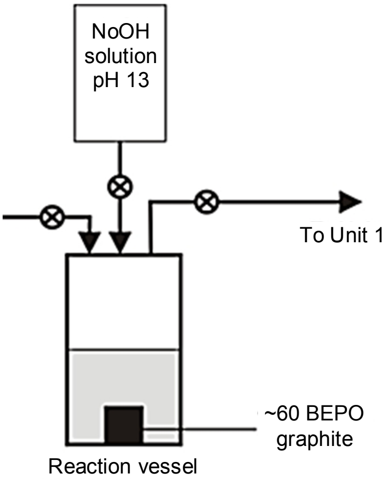

Figure 5.3. Reaction vessel with a graphite sample submerged in a NaOH solution. Purified CO_2-free air is passed over the solution and is subsequently analysed with regard to its content of CO and CH_4. (Detail from figure 2 in Serco 2011.)

The experiment ran for a total of 431 days, over which 87.5 Bq of inorganic ^{14}CO and 24.8 Bq of organic ^{14}C were released to the gas phase, see Figure 5.4. The fractional release was calculated by considering the total ^{14}C inventory of the solid graphite sample, which was approximately 2.1 MBq. The sodium hydroxide was analyzed after termination of the experiment and was found to have a ^{14}C concentration of ~7 Bq/mL, which corresponds to 2.1 kBq in the 300 mL solution used. A fraction of the ^{14}C remained in the solution after acidification, indicating that some carbon may be associated with organic material.

Serco finally notice that the total ^{14}C released as gaseous species represented about 0.005% of the estimated total inventory, while the corresponding figure released from the graphite and retained in solution was 0.10%.

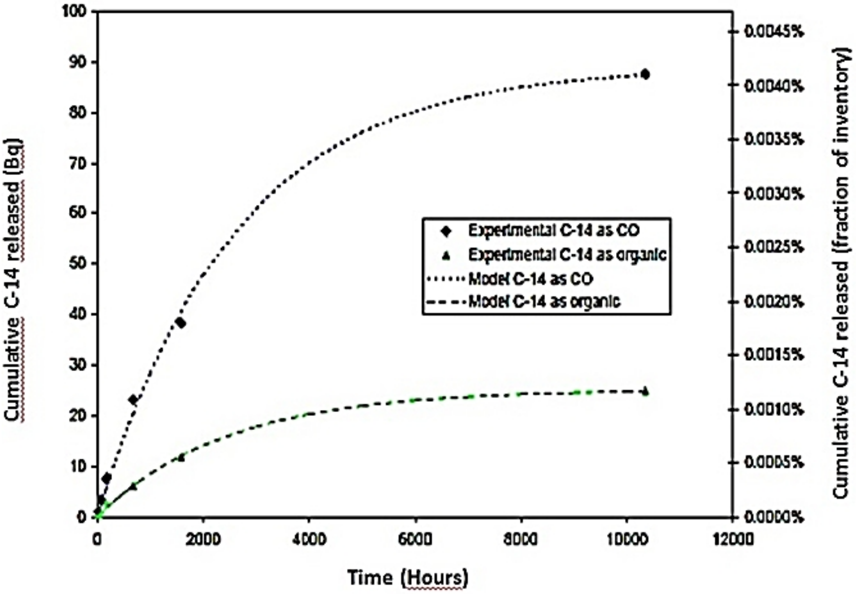

Figure 5.4. Release of inorganic ^{14}CO (upper graph) and organic ^{14}C (lower graph) in the gas phase (Serco 2011).

Handy (2006) describes measurements of the release of, i.a., ^{14}C from samples of irradiated graphite in contact with an alkaline aqueous solution. The experimental set-up was similar to the one described in Figure 5.3. The graphite samples were taken from a spigot ring in the Windscale Advanced Gas-Cooled Reactor (WAGR). The WAGR was a CO_2-cooled, graphite moderated reactor. The graphite content in the core and reflector was 230 tonnes. The WAGR started operations in 1962 and was shut down in 1981 (Mann 2011). The release from ^{14}C was studied for intact and crushed samples during about 30 weeks. Both sample types exhibited similar results, i.e. two forms of ^{14}C were released. It was concluded that these were most likely methane and carbon dioxide. It was also concluded that the released carbon dioxide would be absorbed into the aqueous phase in the experiment, while the methane was released into the gas phase during the experiments.

Handy (2006) also reports that the total releases from the graphite were small compared with the total ^{14}C inventory. Estimated bounding values for the fraction of the total ^{14}C inventory that could be released as hydrocarbon ranged between 0.001% and 1%. It is, however, pointed out that only a small fraction of the ^{14}C inventory would need to be released from the graphite, and migrate from the repository in the gas phase following closure of a deep geological repository, in order for a significant adverse impact to be realised in a performance assessment calculation.

NDA (2012) states that there is presently no mechanistic understanding of the ^{14}C release from irradiated graphite. A simple empirical model describing the release rate of ^{14}C, e.g. from irradiated graphite is (Swift & Rodwell 2006):

$$q_c = k_c \cdot A_c(0) \cdot M_g \cdot exp(-(k_c+\lambda_c)t) \tag{14}$$

where k_c is a rate constant for the release of ^{14}C from the graphite [a^{-1}], $A_c(0)$ is the initial activity of ^{14}C in the graphite [TBq kg-1], t is time [a], M_g is the mass of the graphite [kg], and λ_c is the radioactive decay constant for ^{14}C [a^{-1}].

In France, 23 000 tonnes of graphite waste will be generated during dismantling of the first generation of French reactors (9 gas cooled reactors). Vendé (2012) studied experimentally the release and repartition of organic and inorganic forms of ^{14}C under disposal conditions (Also tritium was studied but this nuclide is of no concern here). As a rationale for his study, Vendé noted that the speciation of ^{14}C strongly affects the migration from the disposal site to the environment. Leaching experiments in 0.1M NaOH solutions were performed on irradiated graphite from the Saint-Laurent A2 and G2 reactors. The results show that ^{14}C exists in both gaseous and aqueous phases. In the gaseous phase, release is weak (<0.1%) and corresponds to oxidizable species. ^{14}C is mainly released in the liquid phase, where it is present as both inorganic and organic species. The inorganic and organic fractions of the released ^{14}C were 65% and 35%, respectively. Figure 5.5 shows a typical example of how the active carbon in the solution phase is distributed between an inorganic and an organic fraction.

Fachinger et al. (2013) mention a new process for producing a graphite-glass composite material called Impermeable Graphite Matrix (IGM), developed at Furnace Nuclear Applications Grenoble (FNAG). The process is said to be applicable to irradiated graphite and allows for the production of an impermeable material without volume increase. Briefly, crushed irradiated graphite is mixed with 20 vol.% of glass and subsequently pressed under vacuum at an elevated temperature in an axial hot vacuum press (HVP). The obtained product is said to have zero or negligible porosity and a water impermeable structure.

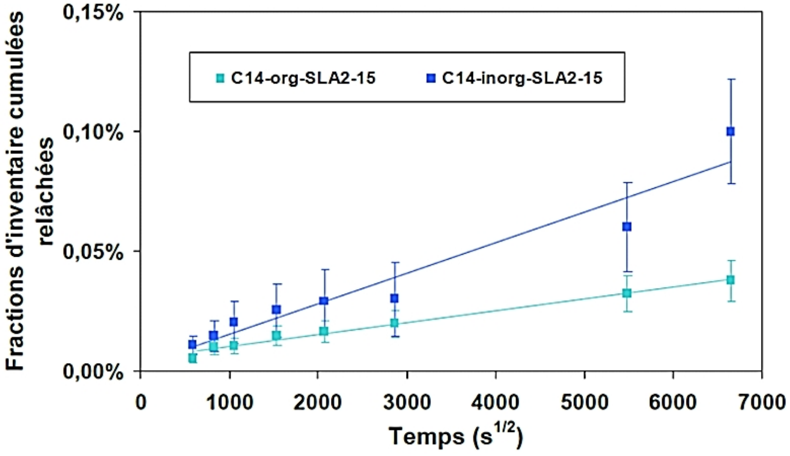

Figure 5.5. Cumulative released fractions of organic and inorganic ^{14}C in solution as a function of the square root of time for sample SLA2-15. Sample: graphite from the Saint-Laurent A2 reactor (Vendé 2012).

The IGM material will allow the encapsulation of irradiated graphite with packing densities higher than 1.5 tonne per m^3, which means that the method offers a huge volume saving. In addition, little or no leaching of radionuclides is observed, due to the impermeability of the material.

Towler et al. (2011) discuss the current UK baseline assumption for the disposal of irradiated graphite waste, i.e. disposal in a geological disposal facility. It is stated that no firm decisions have yet been made concerning the conditioning and packaging of the graphite wastes. Towler et al. stress that irradiated graphite should not be placed in the same container as organic waste in order to minimize the potential for generation of ^{14}C labelled methane. Furthermore, it is stressed that graphite should not be placed in the same container as reactive metals. These precautions would result in a minimum of gas generation.

6. Future research projects

The present overview of studies of management strategies and research activities related to the disposal of metallic aluminium and irradiated graphite was made with the decommissioning of the Finnish FiR 1 reactor in mind. Based on the literature studied, three topics appear to merit further study:

1. The corrosion of aluminium in contact with steel.
2. The corrosion of aluminium in contact with graphite.
3. The release of ^{14}C from irradiated graphite.

However, since the final repository conditions are characterized by pH values above 9 for long periods of time, aluminium will (see Ch. 4) corrode whether it stays in contact with steel or graphite, or not. The aluminium corrosion rate in, say, an 0.1 M NaOH solution will most probably be somewhat affected by a galvanic contact with steel or graphite but based on the literature studied the effect is expected to be minor. Corrosion studies would, however yield measured corrosion rates under the various conditions.

The third research topic is nonetheless important. Experimental studies indicate that the ^{14}C released from irradiated graphite exists in both inorganic and organic forms (see e.g. Magnusson et al. 2004, Serco 2011) and that, inter alia, the relative amounts of these forms influence the total release of ^{14}C to the environment.

The graphite in the future FiR 1 decommissioning waste has so far not been subject to any leach tests and it is therefore not known how ^{14}C will be distributed between inorganic and organic forms under final disposal conditions.

The following presents some preliminary thoughts on how to determine the inorganic and organic forms of ^{14}C released from the FiR 1 decommissioning waste. The leach tests should be carried out in the vicinity of the FiR 1 reactor building to avoid transport of active material outside VTT.

The leach experiments should consist of a pre-tests and subsequent release measurements.

6.1 Pre-tests

1. The pre-tests are suggested to comprise a number of sub-tests, the objectives of which are to fine-tune the experimental set-up. This means choosing proper sample sizes, solid-to-solution ratios, extraction times, pH values, chemical methods for separating inorganic and organic phases, etc. The measuring technique is suggested to be liquid scintillation.

2. The pre-tests are also suggested to produce preliminary leach-rate data, where the amount of ^{14}C released into a solution (Figure 5.5) or into a gas phase gas (Figure 5.4) are shown as a function of time.

6.2 ^{14}C release measurements

3. Once the pre-tests have resulted in a well-working measuring method, the efforts to determine the relative ^{14}C fractions in solution and/or gas phase will be commenced. Since all parts of the reactor graphite may not have experienced the same neutron fluxes, the specific ^{14}C inventory may differ between samples depending on from where they originate in the graphite. The choice of suitable sets of samples as well as the choice of total number of samples needed to get useful data has to be made together with reactor specialists.

The objective of the outlined experimental work is to get an understanding of how the ^{14}C released from the FiR 1 graphite will be distributed between organic and inorganic forms in both an aqueous and a gaseous phase under various pH values in the alkaline region (Figure 6.1).

This literature survey is aimed to give scientific input to the forthcoming decommissioning plan at VTT. As concerns the subsequent safe disposal of decommissioning waste, some waste stream optimisation can be done. For instance, carefully characterising the activity of irradiated aluminium and graphite will help in grading proper packaging requirement for different activity classes, and also in dividing the active material to the category that must be disposed of and to the one that can, according to safety regulations, be exempted.

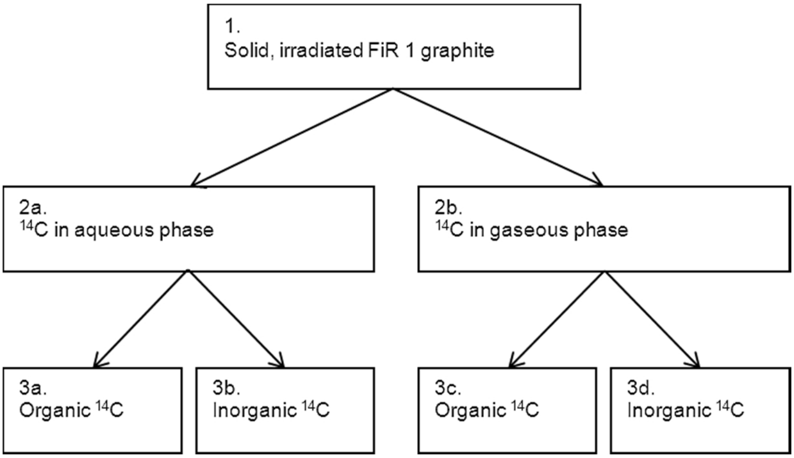

Figure 6.1. Outline of FiR 1 graphite leach test in which the released fractions of organic and inorganic ^{14}C are determined in both an aqueous and a gaseous phase.

7. Summary and discussion

It has been decided to shut down the Finnish FiR 1 TRIGA Mark II reactor after more than 50 years of operation. Decommissioning of the reactor is planned to start during fall 2015 (Vuori & Kotiluoto 2013). Planning of the management and final disposal of the decommissioning waste requires knowledge about, among other things, possible waste-related chemical reactions in disposal conditions and the effects of such reactions on long-term safety of the disposal. For this reason, the present literature study was conducted to collect relevant information on:

i) The chemical behaviour of irradiated aluminium and graphite in FiR 1 decommissioning waste under expected final repository conditions.

ii) The international practices concerning management and final disposal of irradiated aluminium and graphite.

iii) Experimental techniques for determining the form (organic or inorganic) of the ^{14}C released from graphite waste.

The above stated focus of the literature survey was limited by the following factors:

iv) The foreseen final repository environment.

v) The type and mass of the irradiated aluminium and graphite in the FiR 1 decommissioning waste.

vi) The aluminium chemistry under foreseen repository conditions.

vii) The ^{14}C chemistry under foreseen repository conditions.

The FiR 1 decommissioning waste may be disposed of in one of the NPP facilities at Olkiluoto or Loviisa, but there is not yet any final agreement on this matter. However, both disposal alternatives are expected to provide a cementitious environment in which the waste will be exposed to alkaline water for maybe 10^4-10^5 years.

The decommissioning waste considered in this report is aluminium and reactor graphite used in the FiR 1 reactor. The total amount of irradiated aluminium and irradiated graphite were approximately 3 933 and 5 125 kg, respectively. Some part of them can be exempted.

The FiR 1 decommissioning waste discussed here consists briefly of graphite blocks, metallic aluminium and in case of the reflector, of metallic aluminium in close contact with graphite. Potential problems regarding the aluminium chemistry were found to be related to corrosion processes, which lead to the production of hydrogen gas and subsequent build-up of high gas-pressures and possible subsequent cracking of waste-packages. The heat produced by the aluminium corrosion was calculated by Moreno et al. (2001) for the Swedish SFR repository, which is similar to the Finnish repositories. The result indicated that aluminium corrosion might increase the temperature somewhat in the repository, but not more than 5°C, although, locally, the temperature might be higher. The chemical form of the corroded dissolved aluminium is in the form of trivalent Al-species, the concentration of which can exceed acceptable limits for lake and groundwater. Aluminium corrosion is often described in terms of simple E – pH diagrams, showing a pH range (approximately 4–9) where aluminium is generally considered to be protected from corrosion. Recent research indicates, however, that this is not always correct; experimental results show that corrosion is possible also in this ‘corrosion protected’ area.

The surveyed literature indicates that graphite is chemically inert under expected repository conditions. However, water in contact with irradiated graphite is expected to dissolve radionuclides from the graphite body and to offer a transport route towards the environment. The relative amount of ^{14}C released to the environment is coupled to the chemical form in which the element occurs. The organic form of the ^{14}C exhibits a tendency to escape in gaseous form, e.g. like methane, while inorganic ^{14}C is prone to be bound as solid matter, e.g. as calcium carbonate. Thus, the higher portion of organic ^{14}C released from the graphite, the higher the dose to the environment, other things being equal.

Published results from leach tests with irradiated graphite in alkaline solutions indicate the presence of both organic and inorganic forms of ^{14}C. However, such data are reactor-specific and depend on the history of the reactor, and the properties of the graphite, etc.

In the case of the FiR 1 reactor, accurate determinations of the percentages of organic and inorganic ^{14}C in the graphite would mean a series of leach tests being performed. Since the graphite is radioactive, the leach tests should be carried out at VTT, in order to minimize the transportation of radioactive material between the FiR 1 reactor and the laboratory used for the tests. The report suggests preliminarily how such leach tests could be carried out at VTT.

Acknowledgements

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Appendix A: Nuclear graphite

Nuclear graphite, or reactor graphite, is a synthetic material manufactured from filler coke and pitch, see Figure A1. There is a distinction between anisotropic and isotropic graphite. Burchell et al. (2007) mention that graphite with a high degree of anisotropy is not suitable for nuclear applications because the irradiation-induced dimensional changes will also become anisotropic, resulting in high internal stresses, cracking, and shortened irradiation lifetimes. Burchell et al. point out that early nuclear grades, such as AGOT graphite, used in the Hanford Piles exhibited such behaviour. Further information on nuclear graphite is found in Burchell et al. and references therein.

Irradiated graphite, sometimes referred to as i-graphite, contains in addition to ^{14}C, isotopes like ^{3}H, ^{152}Eu, ^{154}Eu and ^{60}Co.

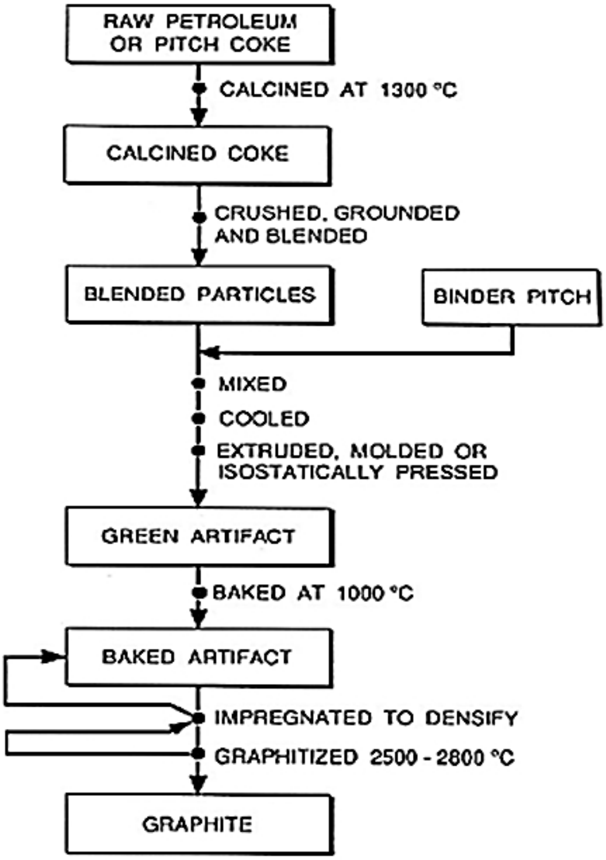

Figure A1. The process steps in the manufacturing of nuclear graphite (from Burchell et al. 2007 and ref. therein).

Series title and number
VTT Technology 156

Title	**Chemical aspects on the final disposal of irradiated graphite and aluminium** **A literature survey**
Author(s)	Torbjörn Carlsson, Petri Kotiluoto, Olli Vilkamo, Tommi Kekki, Iiro Auterinen & Kari Rasilainen
Abstract	The Finnish FiR 1 TRIGA Mark II reactor is facing shut-down after more than 50 years of operation. The decommissioning of the reactor is planned to start during fall 2015. The management and final disposal of the decommissioning waste require knowledge about, among other things, the possible waste-related chemical reactions and the effects of such reactions on long-term safety. The above warrants the rationale for the literature survey, which was conducted to collect information on: i) The chemical behaviour of irradiated aluminium and graphite in FiR 1 decommissioning waste under expected final repository conditions. ii) The international practices concerning the management and final disposal of irradiated aluminium and graphite. iii) The experimental techniques for determining the chemical form (organic or inorganic) of the ^{14}C released from graphite waste. The report describes initially the FiR 1 TRIGA reactor, its associated decommissioning waste and foreseen final disposal conditions. The main part of the report focuses on the chemical behaviour of aluminium and graphite under such conditions. In addition, a few examples are provided concerning available methods for managing irradiated graphitic waste and for measuring the contents of organic and inorganic ^{14}C in irradiated graphite. Finally, the report proposes outlines for some experiments to be conducted at VTT in order to determine the release rates of organic and inorganic ^{14}C from the FiR 1 decommissioning waste.
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Julkaisun sarja ja numero

VTT Technology 156

Nimeke	**Kemiallisia näkökohtia säteilytetyn grafiitin ja alumiinin loppusijoituksesta** **Kirjallisuusselvitys**
Tekijä(t)	Torbjörn Carlsson, Petri Kotiluoto, Olli Vilkamo, Tommi Kekki, Iiro Auterinen & Kari Rasilainen
Tiivistelmä	Suomen FiR 1 TRIGA Mark II reaktori on ollut käytössä yli 50 vuotta ja on nyt päätetty sulkea. Reaktorin käytöstäpoisto on tarkoitus aloittaa syksyllä 2015. Purkujätteen huolto ja loppusijoitus edellyttävät luotettavia tutkimustietoja, muun muassa mahdollisista jätteisiin liittyvistä kemiallisista reaktioista ja tällaisten reaktioiden vaikutuksesta loppusijoituksen pitkäaikaisturvallisuuteen. Tämä kirjallisuustutkimus koostuu pääosin seuraavista aiheista: i) Alumiinin ja grafiitin mahdolliset kemialliset reaktiot loppusijoitusolosuhteissa, ii) Säteilytetyn alumiinin ja grafiitin käsittelyn ja loppusijoituksen raportoidut kansainväliset käytännöt, iii) ^{14}C:n kemiallisen muodon (orgaaninen tai epäorgaaninen) määrittäminen säteilytetylle grafiitille. Raportissa kuvataan aluksi FiR 1 TRIGA reaktoria, sen purkujätettä, ja purkujätteiden odotettavissa olevia loppusijoitusolosuhteita. Suurin osa raportista kohdistuu alumiinin ja grafiitin kemialliseen käyttäytymiseen loppusijoitusolosuhteissa. Raportti antaa esimerkkejä säteilytetyn grafiitin käsittelystä ja loppusijoituksesta ulkomailla ja kuvaa raportoituja kokeellisia menetelmiä orgaanisen ja epäorgaanisen kemiallisen muodon pitoisuuksien määrittämiseksi säteilytetyn grafiitin ^{14}C:sta. Lopuksi pohditaan alustavasti kokeellista tutkimusta, jolla voitaisiin määrittää orgaaninen ja epäorgaanisen ^{14}C:n vapautuminen FiR 1 purkujätteestä.
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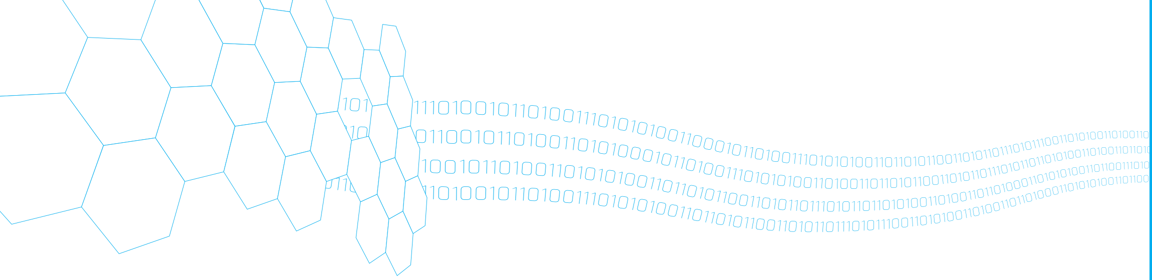

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