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A Review of Anthropogenic Organic Wastes and Their Degradation Behaviour

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MIND

Publishable Summary

Work Package 1 of the MIND project addresses remaining key issues for the geological disposal of ILW concerning the long-term behaviour, fate and consequences of organic materials in the waste along with H_2 generated by corrosion and radiolysis. This review begins this work by collating information concerning the inventory and nature of organic materials present in ILW and some LLW that requires geological disposal. The review has then considered the physical and chemical conditions that the organic materials will be subjected to during storage and geological disposal. The review then provides a summary description of the physical and chemical nature of the main organic materials present in ILW and their known chemical and radiolytic degradation behaviour. The effect of the organic degradation products on radionuclide speciation, which could affect how some radionuclides are transported in groundwater, is then considered to focus subsequent work in this field.

Inventory information concerning the distribution of the different types of organic material present in ILW and some LLW is collated from published national sources. This confirms that the materials selected for study in the MIND project; bitumen, organic ion exchange resins and halogenated polymers (PVC), are present in significant amounts in the national inventories. Cellulose is present in generally lower amounts in most inventories, but it is already established that it is of significance with regard to the strong complexation effect of its alkaline hydrolysis products. Cellulose is included in the Work Package 1 studies, but is not considered in detail by this review because comprehensive reviews exist in peer reviewed literature. The review of organic ILW also collates information relevant to the radiation dose, timescale and chemical conditions that the waste and encapsulant materials will be subjected to during storage and geological disposal. This information, together with information regarding the physical and chemical nature of the organic materials and current understanding of the effects of chemical and radiolytic degradation is used to refine the design of radiolytic and biodegradation experiments that are being undertaken in MIND Work Package 1.

In the next phase of the MIND project ion exchange resin, PVC, bitumen and cellulose materials will be irradiated using ^{60}Co ɣ radiation at a range of dose rates. The first irradiation experiments will be undertaken under a range of relevant pH conditions with air and inert gas headspace. The first experiments will be to ensure that sufficient soluble organic material is produced in order to characterise the compounds present and to use the leachate in subsequent biodegradation experiments. Further experiments will then be undertaken at lower doses. The biodegradation experiments will be inoculated by various cultures, including consortia adapted to high pH conditions and indigenous microbes sampled from underground rock laboratories. Biodegradation studies will utilise a range of electron acceptors, including nitrate and sulfate identified by the review as being of most significance. The process of methane generation under cement buffered ILW conditions will also be explored. The soluble organic species will be characterised before and after biodegradation to identify compounds for complexation studies to draw conclusions regarding the degradation of known complexants such as the cellulose degradation product ISA. The solid residues and biomass materials will also be utilised for microscopy studies including interactions with radionuclides.

The information collated in this review is of prime importance to the design of experimental work undertaken in Task 1.2 of Work Package 1 of the MIND project. The review will also provide a basis of Task 1.3 that examines processes under *in situ* wasteform and repository conditions and modelling and integration in Task 1.4 and wider integration and dissemination through MIND Work Package 3.

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Glossary

ACE	Affinity capillary electrophoresis
AGR	Advanced Gas cooled Reactor
Amberlite™	Organic ion exchange resin
ANDRA	French National Agency for Radioactive Waste Management
ATR-FTIR	Attenuated total reflection - Fourier transform infrared spectroscopy
ATW	Alpha-toxic waste, term used in Switzerland
BBP	Benzyl butyl phthalate
CAC	Asbestos cement containers
CAST	Carbon source term, Framework 7 project
CBF-C'2	Metal fibre reinforced concrete containers
Clab	Central Interim Storage for Spent Nuclear Fuel, Sweden
COVRA	Dutch waste management organisation, Centrale Organisatie Voor Radioactief Afval
CSH	Calcium Silicate Hydrate
CW	Continuous wave (laser spectroscopy)
DBP	Dibutyl phthalate
DECC	Department of Energy and Climate Change, UK
DEHA	Di-2-ethylhexyl adipate
DEHP	Di-ethylhexyl phthalate
DFT	Density functional theory
DIDP	Di-isodecyl phthalate
DIDP	Di-isodecyl phthalate
DINP	Di-isononyl phthalate
DINP	Di-isononyl phthalate
DNA	Deoxyribonucleic acid
DNOP	Di-n-octyl phthalate
DOC	Dissolved organic carbon
DOP	Di-octyl phthalate
DOP	Di-octyl phthalate
DOTP	Dioctyl terephthalate
DTPA	Diethylene triamine pentaacetic acid
DVB	Divinyl benzene
EDF	Energy De France, French power generation company
EDTA	Ethylene diamine tetra acetic acid
EELS	Electron Energy Loss Spectroscopy
ENRESA	Spanish waste management organisation, Empresa Nacional de Residuos Radiactivos, S.A.
ESI-MS	Electrospray ionization mass spectrometry
ESM	Environmental Scanning electron Microscopy
ETFE	Ethylene tetrafluoroethylene
EU	European Union
Eurobitum	Belgian bituminised encapsulated waste
EXAFS	Extended X-ray absorption fine structure spectroscopy
FT-IR	Fourier transform infrared spectroscopy

GC-MS	Gas chromatography mass spectrometry
GDF	Geological Disposal Facility
HLW	High level waste
Hypalon™	Chlorosulfonated polyethylene
IC	Inorganic carbon
IC	ion chromatography
IER	Ion exchange resin
IGD-TP	Implementing geological disposal technical platform
ILW	Intermediate level waste
IR	Infra-red
ISA	Isosaccharinic acid
ITFA	Iterative transformation factor analysis
KAJ	Intermediate activity silo, Finnish
L/ILW	Low- and intermediate-level waste, term used in Switzerland
Lewatit™	Organic ion exchange resin
LILW	Low and intermediate level waste, term used in Belgium, Sweden
LILW-LL	long-lived low- and intermediate level radioactive wastes, term used in Belgium and France
LLW	Low level waste
MAJ	Low activity silo, Finnish
MHLW	Medium high level waste, term used in Spain
MIND	Microbiology In Nuclear waste Disposal
NAGRA	National Cooperative for the Disposal of Radioactive Waste, Swiss waste management organisation
NAPLs	Non aqueous phase liquids
NDA	Nuclear Decommissioning Authority, UK waste management organisation
Neoprene	Polychloroprene
NMR	Nuclear magnetic resonance
NORM	Naturally occurring radioactive material
NPR	Nuclear power reactor
NRVB	Nirex Reference Vault Backfill
NTA	Nitrilotriacetic acid
ONDRAF/NIRAS	The Belgian Agency for Radioactive Waste and Fissile Materials (Organisme National des Déchets Radioactifs et des Matières Fissiles / Nationale Instelling voor Radioactief Afval en Splijtstoffen
OPERA	Onderzoeksprogramma Eindberging Radioactief Afval
PAEs	Phthalic acid esters
PARAFAC	Parallel factor analyses (of the spectral data)
PCE	Polycarboxylate ethers
PCM	Plutonium Contaminated Material
PCTFE	Polychlorotrifluoroethylene
PE	Polyethylene
Powdex™	Organic ion exchange resin
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride

PVDF	Polyvinylidene fluoride
PWR	Pressurised Water Reactor
RAWRA/SÚRAO	Czech Republic Radioactive waste repository authority
SFESEM	Field Emission Scanning Electron Microscopy
SFR	Swedish repository for short-lived low and intermediate level waste
SIT	Specific ion interaction theory
SKB	Svensk Kärnbränslehantering AB, Swedish waste management organisation
SRA	Strategic research agenda
STEM/HAADF	Scanning Transmission Electron Microscopy High Angle Annular Dark Field
TOC	Total organic carbon
TRLFS	Time resolved laser fluorescence spectroscopy
TVO	Teollisuuden Voima Oyj, Finnish power generation and waste management organisation
UK	United Kingdom
UV	Ultra Violet
UV-vis	Ultra violet - visible spectroscopy, TRLFS, ATR-FTIR with
VES	vinylesterstyrene
Vis/NIR	Visible/near infra-red
VLJ	Finnish repository for short-lived low and intermediate level waste
VLLW	Very low level waste
WP	Work package
XAS	X-ray absorption spectroscopy
ZWILAG	Interim storage facility in Würenlingen, Switzerland

1 Introduction

1.1 MIND project overview

The MIND project (Microbiology In Nuclear waste Disposal) is a multidisciplinary project addressing key technical issues that must be tackled to support the implementation of planned geological disposal projects for higher-level radioactive wastes across the EU. Our current understanding of the impact of microbial metabolism on the safety of geological repositories remains tenuous, even though microorganisms may have controlling influences on wasteform evolution *in situ*, multibarrier integrity and ultimately radionuclide migration from the repository.

The MIND project targets a number of high urgency and high importance topics identified in the Strategic Research Agenda, (SRA) (IGD-TP, 2011), focusing mainly on Key topic 2: Waste forms and their behaviour and Key topic 3: Technical feasibility and long-term performance of repository components.

The Scientific Technical Work Programme (Figure 1) is divided into two operative Work Packages (WPs):

WP1 addresses SRA Key topic 2: Remaining key issues for the geological disposal of ILW concerning the long-term behaviour, fate and consequences of organic materials in the waste along with H_2 generated by corrosion and radiolysis. The objectives of WP1 consequently are to reduce the uncertainty of safety-relevant microbial processes controlling radionuclide, chemical and gas release from long-lived intermediate level wastes (ILW) containing organics.

WP2 addresses SRA Key topic 3: Remaining key issues for the geological disposal of HLW concern the factors controlling sulfide production in the geosphere, including to what extent microorganisms can accelerate canister corrosion in the near-field either by hydrogen scavenging or by sulfide and/or acetate production. Further, it is important to identify conditions (including buffer density) under which relevant bentonites inhibit microbial activity, and to understand whether microorganisms can accelerate degradation of bentonite based buffers and influence the long-term behaviour of plug systems and seals.

The third Work Package (WP3) focuses on Integration, Communication and Dissemination. WP3 will evaluate and integrate microbial processes towards the conceptualization and performance assessment of geological repositories and in the respective state of the art knowledge base.

The fourth Work Package (WP4) handles Project Management.
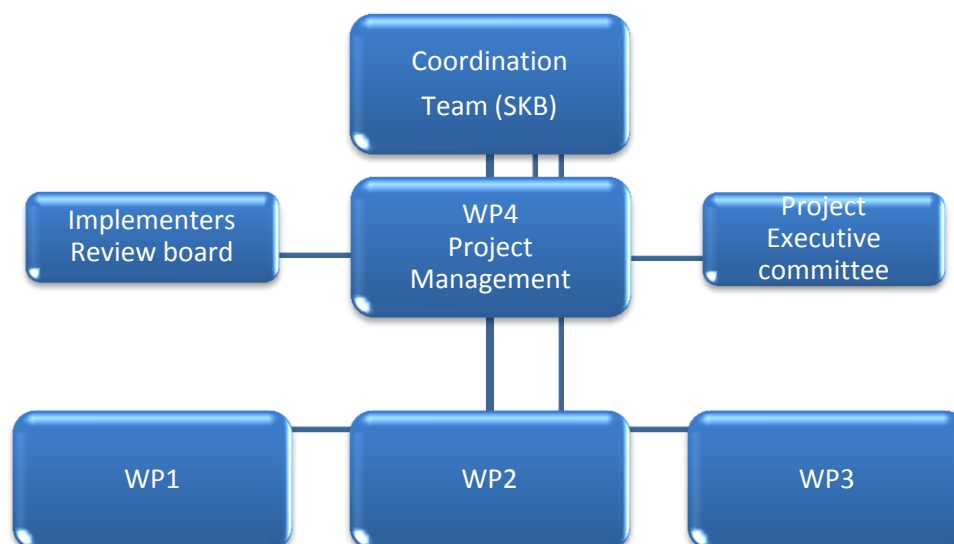
Figure 1 MIND project structure

This review concerns MIND WP1 and forms a first task (Task 1.1) that collates and reviews information concerning anthropogenic organic wastes present in intermediate level waste (ILW) and some low level waste (LLW) considered for geological disposal. The review considers the range of chemical and physical conditions representative of storage and final disposal for established underground operating facilities for LLW and ILW and concept designs for deep geological disposal. This information will be used to define the conditions of degradation studies (Task 1.2) that will explore for the first time the combined effects of chemical hydrolysis, radiolysis and biodegradation of anthropogenic and cellulose organic materials present in ILW and LLW. Work within Task 1.2 will examine how degradation products from anthropogenic polymers and cellulosic materials may fuel microbial metabolic processes leading to microbial gas generation and consumption. In addition effects on radionuclide mobility and speciation will be examined, including; (i) how microbiological processes may affect the stability of organic complexants and (ii) how such organic degradation products may act as electron donors that stabilise the reduced forms of a number of multivalent radionuclides (e.g. Tc, Se, U, Np, Pu).

Other tasks within MIND WP1 comprise: Task 1.3, which will examine microbiological processes relevant to ILW and LLW disposal under *in situ* conditions and Task 1.4, which will develop models of the biogeochemical processes for wider application and consideration by end users.

1.2   Scope and objectives of the review

The main objective of this review is to collate information concerning the organic materials present in ILW and to consider information regarding the treatment, storage and disposal conditions to which the wastes will be subjected in order to define the conditions of subsequent experimental studies with MIND WP1. Further objectives are to review previous work concerning the degradation of anthropogenic organic materials and the radionuclide complexation effects of degradation products which defines the state of knowledge at the outset of the project.

Section 2 of this review compiles information concerning the types of anthropogenic organic wastes present in ILW and some LLW considered for geological disposal. This information is used to select the main anthropogenic organic materials for study in MIND WP1 and to gather other relevant

information concerning the nature of the wastes, conditioning and encapsulation processes, radionuclide inventory and conditions of current operating near surface repositories (e.g. SFR, Sweden; VLJ Olkiluoto Finland and repositories in the Czech Republic).

Section 3 considers the range of chemical and physical conditions representative of storage and final disposal for established underground operating facilities and concept designs for deep geological repositories (e.g. in Belgium, France, Switzerland and the UK). This information is used to discuss the range of chemical conditions (pH and redox potential, Eh) of relevance to the experiments. Information is also presented concerning the effects of radiation on microbial processes and the degradation of organic materials that will input into the consideration of the total adsorbed dose and dose rate of irradiation experiments that will be undertaken in the MIND project. This discussion of the scenarios describing the evolution of organic-containing ILW under deep disposal conditions provides a basis for further integration of the microbiological research within WP3.

Section 4 summarises the existing knowledge concerning hydrolysis and radiolysis products of the main anthropogenic polymers and materials (halogenated plastics, ion exchange resins and bitumen) under neutral and cement buffered pH conditions, and their known or hypothesised potential for further biodegradation. The degradation of cellulose wastes while important to research undertaken in WP1 will not be reviewed in detail, because the knowledge in this areas is well established in peer reviewed and safety case literature (e.g. Greenfield *et al*, 1992; Van Loon *et al*, 1997; Van Loon and Glaus 1997; Glaus *et al*, 1999; Van Loon *et al*, 1999; Vercammen *et al*, 2001; Pavasars *et al*,2003; Glaus, and Van Loon 2008; Humphreys *et al,* 2009; Bassil *et al,* 2015).

Section 5 reviews previous literature concerning radionuclide complexation by water soluble degradation products of the main anthropogenic polymers and materials. This part of the review identifies those complexing ligands that may significantly affect radionuclide migration so that the subsequent biodegradation and complexation experiments focus on the most relevant organic waste materials and ligands.

Section 6 presents a summary of the key points of the review and identifies key knowledge gaps that will be investigated by the MIND project.

1.3   ILW and LLW terminology

The focus of MIND WP1 is the study of intermediate level waste (ILW) and some low level waste (LLW) that requires underground near surface or deep geological disposal. LLW that requires geological disposal normally includes wastes with alpha emitting radionuclides such as plutonium contaminated materials. In this review where discussion is generic the abbreviations ILW and LLW are used where appropriate. Other abbreviations are also in common use in different countries, which categorise the wastes by half-life, for example the term long-lived low and intermediate level radioactive wastes (LILW-LL) is used in Belgium. In this review (mainly in Section 2) these country specific abbreviations are defined and used when describing specific wastes.

2   The inventory of organic materials in ILW and LLW

A variety of natural and anthropogenic polymers are present in ILW and some LLW that requires geological disposal. Organic materials present in ILW result from the following main sources:

- Organic ion exchange resins (IERs) used in nuclear facilities to remove activity from process liquids and wastes streams. Significant amount of IERs are used to remove activity from water reactor coolants. Organic IERs may also be used to reduce levels of activity in fuel storage ponds and to treat effluents from reprocessing plants. IERs for use in the nuclear industry have been designed to be radiation resistant.

- Organic materials such as bitumen and some specific polymers (e.g. vinylesterstyrene (VES) and epoxy resins) are used to encapsulate ILW. These materials are typically used to encapsulate water soluble residues from reprocessing and effluent treatment or reactive metal wastes. Bitumen and other polymers are also used to encapsulate IERs to reduce the release of contaminants.

- Miscellaneous ILW such as arising from maintenance and decommissioning operations at nuclear power plants and waste arising from reprocessing plants and laboratories. Such wastes are generally less well characterised and more variable in their composition and physical nature than IERs and organic encapsulants. These miscellaneous organic wastes mainly comprise halogenated polymers (e.g. polyvinyl chloride, PVC) and non-halogenated polymers (e.g. polythene, PE), rubber and cellulose materials.

A further category of organic materials of significance to ILW disposal comprises additives present in cement encapsulants, which are used to decrease the viscosity and reduce the water content of cement slurry and to optimise the encapsulation and curing process. A variety of soluble organic compounds have been used as superplasticiser additives. Older additives were based on vinyl co-polymers, but more recently developed reagents based on polycarboxylate ethers (PCE) are used at lower dose. Both types of surfactant have the potential to complex with radionuclides in free solution, but PCE additives are of higher molecular weight and less likely to migrate out of the cement grout. Other organic complexants such as amino carboxylic acids (EDTA, DTPA and NTA) may also be present in trace amounts in some ILW streams. Such additives and complexants are present in lower concentrations in ILW and are not included in the scope of the MIND project as they represent a relatively small mass of organic carbon that could be utilised by microbial processes.

2.1   Overview of the nature of anthropogenic organic polymers and materials

In this subsection the chemical structure and nature of organic polymers, ion exchange and organic encapsulation ILW materials are described in more detail as an introduction to the presentation of national inventory information from partner states.

Organic polymers can be classified in terms of their mode of polymerisation, which reflects the chemical structure and stability of the polymer:

- Addition polymers form by polymerisation of unsaturated monomers that typically contain a C=C double bond. Important addition polymers include PE and PVC which are formed by polymerisation of ethane (CH_2CH_2) and vinyl choride (chloroethene; CH_2CHCl) respectively. Addition polymers are formed of chains of carbon atoms with strong C-H bonds and are resistant to biodegradation.

- Condensation polymers are formed by the elimination of water or other small molecules from two or more reactant monomers. Common condensation polymers include polyamides and polyesters; here the polymer structure contains polar amide or ester groups, which are

susceptible to biodegradation. Cellulose is a natural condensation polymer comprised of glucose monomers.

Polymers comprised of chains of monomers formed by addition or condensation reactions may form cross linked structures, which are induced by heat, pressure and radiation, or by chemical effects e.g. pH. Vulcanisation of rubber is a common example of cross linking in response to temperature, which can be accelerated by addition of sulfur or specific sulfur catalysts. Thermo plastic polymers such as PE may become brittle under UV radiation due to cross linking. Co-polymers formed by two monomers can be used to form highly cross linked structures. Styrene and divinylbenzene (DVB) react together to form the copolymer styrene-divinylbenzene, which is a commonly used ion exchange resin. Under irradiation, some polymer structures tend to cross-link and are stable, whilst others will degrade. This allows the allocation of polymers into two broad groups, as shown in Table 1.

Table 1 Polymer behaviour upon irradiation (Walters, 2004 after Chapiro, 1962)

Group 1 Cross-linking polymers	Group 2 Degrading polymers
Polyethylene	Polyisobutylene
Polypropylene	Poly(α-methylstyrene)
Polystyrene	Polymethacrylates
Polyacrylates	Polymethacrylamide
Polyacrylamide	PolyVinylideneChloride
PolyVinylChloride	Cellulose and derivatives
Polyamides	Polytetrafluoroethylene
Polyesters	Polytrifluorochloroethylene
Polyvinylpyrrolidone	
Rubbers	
Polysiloxanes	
Poly(vinylalcohol)	
Polyacroleine	

Bitumen is a highly viscous form of petroleum, which in its refined form is used in the nuclear industry as a thermoplastic encapsulant. Bitumen is not a polymer material, rather it is a mixture (solution) of saturated hydrocarbons, aromatics, polar aromatics and heterocyclic compounds. The viscosity is related to the content and molecular weight of saturated hydrocarbons present in which other more complex organics are dissolved. Although it occurs in natural deposits, bitumen used in industry is a by-product of crude oil refining, representing the residue following distillation of lighter hydrocarbons.

2.2 Example national inventories

In this section inventory information concerning the nature and quantities of organic containing ILW and LLW is presented. Inventory information is presented in alphabetical order for countries with stocks of organic wastes that may be considered for geological disposal. Additional information is also provided for operating underground disposal facilities for ILW and LLW disposal in the Czech Republic, Finland and Sweden.

2.2.1 Belgium

In Belgium, ONDRAF/NIRAS implemented a four-level hierarchical classification system for conditioned radioactive waste (Figure 2). This system is consistent with the main international classification system adopted by countries challenged with the issue of radioactive waste management. At the first level, the waste is divided in two groups according to the possible disposal solutions. Next, the groups are divided in three main internationally defined categories (e.g. LLW, ILW, HLW). At this second level, distinctions are made based at the radiological activities of the waste and possible heat generation. At the third level conditioned waste that has similar packaging, storage and potential disposal methods are assigned to twenty classes (ONDRAF/NIRAS, 2001) that are finally allocated to about 60 families (ONDRAF/NIRAS, 2013a). Each waste family gathers waste packages whose individual characteristics are sufficiently close to that of the family average to not produce a significantly different impact of any type during any step subsequent to its production (ONDRAF/NIRAS, 2013a).
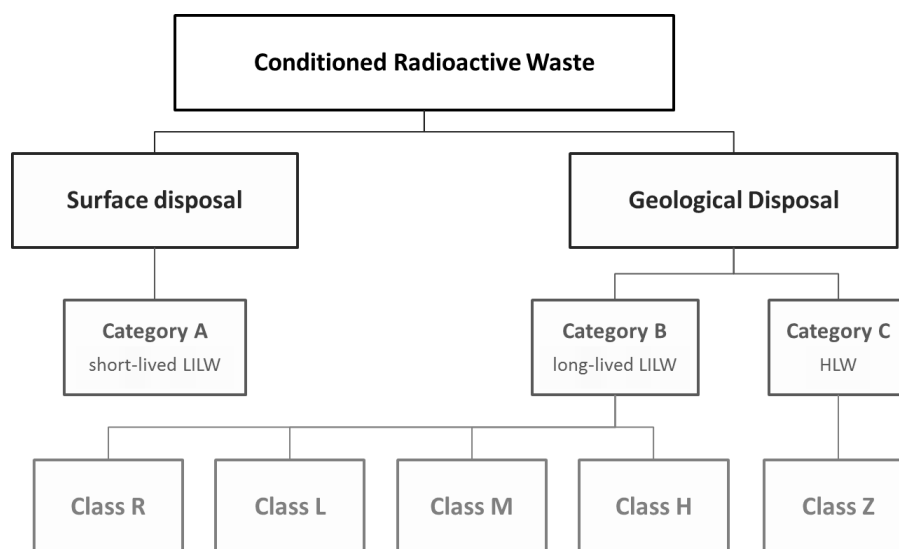
Figure 2: Classification of conditioned radioactive waste in Belgium. LILW: low- and intermediate level waste; HLW: high level waste

Belgoprocess is the leading company for processing and conditioning of radioactive waste in Belgium. Processing of radioactive waste is important to reduce its volume and to convert the physical and chemical conditions of the waste for safe and long-term conditioning. Depending on the physicochemical properties of the waste, different processing techniques can be applied.

- Solid combustible waste is incinerated at up to 900°C. The resulting ash has on average a volume 50 times lower than the original waste.

- Solid incombustible but compressible waste is collected in steel 220 litre drums and compressed with a press of 2000 ton into 25 cm thick slices, leading on average to a volume reduction of a factor 3.
- Incombustible and incompressible waste is cut to pieces.
- Liquid waste undergoes a physicochemical or thermal treatment to transform the waste into a small amount of sludge which can be further processed as solid waste.
- Small amounts of effluents such as oils and solvents from laboratories are injected in the oven for solid combustible waste.

Afterwards, the processed waste is immobilised and encapsulated to prevent spreading of the radionuclides. Depending on the activity, different techniques are used (www.belgoprocess.be; ONDRAF/NIRAS, 2008). In 2010, about 80 % of the total volume of LILW-LL in Belgium was stabilised in a bituminous matrix. These are mainly liquid wastes and sludges. There are two different types of bituminised waste in Belgium, depending on the conditioning. One type is conditioned in the Mummie installation in a matrix of distilled bitumen i.e. soft bitumen, while the other part is conditioned in a matrix of blown bitumen i.e. hard bitumen in the Eurobitum installation (ONDRAF/NIRAS, 2001). Both installations were shutdown in 2004 and 1999, respectively. After all radioactive waste intended for geological disposal has been produced, the volume fraction of bituminised waste will drop to approximately 35 %, however bitumen remains the most important organic fraction of the waste (90 %). The other part of the LILW-LL has been encapsulated in a cementitious matrix sometimes preceded by compaction of the raw waste, except for waste originating from the Eurochemic Pamela facility that has been vitrified, and combustible waste which has been incinerated before encapsulation in cement. It should be noted that the former waste is considered as non-heat producing due to its advanced age and is therefore classified as LILW-LL (ONDRAF/NIRAS, 2013b). Hence, bitumen and cement are the most commonly used immobilisation matrices in Belgium.

A summary of the relative amounts of organics comprised in the Belgian LILW-LL waste is presented in Figure 3. The organic cement additive present in the encapsulation matrix will mainly be Rheobuild 1100 (Napthalene Sulfonate based). About 90 % of the organics present in the LILW-LL comprises of bitumen, 4 % are halogenated polymers which are mostly PVC (including phthalates), 2.5 % comprises of cellulose (wood, paper, cotton etc), 2 % consist of non-halogenated polymers, including resins (mostly polystyrene-based) and polyethylene. Among others the following contaminants will probably also be present in the waste at very low concentrations: EDTA, citrate, tributylphosphate, oxalic acid, tartaric acid (Benny de Blochouse, ONDRAF/NIRAS, pers. Communication, 2015).
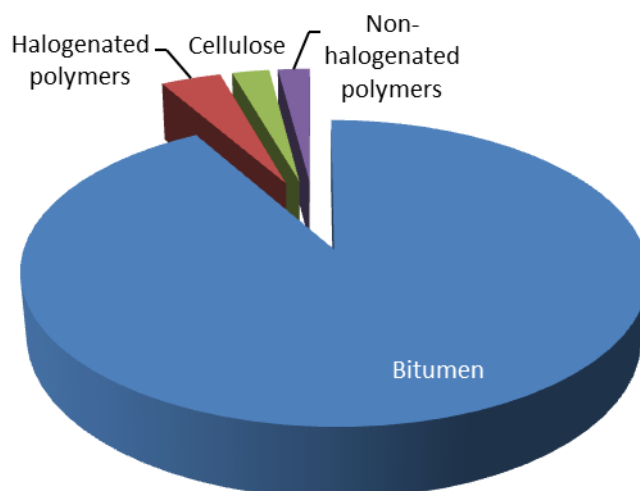
Figure 3: Percentages of the different groups of organics present in the LILW-LL waste in Belgium

2.2.2 Czech Republic

In the Czech Republic, radioactive waste is classified as recommended by the IAEA into low-level waste LLW (A <10^9 Bq.m^{-3}, zero heat generation), intermediate level waste ILW moderately active (A ~ 10^9-10^{14} Bq.m^{-3}, low heat generation), and high-level waste HLW (A > 10^{14} Bq.m^{-3}, high heat generation). LLW and ILW is also classified by the half-life and the prevailing radionuclides into short-term (half-life about 30 years) and long-term (SÚRAO 2011). Operation and monitoring of all repositories, as well as the construction of a deep geological repository is the responsibility of the Radioactive Waste Repository Authority (RAWRA / SÚRAO).

The majority (around 80% volume) of radioactive waste produced in the Czech Republic arises from nuclear power plant operations. Institutional radioactive waste generated in hospitals, agriculture, industry and research accounts for roughly 20% of the total amount of radioactive waste in the Czech Republic. Annually, around 450 tons of LLW and ILW originates from medicine, research and other nuclear technologies (SÚJB 2015). There are several hundreds of producers of institutional radioactive waste. The most important producer of institutional radioactive waste is ÚJV Řež a.s., which produces about 90% of this kind of waste. Moreover, ÚJV Řež provides services for other producers in the field of radioactive waste management including identification, collection, sorting, treatment and transportation of radioactive waste for disposal in a repository. Institutional radioactive waste comprises a wide range of material type (Figure 4) and is more variable than that from nuclear power plants. Around half of the institutional waste comprises organic materials and plastic comprising 15% of the waste (Figure 4).
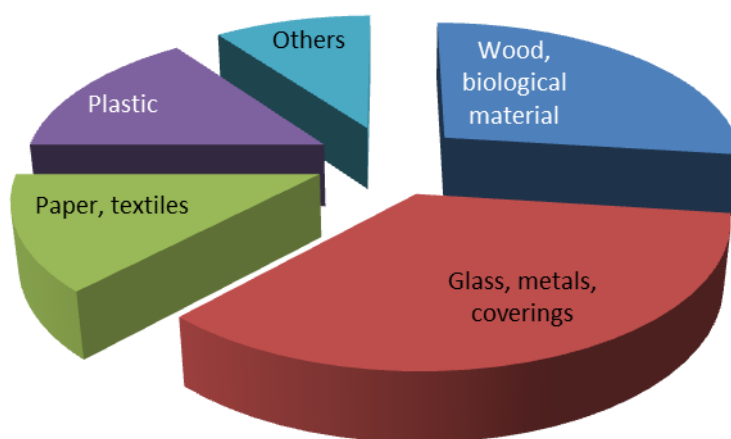
Figure 4 Distribution, by volume, of Institutional radioactive wastes in the Czech Republic (Bromová 2013)

Institutional radioactive waste is classified and segregated (based on materials used, such as paper, used syringes from hospitals, glass, plastics, filters from devices using ionizing radiation, protective clothes and many other different materials), and then compressed. The compacted waste is placed into 100 l barrels and filled with concrete. These barrels are inserted into larger, usually 200 l barrels (Figure 5a). The space between the barrels is filled with concrete mixture which is at least 5 cm thick. The barrels and the outer surface are coated with bitumen. Approximately 500 barrels of institutional waste are disposed each year. In contrast, the LLW and ILW from nuclear power plants comprise 2000 barrels (SÚRAO, 2014a).

LLW and ILW from the operation of nuclear power plants comprise mainly of materials arising from water treatment. Radioactive water is treated by selected processes including mechanical filtration and ion exchange, sorption, sedimentation, centrifugation and evaporation. The concentrated liquid waste, sludge and spent ion exchangers from the current nuclear power plants are encapsulated in bitumen, concrete or aluminosilicate (Geopolymer) matrices. Solid or solidified radioactive waste in 200 l barrels is characterised and subsequently transported to a repository at Dukovany.

ILW is stored in surface or near-surface repositories in the Czech Republic. The largest near-surface storage is situated in the Dukovany nuclear power plant. It has been in continuous operation since 1995 and is designed for LLW and ILW for waste produced during the operation of nuclear power plants. The total volume of storage space (55,000 m^3) is sufficient to store all operational waste from both nuclear plants in the Czech Republic (Dukovany and Temelin), even if their planned lifetime will be extended up to 40 years. Radioactive waste immobilised in bitumen is disposed of in the Dukovany repository. Since 2010, an aluminosilicate Geopolymer matrix has been used for sludge disposal and spent polystyrene ion exchangers. The number of stored 200 l barrels is published annually. In 2014, 1189 barrels of bitumen and 1053 barrels of aluminosilicate conditioned waste were stored (SÚRAO 2014a). The number of bitumen barrels each year remains constant, but there has been an increase in the numbers of barrels using the aluminosilicate matrix since 2010.

The waste producers in the Czech Republic sort LLW and ILW by the type of radionuclides and total activity in each barrel. Due to the disposal of radioactive waste mainly by solidification, the type of waste is less important for the repository authorities. Table 2 provides a listing of the volumes and

radionuclides disposed at the main Dukovany repository at the end of 2014. The majority of the radionuclide inventory comprises ^{137}Cs and [63]Ni, which have half-lives of around 30 and 100 years, respectively. The inventory also includes longer lived radionuclides ^{14}C and [239]Pu and [241]Am, which are both alpha emitters.

Table 2 Overview of the utilisation of the volume and inventory limits of the Dukovany repository as at 31 December 2014 (SÚRAO 2014)

		Limit	Disposed of	Utilisation [%]	Remaining capacity
Volume	[m³]	55,000	10,764	19.57	44 236
[14]C	[bq]	1,00E+13	1.99E+11	1.99	9.80E+12
[41]Ca		3,00E+11	3.15E+08	0.11	3.00E+11
[59]Ni		3,00E+12	7.82E+09	0.26	2.99E+12
[63]Ni		3,50E+13	1.08E+12	3.08	3.39E+13
[90]Sr		1,00E+13	9.44E+10	0.94	9.91E+12
[94]Nb		3,00E+10	1.56E+09	5.21	2.84E+10
[99]Tc		1,00E+12	1.39E+09	0.14	9.99E+11
[129]I		1,00E+11	5.60E+08	0.56	9.94E+10
[137]Cs		3,00E+14	9.65E+12	3.22	2.90E+14
[239]Pu		6,00E+09	1.44E+08	2.40	5.86E+09
[241]Am		1,00E+10	6.42E+08	6.42	9.36E+09

(a)   (b)

Figure 5 Examples of disposed organic wastes in the Czech Republic (a) Compressed plastic LLW and ILW, cut section of a 200 l barrel (b) waste drums stacked in a disposal chamber at the Richard Repository.

The former mine Richard near Litomerice and Bratrství mine near Jáchymov serve as subsurface storage. The Richard repository is designed for disposal of institutional LLW and ILW from research, industry, agriculture and medicine (Figure 5b). It was established in a former limestone mine Richard II in 1964. Its storage capacity is about 8,500 m³ and at present has sufficient capacity until at least 2070 (SÚRAO 2012b). Waste is characterized in ÚJV Řež a.s., and subsequently stored based on quantities and specific activities of critical radionuclides (SÚRAO 2011). The overburden and bedrock of this former mining complex is made up of impermeable marlite with a thickness of over 50 m. The repository temperature is stable throughout the whole year (about 10 °C). The total volume of used space exceeds 19,000 m³ and the space designated for storage is 8,500 m³ of which 67% has been filled to date. There have been 3825 barrels disposed since 2000 and more than 24,000 packages in total (SÚRAO 2012a). Repository Richard also accepts wastes of high activity exceeding the limit of

radionuclide content, but only as a temporary measure until they are stored permanently in a deep underground repository.

Bratrství repository stores LLW and ILW containing only naturally occurring radionuclides. The repository was established in the former uranium mine at Bratrství in 1974. More than 80% of the available capacity of approximately 1,200 m^3 has been used. The final closure date and method of storage is dependent on the volume of the future radioactive wastes (SÚRAO 2012a).

A certain amount of ILW cannot be disposed of in existing near-surface facilities. For this type of waste, special requirements must be met concerning the method and quality of conditioning necessary for its storage and subsequent disposal in a deep geological repository (DGR). Until the time that the DGR comes into operation, such waste is stored either by waste producers or by SÚRAO. The future concept is to minimize the amount of radioactive waste (SÚRAO 2014b). SÚRAO plans to monitor the composition of radioactive waste materials in more detail, although it is not required to by law. The Dukovany repository has sufficient capacity for wastes from the two nuclear power plants. Expansion of usable space is planned in the Richard repository. Bratrství repository expects to have no increase in the amounts of uranium from mining.

2.2.3 Finland

In Finland, nuclear waste is primarily generated in the nuclear power plants in Loviisa and Olkiluoto. Radioactive waste is categorised according to the activity level into high-level waste (activity more than 10 GBq kg^{-1}; spent fuel), intermediate-level waste (1 MBq kg^{-1} - 10 GBq kg^{-1}) and low-level waste (not more than 1 Mbq kg^{-1}) (STUK, 2015). According to the Finnish Law Nuclear Energy Act (990/1987) and the Nuclear Energy Decree (161/1988) that came into force in 1988, all nuclear waste must be treated, stored and disposed of within Finnish borders. The Finnish nuclear power companies Fortum Power and Heat Oy (Fortum, Loviisa, Finland) and Teollisuuden Voima Oyj (TVO, Olkiluoto, Finland) process and dispose of the LLW and ILW arising from power plants at Loviisa and Olkiluoto. Waste generated from the eventual decommissioning of the power plants is to be disposed of in the same facilities. In order to organise the management of spent nuclear fuel, TVO and Fortum established Posiva Oy (Posiva) in 1995 to take care of the disposal of its owners' spent nuclear fuel.

Table 3 and Table 4 list the inventories of LLW and ILW disposed, as of 2014, at the Olkiluoto and Loviisa facilities, respectively. The Olkiluoto repository for operational waste (VLJ repository) was commissioned in 1992. The repository consists of two rock silos, a hall connecting the two and of auxiliary facilities constructed at a depth of 60–100 metres inside the bedrock (Figure 6). The capacities for silos (as volumes of waste placed in 200 l drums) are about 5,000 m^3 (low activity silo, MAJ-siilo) and 3,500 m^3 (intermediate activity silo, KAJ-siilo). Low-level waste is deposited in the rock silo inside a concrete box. Intermediate-level waste is deposited in the rock silo comprised of steel-reinforced concrete (Posiva, 2012). A large-scale waste degradation experiment is located in a construction tunnel (Figure 6), which will be utilised as part of Task 1.3 of the MIND project.

The organic components of ILW at Olkiluoto comprise ion exchange resins, while the organic components of LLW are maintenance wastes comprising cellulose and other polymers. At Olkiluoto ILW ion exchange resins are encapsulated in bitumen in 200 l steel drums. Figure 7 further illustrates the distribution of these LLW and ILW organic wastes from Olkiluoto.

Table 3 Total amount of low level and intermediate level waste in Olkiluoto in 2014 (Posiva, 2015).

Waste type	Description	Amount (m^3)
Low level waste		
Scrap		2962
Unpacked scrap		23
Maintenance waste	approximately 80% organic material: 41% cellulose (cotton cloth, paper, paper board, oily paper and cotton cloth), 30% PE, 3% latex, 2% PVC	1020
Miscellaneous liquids	organic solvents, water, acids etc.	14
Solidified liquids (bitumen)		98
Waste oil		11
Intermediate level waste		
Scrap		362
Resin powders		1424
Resin granules		299
Total		**6214**

The inventory of the wastes generated by Fortum (Table 4) comprise similar materials, with the ion exchange resins representing the majority (90%) of the radioactivity. Currently, ion exchange wastes are stored in liquid prior to solidification in cement. LLW and ILW generated during operation of the Loviisa power plant is disposed in the bedrock-excavated final repository (VLJ cave) owned and used by Fortum. Final repository consists of a 1,170-metre-long access tunnel and hall facilities situated at a depth of about 110 metres. The plan is to enlarge the final repository so that all LLW and ILW and decommissioning waste generated at the power plant can be placed there. The dry maintenance waste generated during operation is packed into 200-litre steel drums and compressible waste is pressed into the drums using a baling press. Used ion exchange resins and evaporator concentrates are stored in tanks in the liquid waste storage. Trial operation runs of the solidification plant for liquid operating waste have been performed since 2007 and the plan is to commission the plant by 2016.

Table 4 Total amount of low and intermediate level waste in Loviisa in 2014 (Posiva, 2012, 2015).

WASTE TYPE	AMOUNT (M^3)	Activity (GBq) at 2011
Used ion exchange resins	566	15,000
Evaporation residues	658	1,180
Solidified evaporation liquids and ion exchange resins	31	<1
Solvents solidified by absorption, low level ion exchange resins and active carbon	66,8	<1
Maintenance waste	2172,4	648
Total	**3521,2**	
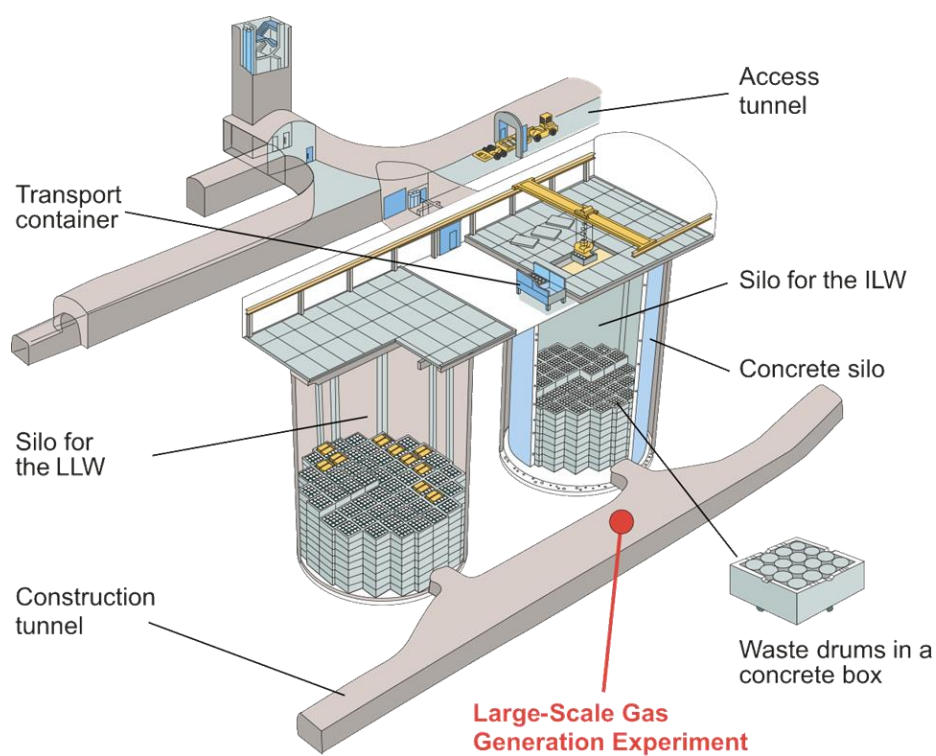
Figure 6 Schematic of the VLJ repository, Olkiluoto, (TVO)
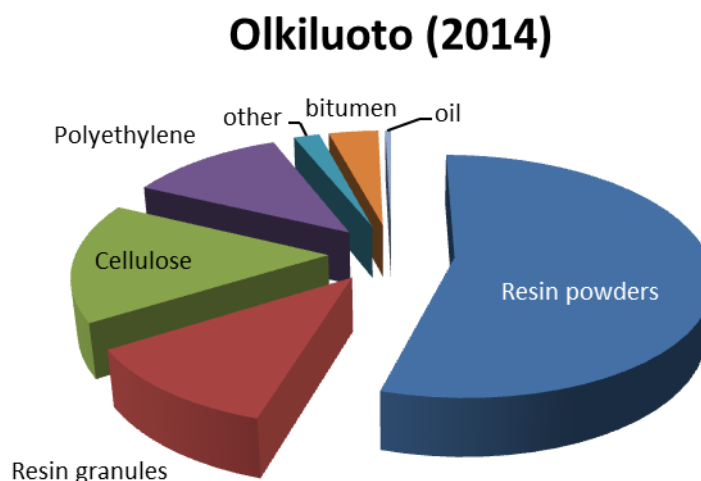
Figure 7 Distribution (by volume) of organic LLW and ILW (resins) disposed at Olkiluoto as of 2014. Note: excludes bitumen used to encapsulate ion exchange resins.

2.2.4 France

The French National Inventory (Andra, 2012) includes sources of radioactive waste from five economic sectors: nuclear power, defence, research, industry and medical. Radioactive waste is classified into 4 main categories; high level, intermediate level, low level and very low level. Waste is also classified according to its half-life, where long-lived waste contains a large quantity of radionuclides with half-lives longer than 31 years. High level waste and long-lived intermediate level waste is currently being stored until such time as a definitive disposal site is made available. The organic inventory of long-lived intermediate level waste (LL-ILW) is of main relevance to the MIND project.

LL-ILW is comprised of a number of waste package types with designation B1 to B9 (e.g. see Andra, 2005), and of these, the B2 wastes are notable in that they contain bituminised waste, while the B3 wastes packages contain a variety of organic wastes encapsulated in a cement matrix. Figure 8 shows the distribution of organic materials present in some example B wastes. B3.1.2 includes wastes from the La Hague reprocessing site. Here the organic wastes comprise mainly chlorinated and non-chlorinated plastics (Figure 8) contained in metal drums or polythene sacks within 400 l concrete packages encapsulated in a cement matrix. Prior to 1994 asbestos cement containers (CAC) were used. Since then metal fibre reinforced concrete containers (CBF-C'2) have been used. The chlorinated plastics include PVC, Hypalon™ and neoprene. The non-chlorinated plastics comprise polyethylene and polypropylene (Andra, 2009). A lower proportion of chlorinated organics is present in the more recent CBF-C'2 B3.1.2 wastes (Figure 8). B3.1.3 waste (Figure 8) also comprises a large proportion of chlorinated plastics. This wastestream represents repackaged waste from the Le Manche facility and includes various kinds of sheets of PVC or polyethylene, clothing, overshoes, laboratory glassware, various metal parts, cotton and fabrics, small tools and irradiated metal residues from examining fuels. Large items of dismantled waste include pipes, tanks, ventilation ducting, glove boxes, cutting and machining tools may also comprise organic materials. (Andra, 2009). B3.3.7 (Figure 8) comprise metallic and organic technological waste from maintenance and operation at the Marcoule site, which include higher proportions of cellulose.
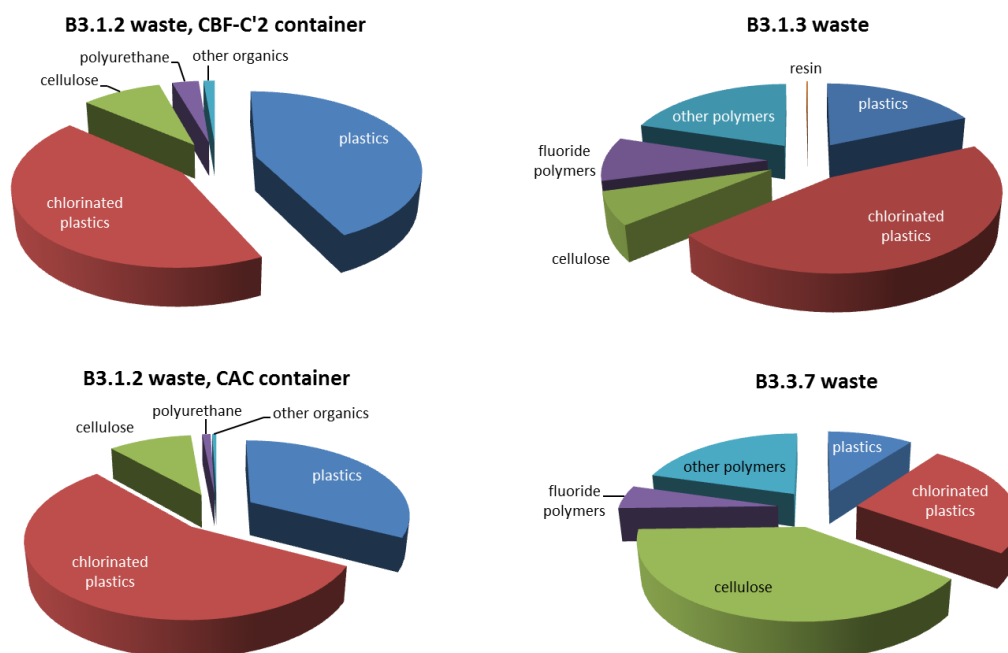
Figure 8 Distribution (by mass) of organic materials in some French LL-ILW wastes (Andra, 2009)

Information concerning the radionuclide inventory of chlorinated plastic-rich wastes present in the B3.1.2 waste is provided in Figure 9. After 10 years storage, the activity is dominated (~60%) by [241]Pu together with equal activities (~15%) of ^{90}Sr and ^{137}Cs the remaining 10% of the activity comprises [238]Pu, [240]Pu and [241]Am. After 200 years, the total activity will have decayed by a factor 50 and be dominated by [241]Am that in-grows from [241]Pu decay. [90]Sr and ^{137}Cs will have also decayed and after 200 years will represent less than 10% of the activity. After 1,000 years, the total activity will have decayed by 2 orders of magnitude and will be comprised of [241]Am and the longer lived [239]Pu and [240]Pu, which will dominate after 4,000 years. After 100,000 years, most remaining activity will be from [240]Pu. This information is useful to consider the types of radiation, dose and time period that the chlorinated plastic waste will be exposed to.
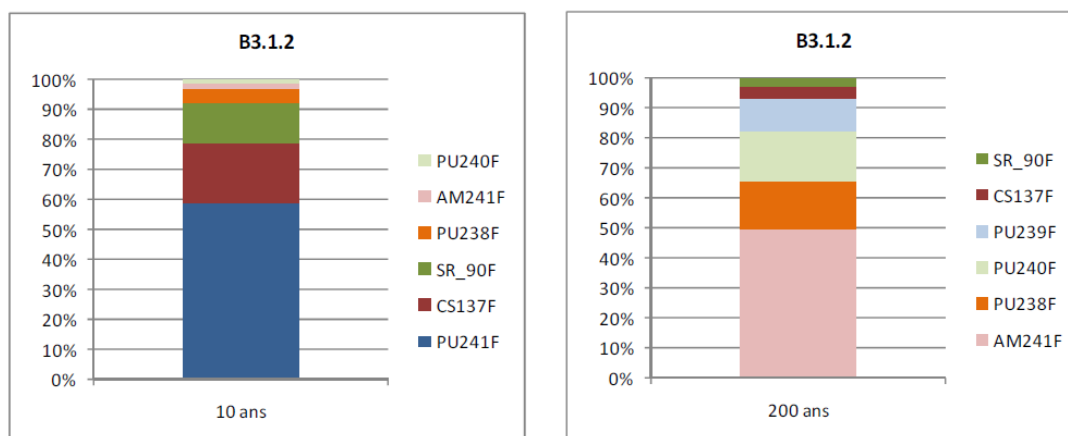
(a)
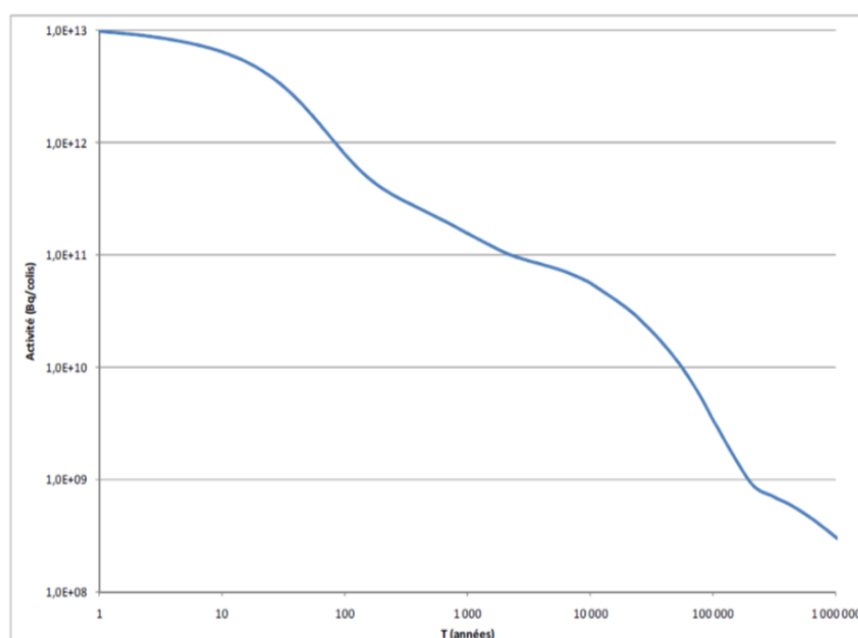
(b)

Figure 9 (a) summary of main radionuclides contributing to activity in waste B3.1.2 at 10 and 200 years (b) temporal evolution of activity of the B3.1.2 wastepackage (Andra, 2009).

In addition to the organic wastes that arise from reprocessing and laboratory operations, a significant inventory of organic ion exchange resins arises from nuclear power reactors in France operated by EDF. The EU Framework 7 CAST project (Rizzato *et al*, 2015) has reviewed information concerning organic exchange materials used to clean cooling water in pressurised water reactors in France. Polystyrene DVB copolymer resins are used with cation resins, being of the acid sulfonated type, in hydrogen or lithium form depending on the application. Anion exchange resins are of the strong base quaternary trimethylamine type, in hydroxide form. Resins degrade in the harsh radioactive thermal and chemical conditions in which they are used and have a maximum lifetime of 7 years. Spent resins are stored under water for several months for short-lived radioactivity to decay. The resins are then processed using the Mercure process that encapsulates the materials in an epoxy resin in C1PG type

concrete containers for surface disposal. The Mercure process is suitable for treating resins containing short-lived radionuclides e.g. [58]Co, ^{60}Co, [110m]Ag, [54]Mn, [57]Co, [134]Cs, [137]Cs (non-exhaustive list) and that are suitable for surface disposal. Other exchange resins containing long-lived radionuclides would be classified as LL-ILW requiring deep geological disposal.

Figure 10 illustrates a distribution of organic wastes considered for geological disposal in the Dossier Argile (Andra, 2005). This projected inventory represents the waste arising from a scenario (S1a) which assumes that all the spent fuel unloaded by EDF power plants in France currently operating will be reprocessed. The total mass of organic waste is estimated to be 2.6×10^6 kg. This inventory of organic waste does not include the bitumen present in the B2 wastes (Andra, 2005) which have a mass of approximately 1.37×10^7 kg.
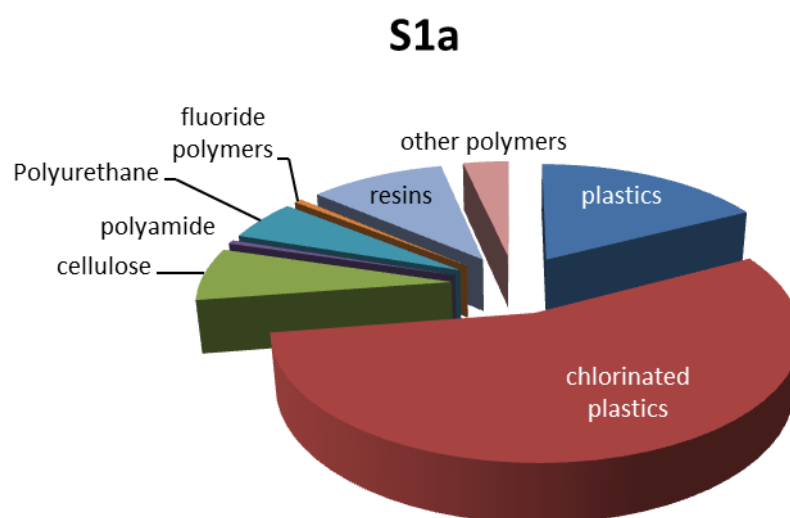
Figure 10 Distribution of the forward inventory of organic LL-ILW materials by mass (Andra, 2005)

2.2.5   Spain

The classification of radioactive waste in Spain defines two main categories (Enresa, 2006):

- Waste with low and medium level activity and short life (LILW) contains mainly beta-gamma emitting radionuclides with short or medium half-life (less than 30 years) and which contain very low levels of long-lived radionuclides. LILW is disposed at the El Cabril nuclear facility.

- High level activity waste (HLW) contains long-lived alpha emitting radionuclides in appreciable concentrations above 0.37 GBq/t, with a half-life of more than 30 years. This mainly includes spent fuel and vitrified waste, but also includes medium high level waste (MHLW), which is not suitable for disposal at the El Cabril facility.

A summary of the inventory of LILW at 31st December 2004 is published (Enresa, 2006). Nuclear waste primarily arises from nuclear power plants (93 %). The total inventory of LILW generated by the operation of nuclear power plants from start-up to the end of their useful lives (2028) is 36,300 m^3, of which 18,500 m^3 had been removed as of 31 December 2004 (Enresa, 2006). Figure 11 illustrates the distribution of all the materials present in Spanish LILW that has been conditioned, excluding materials present at the nuclear power plants at that time. A quarter (25%) of the

conditioned LILW inventory comprises resins used to clean cooling water of the light water reactor power plants operating in Spain. A further 25% of the conditioned LILW comprise evaporator concentrates and smaller quantities of sludge and filters resulting from the treatment of cooling water and other liquid wastes produced at nuclear power plants. The resin, concentrate, sludge and filter materials are conditioned in a cement matrix within 220 l drums.
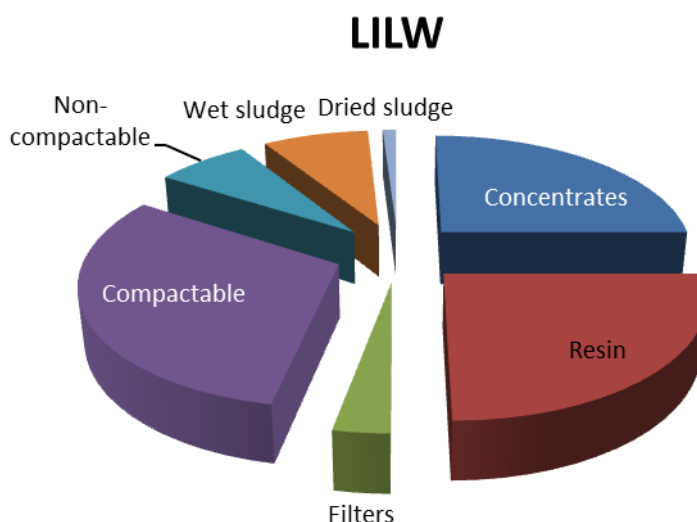
Figure 11 Distribution (by volume) of conditioned LILW in Spain at 2004 (from Enresa, 2006)

The remaining solid waste comprising cloth, debris, metal components, personal protective equipment, paper, wood, etc. is divided into compactable and non-compactable LILW. Ion exchange resins thus comprise the main organic material present in Spanish LILW, with compactable waste likely including cellulose and polymer materials. The amount and proportion of compactable and non-compactable solid wastes is anticipated to increase as nuclear sites are decommissioned (Enresa, 2006).

2.2.6   Sweden

In Sweden, radioactive waste is classified into five categories: Very low level waste (VLLW); Short-lived Low and intermediate level waste (LILW); Long-lived LILW and Spent Fuel. The focus of MIND Work Package 1 concerns short-lived LILW, which since 1988 has been disposed at the SFR 1 facility situated close to the Forsmark nuclear power plant in the northern part of Uppland, Sweden. It is designed for the disposal of low and intermediate level wastes from Swedish nuclear power plants and is the Central Interim Storage for Spent Nuclear Fuel (Clab) and wastes from other industries and research. The repository's total volumetric capacity is 90,000 m^3 of waste with a total radioactivity of 10^{16} Bq. Waste materials are encapsulated in either cement or bitumen.

SFR 1 is located at a depth of around 50m below the Baltic Sea and is divided into four 160m long rock vaults (1BMA, 1BLA, 2BTF and 1BTF) and a main Silo (Almkvist and Gordon, 2007, Figure 12).
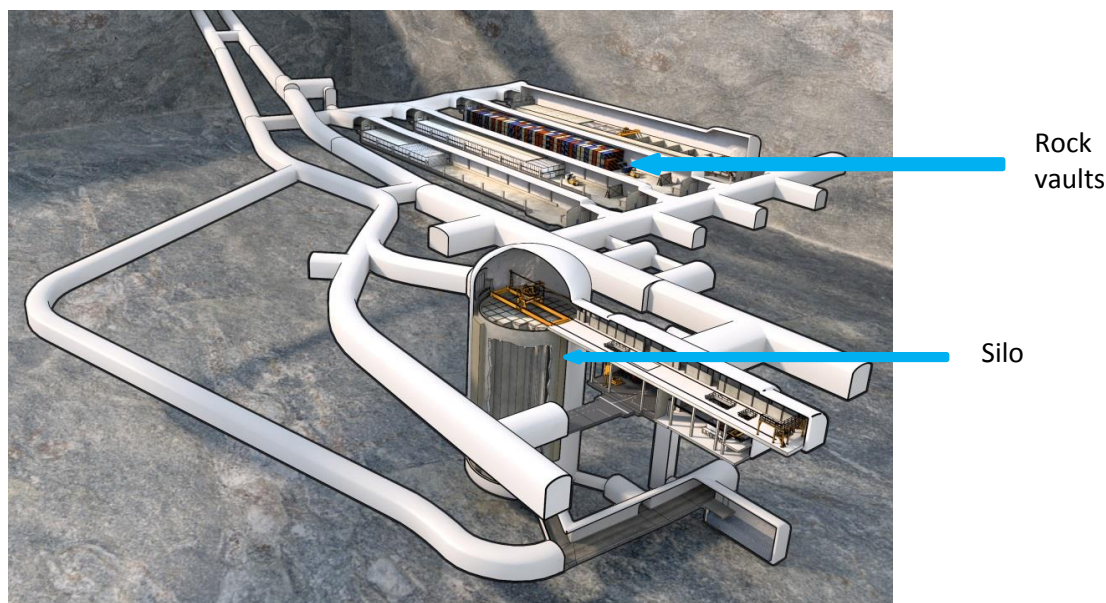
Figure 12 Overview of the SFR 1 repository at Forsmark (adapted from skb.se)

Pending regulatory approval it is planned that the SFR will be extended to around 200,000 m^3 to accommodate LILW from decommissioning the Swedish power plants (SKB, 2014).

The Silo

The main part of the radioactivity in the waste in SFR 1 (92%) is intended for disposal in the Silo. The waste is mainly composed of ion-exchange resin in a concrete or bitumen matrix. The Silo consists of a concrete cylinder with the height of approximately 50 m and a diameter of approximately 30 m. The Silo is divided into vertical shafts with intervening concrete walls. The waste packages are placed in the shafts, normally in levels with four moulds or 16 drums. The voids between the waste packages are gradually backfilled with porous concrete. The walls of the Silo are made of reinforced concrete with a thickness of 0.8 m. In between the Silo walls and the surrounding rock, there is a bentonite backfill, on average 1.2 m thick. The 1 m thick concrete floor in the bottom of the Silo is placed on a layer of 90/10 sand/bentonite mixture. According to present plans, the top of the Silo will be a 1 m thick concrete lid (Almkvist and Gordon, 2007). The top of the lid will be covered with a thin layer of sand and then 1.5 m of sand/bentonite mixture (90/10). The remaining void above the sand/bentonite in the top will be filled with sand or gravel or sand stabilised in cement.

Rock Vault for Intermediate Level Waste (BMA)

The radioactivity in the waste deposited in the BMA is mainly lower than in the Silo waste. The waste consists of ion exchange resins, scrap metal and trash in a concrete or bitumen matrix. The waste packages are of the same type as in the Silo, i.e. moulds and drums. The rock vault is 160 m long and has a width of 19.5 m. The concrete structure in the vault is divided into 15 compartments. The compartments comprise large boxed regions with concrete walls in between. The waste is piled on top of the concrete floor in a way that allows the concrete moulds to act as support for pre-fabricated concrete lids. The lids are put in position as soon as the compartments are filled. Finally a layer of concrete is cast on top of the lid. Between the concrete structure and the rock wall there is a 2 m wide space. This space will be filled with sand. The space above the concrete structure could be left unfilled but could also be backfilled. Plugs will be placed in the two entrances to the vault when the repository is closed.

Rock Vault for Low Level Waste (BLA)

The waste deposited in BLA is mainly low level scrap metal and refuse placed in standard steel containers. Some of the waste inside the containers is placed in steel drums and others in bales. The rock vault is 160 m long and has a width of 15 m. There are no concrete structures in BLA except the floor. The containers are placed two in a row and three full height containers or six half height containers in height. Most of the containers are half height. No backfill is planned.

Rock Vaults for Concrete Tanks (BTF)

In SFR 1 there are two rock vaults for concrete tanks, 1BTF and 2BTF. The waste placed in BTF is de-watered low-level ion exchange resin in concrete tanks. In addition, some drums with ashes are stored in 1BTF. The rock vaults are 160 m long and have a width of 15 m. The concrete tanks, each with a volume of 10 m^3, are piled in two levels with four tanks in each row. A concrete radiation protection lid is placed on top of the pile. The space between the different tanks is backfilled with concrete and the space between the tanks and the rock wall will be filled with, for example, sand stabilised in cement.

Waste materials

Table 5 shows the expected quantities of wastes to be disposed in SFR 1, based on the full inventory at the time of repository closure estimated in 2007[1] (Almkvist and Gordon, 2007). The items in bold are those which are of direct interest to the MIND Work Package 1 studies, i.e. anthropogenic organic materials. Note that these data include both the mass of unconditioned waste material (e.g. ion-exchange resin) and the encapsulant used to condition the waste (e.g. bitumen) as separate material items, even though one will be incorporated within the other. In addition to bitumen, some ion exchange resins are conditioned in a cement matrix. Figure 13 illustrates that for the Silo, ion exchange resins and bitumen dominate the inventory of organic LILW. Similar quantities of resin and bitumen are present in the BMA rock vault inventory, which is designed to take waste not suitable for the silo. Resin is the main organic material in the 1BTF and 2BTF rock vault inventories. The BLA rock vault is designed mainly to contain scrap metals and refuse and its inventory mainly comprises other organic materials, such as plastics, rubber and cable.

Waste Processing Methods

The following methods are utilised to prepare wastes for packaging and disposal:

- **Cement solidification**. Ion-exchange resins or sludge are mixed with cement in drums or moulds.
- **Cement stabilisation**. Scrap metal and refuse are placed in moulds and cement is poured over it. In certain cases the waste is placed in 100-litre drums, which are then put inside standard 200-litre drums. Concrete is then poured in-between the drums.
- **Bitumen stabilisation**. Ion-exchange resins are dried and mixed with bitumen and then poured into moulds or drums.
- **De-watering**. Wet ion-exchange resin is pumped into a concrete tank and water is removed by suction.

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[1] At time of writing an updated inventory has been published (SKB, 2015), this includes information on decommissioning waste and the planned extension of SFR , but the expected amounts of wastes in SFR 1 are not significantly different.

Table 5. Summarised expected amounts of wastes in the SFR 1 at the time of closure, full inventory Almkvist and Gordon, (2007)

Material	Mass in Silo (kg)	Mass in BMA (kg)	Mass in BLA (kg)	Mass in 1BTF (kg)	Mass in 2BTF (kg)
Ion-exchange resin	**2.45E+06**	**1.65E+06**	**9.77E+04**	**5.21E+05**	**8.06E+05**
Other organics (plastics, rubber, cable)	**4.32E+04**	**2.91E+05**	**1.55E+06**	**3.58E+04**	**6.00E+04**
Bitumen	**1.36E+06**	**1.79E+06**	**1.17E+05**		
Cellulose	7.95E+03	1.47E+05	4.50E+05	1.68E+03	1.66E+02
Sludge	2.00E+04	6.00E+04		3.00E+04	4.35E+04
Evaporator bottoms		6.51E+05			
Iron/Steel	3.83E+06	2.76E+06	3.92E+06	7.79E+05	6.34E+05
Aluminium	5.99E+02	7.26E+03	6.50E+04	3.42E+04	2.54E+03
Cement & concrete	2.16E+07	1.27E+07		5.68E+06	3.70E+06
Other inorganic	2.78E+04	3.54E+04	1.05E+05	1.76E+04	4.47E+03
Ashes				1.89E+05	2.48E+04
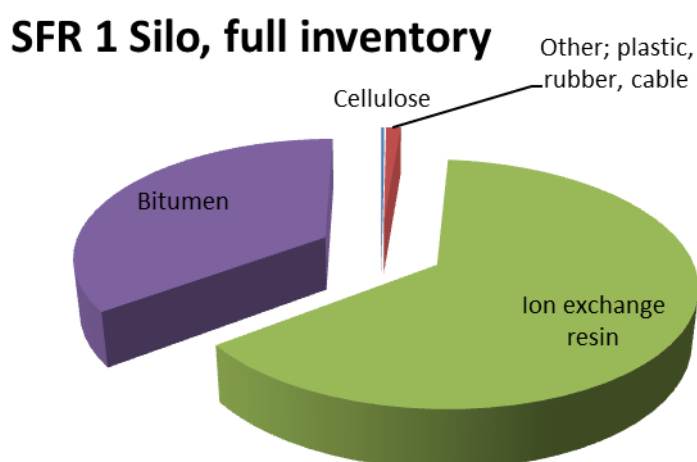
Figure 13 Distribution of organic materials (by mass) estimated for the SFR1 Silo at time of closure

2.2.7 Switzerland

In Switzerland, radioactive waste requiring deep geological disposal is categorised into:

- High-level waste (HLW) comprising, spent fuel assemblies not destined for reprocessing and vitrified fission product solutions from reprocessing of spent fuel.

- Alpha-toxic waste (ATW), with a content of alpha-emitters exceeding a value of 20,000 Bq g^{-1} of conditioned waste.

- Low- and intermediate-level waste (L/ILW)

The Swiss waste management organisation Nagra has developed a deep geological disposal concept for radioactive wastes, including L/ILW. Such L/ILW is prepared for deep disposal either at the power plant sites or at the ZWILAG interim storage facility in Würenlingen. Raw wastes from medicine, industry and research are processed into a form suitable for disposal at the Paul Scherrer Institute or at ZWILAG and are then stored in the Federal Government's interim storage facility (BZL) in Würenlingen.

The estimated mass of organic materials present in conditioned L/ILW is around 3×10^6 kg (Nagra, 2014). The distribution of organic materials in this inventory is illustrated in Figure 14. This distribution includes waste materials (e.g. ion exchange resins) as well as the mass of organic encapsulants such as bitumen or polystyrene used to condition certain L/ILW. Polystyrene (PS) based resins are the largest category of organic material. The inventory delineates these resins into PS sulfonate resins (4.3×10^5 kg) and PS quaternary amino resins (7×10^5 kg). PVC materials comprise around a quarter of the inventory, followed by plastics and bitumen.
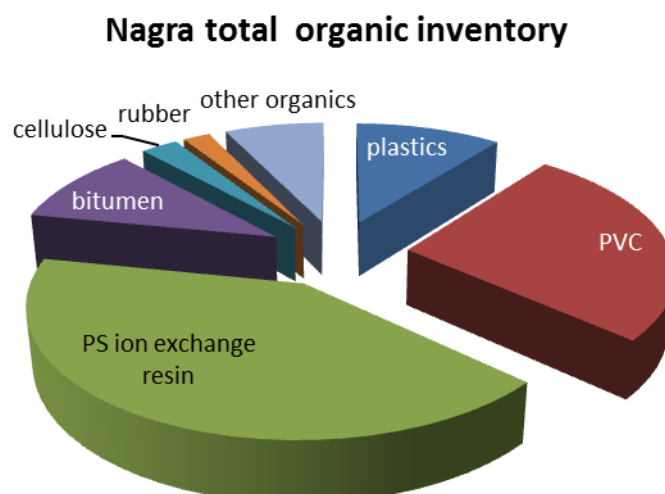
Figure 14 Distribution (by mass) of the organic materials in the Swiss L/ILW inventory for deep geological disposal (data from Nagra, 2014).

A number of different waste package designs exist for L/ILW. Figure 15 shows the design of package type BA-L-H-F2-SMA (Nagra, 2014), where resins and concentrates are conditioned in a cement mortar within a 200 l drum. Similar designs are used for the encapsulation of concentrates in bitumen (e.g. Package BA-G-KB-F2-SMA). Figure 16 shows the design of a package where resin is conditioned in a drum with polystyrene. Here a small 60 l concrete cask containing resin is

encapsulated in a 200 l drum containing an annulus of polystyrene. For each waste stream, the Miram 14 inventory report (Nagra, 2014) details the radionuclide content and calculates the in-growth and decay of radioactivity. Figure 17 shows an example of the estimated activity (Bq) for the resin waste (BA-B-HP-F2-SMA) where the beta/gamma activity appears to be maintained for several hundreds of years by the decay of alpha emitting radionuclides. This information is useful to understand the period that these ion exchange resins may be subject to higher radiation dose.
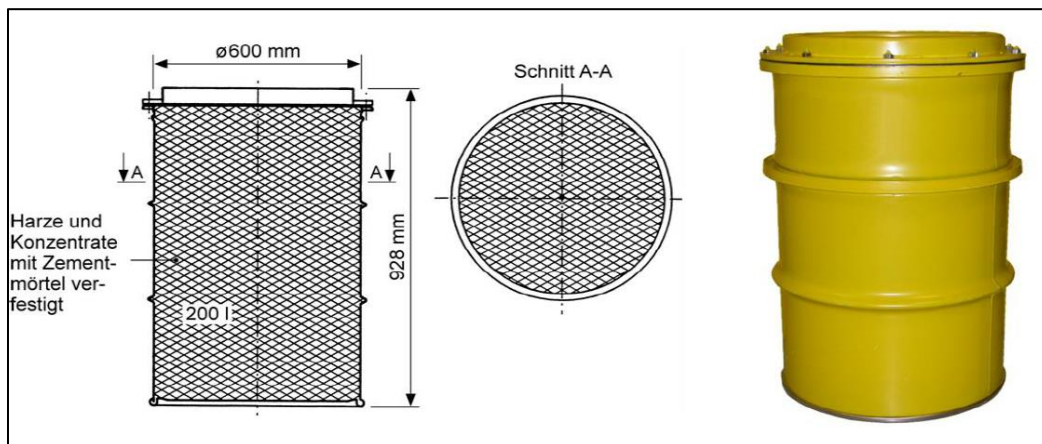
Figure 15 Swiss waste package BA-L-H-F2-SMA, an example of a cement encapsulated ion exchange resin (Nagra, 2014)
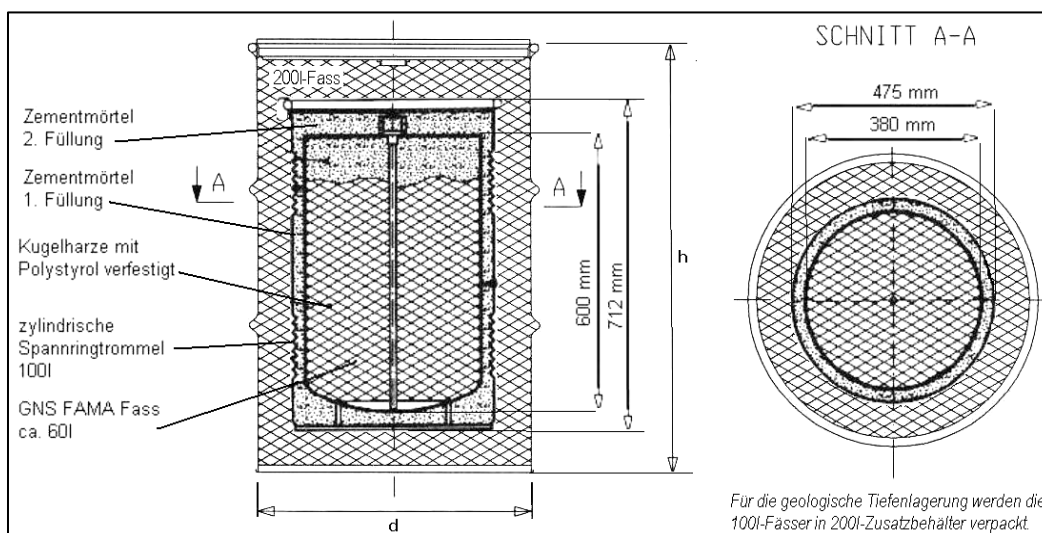
Figure 16 Swiss waste package BA-B-HP-F2-SMA, an example of a polystyrene encapsulated ion exchange resin (Nagra, 2014)
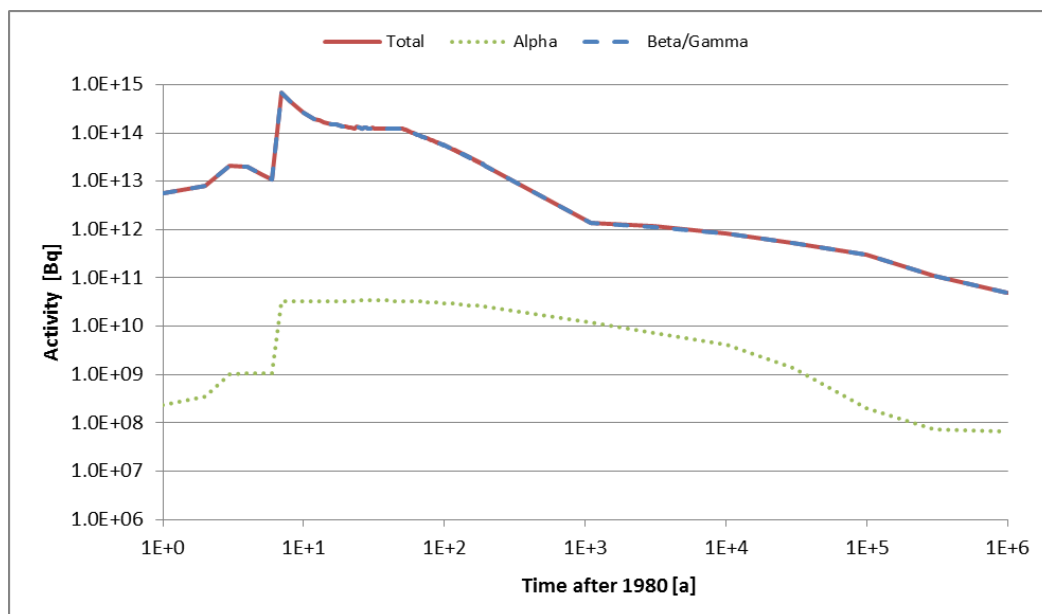
Figure 17 Modelled activity of Swiss resin waste package BA-B-HP-F2-SMA (data from Nagra, 2014)

2.2.8   The Netherlands

In the Netherlands, there is a single nuclear power reactor (NPR), the Borssele pressurised water reactor, and two research reactors, the High Flux Reactor of the EU Joint Research Centre and the Hoger Onderwijs Reactor at the Reactor institute Delft, all still in operation. The NPR Dodewaard boiling water reactor was shut down in 1997 and is in decommissioning and the Low Flux Research Reactor on the Research Location Petten was taken out of operation in 2010 and is prepared for decommissioning. In addition, uranium enrichment facilities are present. The nuclear program in the Netherlands is relatively small, hence the amounts of radioactive wastes that have to be managed are modest. Most of the radioactive waste from nuclear and non-nuclear origin is collected, treated and stored by the waste management organisation COVRA (Centrale Organisatie Voor Radioactief Afval). Exceptions are radioactive waste with a half-life less than 100 days, which is allowed to decay at the sites where it is being generated, and large amount of NORM (naturally occurring radioactive material) waste, which is disposed of (or reused) at landfills. The Dutch policy is that all radioactive waste must be isolated, controlled and monitored. The waste will be stored above ground for at least 100 years so in this period a thorough study of the best long-term solution for deep geological disposal can be performed. In addition, a research programme dealing with geological disposal is required, with the current programme being named OPERA (Onderzoeksprogramma Eindberging Radioactief Afval) (Ministry of Economic Affairs, 2014).

As shallow land burial is not applicable for the Netherlands, there is no distinction between short-lived and long-lived low- and intermediate level radioactive waste (LILW) Ministry of Economic Affairs, 2014). The waste inventory includes three types of radioactive waste, namely high-level waste (HLW), LILW, and NORM waste (Verhoef *et al*, 2014a). NORM waste is actually a special case of LILW and comprises depleted uranium and waste produced during ore reprocessing. At COVRA, it is stored in separate facilities than the other LILW and it is not conditioned in concrete during interim storage (Ministry of Economic Affairs, 2014).

Until now, the radioactive waste disposal process in the Netherlands is only at an early, conceptual phase (Verhoef *et al*, 2014b). Deep geological disposal in poorly indurated clay formations within the

Boom Clay (or Rupel Clay according to Dutch geological stratigraphy) or in a Zechstein rock salt formation is being investigated. The disposal facility should be constructed in such a way that the waste is retrievable, i.e. it is reversible for the long-term by proven technology without re-mining (Ministry of Economic Affairs, 2014). In OPERA it is proposed to include a post-operational phase after emplacement of the waste during which recovery of the waste is possible.

At COVRA, waste drums with LILW are sorted according to the type and processing method that will be applied. Cement is always used as an immobilisation matrix. Generally, packages with a final volume of 200 l or 1000 l are produced. The 200 l drum is a galvanised steel drum with a layer of 5 cm of clean, uncontaminated concrete inside, surrounding the waste. The 1000 l packages are concrete packages wherein a cemented waste form is present. In each package there is at least as much cement as waste volume. The waste is processed by various methods including compaction, incineration of biological materials and organic liquids, water treatment and cement grout encapsulation (Ministry of Economic Affairs, 2014; Verhoef *et al*, 2015; www.covra.nl). Of these wastes compacted LILW and ion exchange materials resulting from water treatment are of relevance to the MIND project.

Compacted waste

About 7 compacted 90 l cans are loaded in a 200 l waste drum. An estimate of the materials present in the waste cans prior to compaction is presented in Table 6. The uncertainty in these estimates is large as indicated by the margin % (Table 6) however the wastes contain significant proportions of cellulose materials and plastics, the latter being dominated by non-halogenated types. The residual space around the compacted 90 l cans is filled with concrete made of Blast Furnace Slag cement (Table 7). The waste drums are galvanised with a thickness of 40 µm zinc and varnished with a vinylcopolymer resin (www.covra.nl).

Table 6 Estimate of the composition of Dutch LILW present in 90 l cans prior to compaction (Verhoef et al, 2015)

Matrix	Specification	Fraction of matrix	Volume %	Margin %
Organic material	Cellulose (clothing, paper, tissue) organic sludge etc	1	35	20
Metals	Steel	0.75	30	20
	Aluminium	0.25		
Plastics	Halogenated	0.10	25	20
	Non-halogenated	0.90		
Other	Glass, rubber, concrete, inorganic adsorption materials, salts etc	1	10	10

Processed liquid waste with spent ion exchangers

Ion exchangers are used to treat liquids from nuclear power plants, where they effectively transfer the radioactive content of a large volume of liquid into a small volume of solid. Ion exchangers from Dutch nuclear power plants are conditioned in cement and will be the only ion exchangers discussed here. Two waste streams, with characteristics specified in Table 8 are processed and conditioned with concrete (Verhoef *et al*, 2015). It is assumed that the most common form of synthetic ion exchange resin is used, namely polystyrene divinylbenzene in powdered form with diameters from 5-150 µm or in beads with diameters from 0.5-2 mm. The resin is conditioned in a cement grout and

poured into 200 l drums. The overall composition of the processed liquid waste and cement encapsulating material is presented in Table 9.

Table 7 Composition of Blast Furnace Slag cement used to encapsulate Dutch LILW (Verhoef et al, 2015)

Component	Type	Quantity (kg m^{-3})
Cement	CEM III/B 42.5 LH HS*	407-430
Water	-	175-185
Plasticiser	TM OFT-II B84/39 CON. 35% (BT-SPL)	3-5
Fine aggregate	Quartz sand : 0-4 mm	819-972
Coarse aggregate	Quartz gravel : 2-8 mm	891-763

* LH: Low Hydration heat; HS High Sulfate resistance

Table 8 Main characteristics of ion exchange processed liquid waste streams (Verhoef et al, 2015; COVRA, 2013).

Component	Waste stream 1	Waste stream 2
Ion exchange resin	Powder max 4.3 kg (wet 8.6 kg) per waste container	Powder max 2.7 kg (wet 5.4 kg) per 200 litre drum
		Beads max 16.8 kg (wet 40 kg) per 200 litre drum
Max activity per waste container	^{60}Co : 10 GBq	^{60}Co: max 400 GBq* ^{137}Cs: max 600 GBq*

* radionuclide specific maximum activities that a vessel of radioactive waste may contain upon collection by COVRA

Table 9 Composition of processed ion exchange resin per 200 litre drum

Component	Type	Weight for waste stream with powder and sludge (kg)	Weight for waste stream with beads, powder and sludge (kg)
Spent ion exchanger	Resin beads	-	16.8 dry resin
			23.2 absorbed water
	Resin powder mixed with sludge	94	45
Cement	CEMIII/B 42.5 LH HS*	242	181
Plasticiser	Sikament	-	3.6
Retarder	Sika retarder	2.4	1.8
Admixture	Zeolite / Klino type 1 $(Na_2K)_6(Al_6Si_{30}O_{72})_{20} \bullet H_2O$	12.1	9.1
Admixture	$Ca(OH)_2$	15	12
Water	-	97	63.5

* LH: Low Hydration heat; HS High Sulfate resistance

2.2.9 UK

UK Government policy is that geological disposal is the way that higher activity radioactive wastes will be managed in the long term; this will be preceded by safe and secure interim storage until a geological disposal facility (GDF) is available and can receive waste. The White Paper, "Implementing Geological Disposal" (DECC, 2014) sets out the UK Government's framework for managing higher activity radioactive waste in the long term through geological disposal. In the UK, higher activity radioactive waste comprises a number of categories: high level waste (HLW), intermediate level waste (ILW), and low level waste (LLW) that is not suitable for near-surface disposal in current facilities. ILW is defined in the UK as waste with radioactivity levels exceeding the upper boundaries for LLW, but which does not require heat to be taken into account in the design of storage or disposal facilities. ILW arises mainly from the reprocessing of spent fuel and from general operations and maintenance at nuclear sites, and can include solid metal items such as fuel cladding and reactor components, and sludges from the treatment of radioactive liquid effluents. As decommissioning and clean-up of nuclear sites proceed, more ILW will arise. Typically, ILW is treated in solid form and packaged in purpose-designed containers, manufactured from stainless steel, iron or concrete.

The UK National Inventory (NDA/DECC, 2014) provides a database of HLW, ILW and LLW waste streams from all UK nuclear facilities and categorises the information by activity and by material type (mass). The National Inventory provides information concerning the current stock of waste and the total that is forecast to arise in future. Figure 18 provides a summary of the total inventory of current stock and future arising of organic ILW materials. This total inventory or organic ILW has a mass of 3.7×10^7 kg.
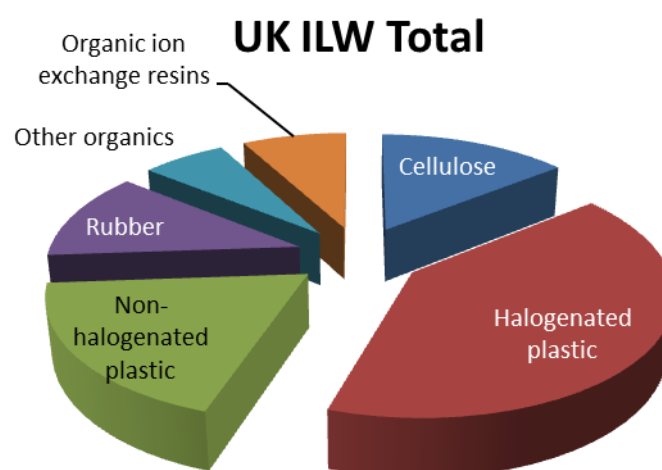
Figure 18 Distribution (by mass) of the total UK ILW inventory of organic ILW (source 2013 National Inventory)

Halogenated plastics comprise the largest component of the inventory (5×10^6 kg). Non-halogenated plastics and cellulose material each comprise around 2.8×10^6 kg and rubber 2.0×10^6 kg. Much of this organic plastic waste arises from reprocessing and research operations and in this respect the UK inventory has a similar distribution to the French inventory (Figure 10). Halogenated plastic is dominated by PVC (NDA, 2012a) which results from use of plastic sheeting to wrap miscellaneous waste and its use in glove box posting bags, protective suits, barriers and other packaging (Smith *et*

al, 2013). Plutonium contaminated material (PCM) wastes generated at the Sellafield site include 2.6 x 10^6 kg of halogenated plastic and 1.6 x 10^6 kg of non-halogenated plastic which is more than half the total UK inventory of these materials. The PCM wastes also comprise around 40% of the UK ILW inventory of cellulose. These organic-rich PCM wastes are collected and stored in 200 l carbon steel drums, which are then compacted and stacked in a 500 l stainless steel drum encapsulated with an annulus of cement grout encapsulant (Figure 19).

Figure 19 Example of compacted organic containing ILW enclosed in an annulus of cement grout (NDA, 2010a)

Compared to other national inventories relatively small quantities or organic ion exchange resin (4.1 x 10^5 kg) are present in the UK inventory, which reflects the UKs fleet of mainly gas cooled reactors, which have lower requirements for liquid effluent treatment than water reactors. The UK's only PWR nuclear power reactor, Sizewell B, has a stock of ILW resin that is proposed to be contained in thick walled ductile cast iron containers for storage, transport and final disposal (NDA, 2012b). In this concept, resins would be dewatered (<1 % free water) and loaded into the sealed and unvented containers without any encapsulant. Gas generation and pressurisation of the containers through radiolysis has been assessed to be insignificant due to the mainly short-lived radionuclides (^{60}Co and ^{137}Cs) present (NDA, 2012b). The Trawsfynydd Magnox gas cooled reactor station (now in decommissioning) is notable in its use of ion exchange resins to achieve required low activity levels of liquid discharges to an inland lake. The ion exchange resins from Trawsfynydd are encapsulated in a vinyl ester styrene resin (Dawson, 2013a). At other Magnox and Advanced Gas Reactor (AGR) stations lower quantities of resins have been used.

A number of other organic polymeric encapsulants have been considered for certain types of ILW, such as where reactive metal wastes (Al, Mg, U) may react with alkaline cement porewater and affect the stability of the cement-based wasteform (NDA, 2010a). In the UK, epoxy and vinyl ester styrene resins are under consideration for immobilisation of certain wastes. These materials are examples of thermoset polymers, which cannot be reformed and have the disadvantage as a waste encapsulant that they can crack. Thermoplastic polymers such as polyethylene which are soft and can be moulded and welded when heated are also identified as candidate wasteform materials (NDA, 2010a). Bitumen and urea-formaldehyde resins have not been employed for general waste encapsulation in the UK.

2.3 Organic ILW materials selected for study

Consideration of the inventory of organic ILW materials of European programmes for geological disposal shows that the following main groups of materials are volumetrically important:

- Organic ion exchange resins
- Halogenated plastics
- Bitumen

The amounts and proportions of these organic materials vary by country and this reflects the different nuclear industry and power generation activities. In many countries ion exchange resins dominate the inventory of organic ILW, where it results from nuclear power generation using light water reactors (e.g. Finland, Sweden, Switzerland). Higher inventories of halogenated plastics and other related plastic and cellulose wastes result from countries (e.g. France and the UK) which undertake fuel reprocessing and have a larger inventory from nuclear research. Bitumen is used as an encapsulant material for both nuclear power plant and reprocessing wastes and is notable in the Belgian and French inventories. These three main organic materials were selected when the proposal for the MIND project was developed, taking account of the views of waste management organisations.

These materials provide a major source of organic carbon that has the potential to fuel anaerobic microbial processes including methane gas generation in a geological repository, but which may also stimulate the consumption of H_2 gas (e.g. arising from corrosion) and the biodegradation of organic complexants. The three anthropogenic organic materials selected for study are of differing physical and chemical nature and structure and their degradation will involve a range of different processes e.g.

- Ion exchange resins are comprised of an aromatic (polystyrene) structure with attached functional sulfonyl or amine groups. The latter being released more easily, leaving the aromatic structure that will be more resistant to radiolysis and biodegradation.
- Halogenated plastics principally concern PVC, which can include a variety of organic additives, which are not bound to the polymer and so may be easily leached and biodegraded. The PVC polymer is aliphatic and may be less resistant to radiolysis than resins and its radiolysis products might be more readily biodegraded. Radiolysis of PVC will liberate the strong acid HCl, which may be significant to pH buffering.
- Bitumen degradation will firstly involve the diffusion of water into the complex mixture of aromatic and aliphatic compounds, with the leaching of a water soluble fraction. Complex

> radiolytic interactions will occur in the original and partially hydrated bitumen. Biodegradation is more likely to occur at the bitumen-water interface.

Study of the combined radiolytic and biodegradation of these three organic materials should also yield information relevant to understanding the degradation of other materials in the ILW inventory e.g. the non-halogenated polymer polyethylene (PE), rubber and other resins used as waste encapsulants.

Of the other organic materials, the naturally occurring polymer cellulose is present in most national inventories. The UK has the largest inventory of cellulose, where it comprises around 20 wt% of the organic ILW. Cellulose is recognised as being of increased potential importance compared to other organic materials due the strong radionuclide complexation effects of its hydrolysis products formed under alkaline (cementitious) conditions. Research understanding alkaline cellulose degradation is well established (Section 1.2), and following recent advances (e.g. Bassil *et al*, 2015) current research within MIND will focus on the biodegradation of the radiolysis and alkaline hydrolysis products.

3 Storage and disposal conditions

In this section the chemical conditions under which organic wastes are subjected are summarised taking account of the concept designs proposed for deep geological disposal of long-lived ILW and LLW. The aim of this discussion is to constrain the conditions and processes of most relevance for irradiation and biodegradation studies that will be undertaken within the MIND project.

3.1 Deep geological disposal concepts
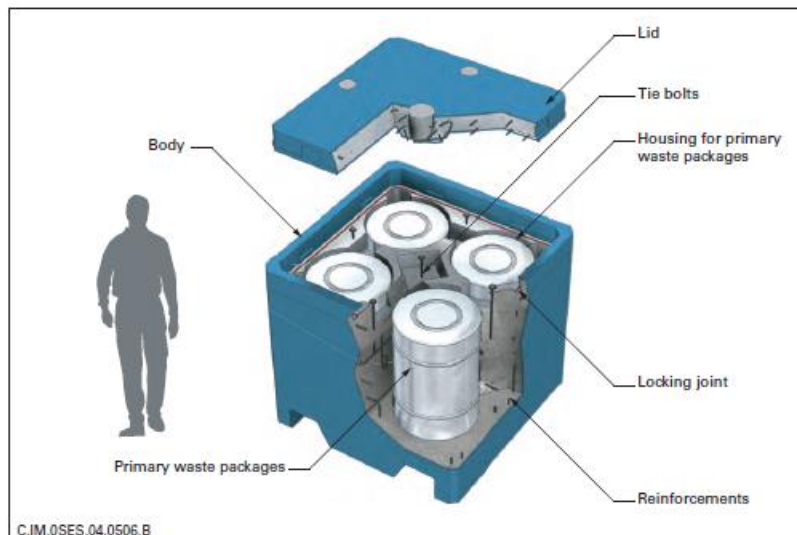
Most geological disposal concepts for long-lived ILW and LLW (LILW) are based on the use of cementitious materials that may be used in the following components of the engineered barrier system:

- Cementitious encapsulation of wastes in metal or concrete containers to condition wastes during storage.

- Concrete overpack containers used in some concepts to transport and emplace containers to the repository.

- Construction materials e.g. shotcrete used to support excavations in some host rocks.

- Backfill materials used to fill voidspace between waste packages.

Examples of cement-encapsulated wastes are shown in the preceding section (e.g. Figure 5, Figure 15, Figure 19). Current examples of concrete overpack containers include concrete boxes used to contain waste drums of LLW and ILW at the VLJ repository, Olkiluoto (Figure 6). The concepts for LILW disposal in France (Figure 20) and Belgium (Figure 21) also propose the use of concrete overpack containers that minimise the voidage in the disposal galleries.

The French concept for the disposal of B wastes is modular, permitting the separation of different types of package. Type B cells are sub-horizontal tunnels, with a maximum length and diameter of 250 m and 12 m, respectively, in which packages are stacked on several levels (Figure 20b). A concrete lining provides the structure with mechanical stability. Concrete also provides a chemical barrier function for the packages and thus contributes to the retention of radionuclides. There is

limited clearance between the package and the disposal cell and this small volume will not be filled, in order to facilitate the closure operations and, if decided at a later date, possible retrieval of waste packages.

(a)
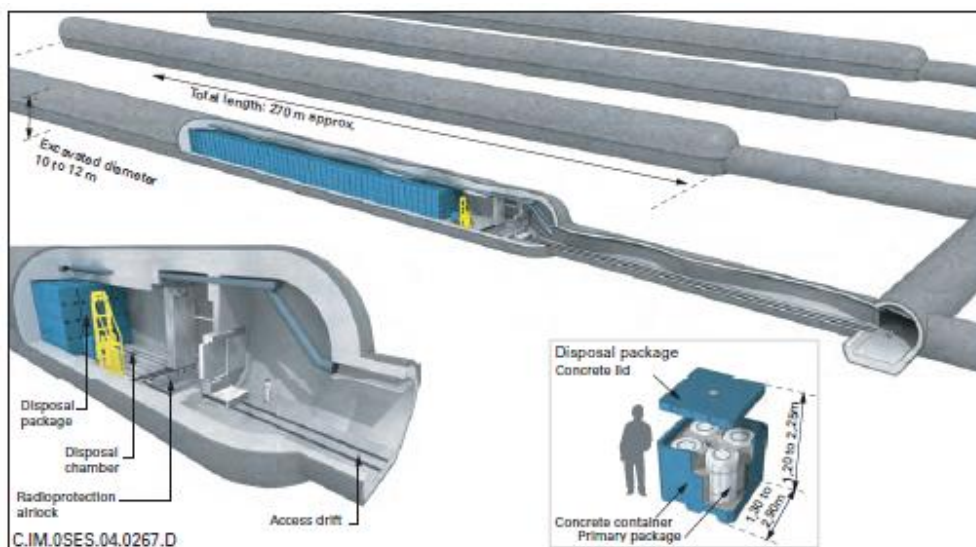
(b)

Figure 20 Illustrations of (a) a B type waste container and (b) disposal cells proposed for disposal of L-ILW in France (Andra, 2005).

In the case of the Belgian concept, primary waste containers for most of the LILW-LL wastes that have been immobilised in cement or bitumen are 200 and 400 l carbon or stainless steel drums. The remaining wastes are stored in various primary containers constructed from a variety of steels, including mild steel, galvanised steel, low-alloy Cr steel and stainless steel. It is proposed that these various waste drums are contained within a prefabricated concrete container (Figure 21a). Numerous

functions that contribute to the operational and long-term safety are accomplished by this so called category B waste monolith, including shielding of radiation during operation and mediating chemical conditions that should retard radionuclide release and transport. In addition, under repository conditions, the uniform anaerobic corrosion rate (i.e. the main corrosion mechanism) of the steel will be decreased as the steel will become passivated by the high pH originating from the concrete of the category B waste monolith. The number of primary waste packages inside is determined by the dimensions and the radiological activity of the packages and, for Eurobitum, on the maximum number of drums that can be disposed per metre of gallery without risking an unacceptably high mechanical perturbation of the Boom clay by osmosis-induced water uptake and swelling of this waste. It is proposed to use Mortar to backfill the void space around the primary waste drums (Figure 21a) and further cement backfill would be used around the prefabricated concrete container (Figure 21b).

(a)

(b)
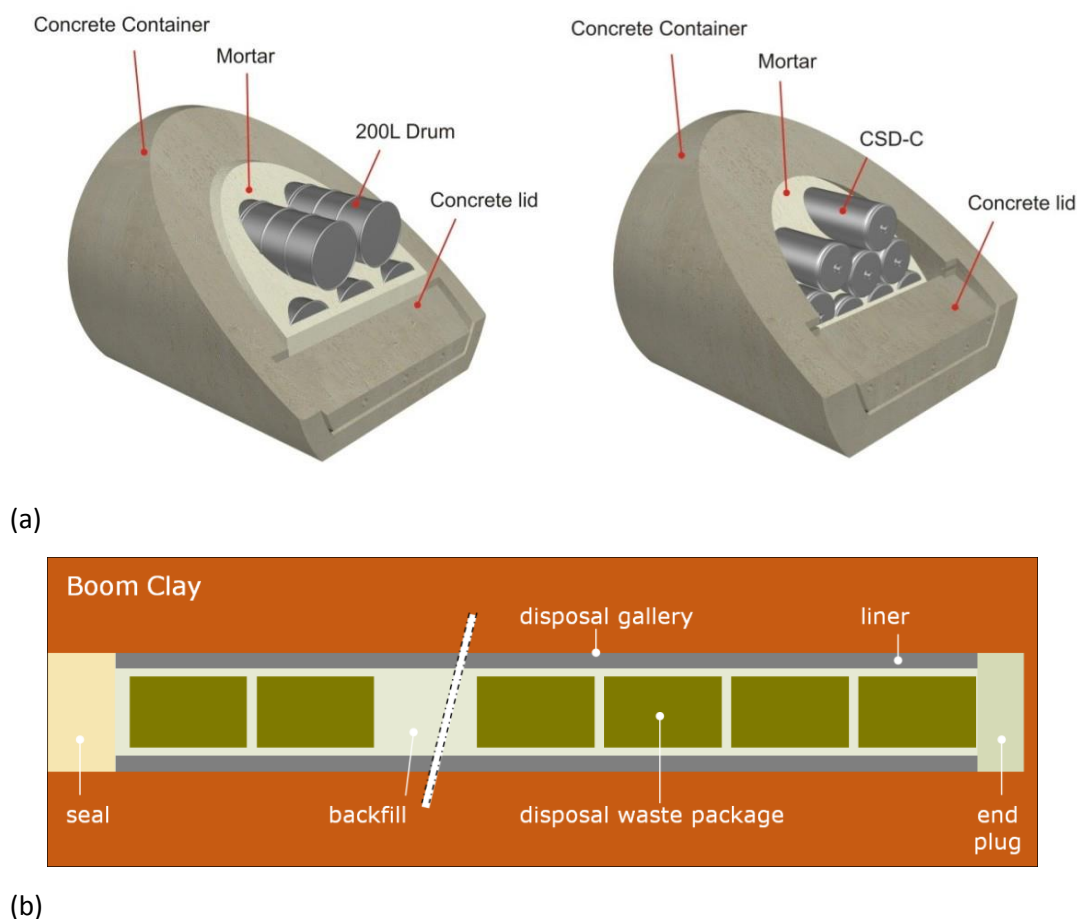
Figure 21: Schematic illustrations of (a) cross sections through category B waste monoliths containing drums or canisters as primary waste packages and (b) configuration of waste packages within a disposal gallery for the disposal concept in Boom Clay proposed in Belgium (ONDRAF/NIRAS, 2013)

Other concepts for LILW geological disposal such as those proposed in Switzerland and the UK involve the emplacement of stacks of conditioned waste packages in excavated vaults (e.g. Figure 22). In this type of concept, waste packages are stacked in underground caverns, and the void space around the packages would be backfilled by a cementitious material. In the case of the UK concept, wastes may be stored for a period of time before backfilling, such as to ease retrieval of waste packages (NDA, 2010b). The specific dimensions and geometry of the excavated vaults in such

concept designs would change as a result of the type of host rock selected for a geological disposal facility in the UK (NDA, 2010b). The backfill material that has been developed in the UK for use in higher strength host rock (Nirex Reference Vault Backfill, NRVB) provides a number of safety relevant functions. The composition of NRVB enables the long-term maintenance of alkaline porewater chemistry, which supresses the concentration of many important radionuclides and maintains a high active surface area for radionuclide sorption. NRVB has relatively high permeability and porosity to ensure homogeneous chemical conditions and to permit the escape of gas (NDA, 2010c).
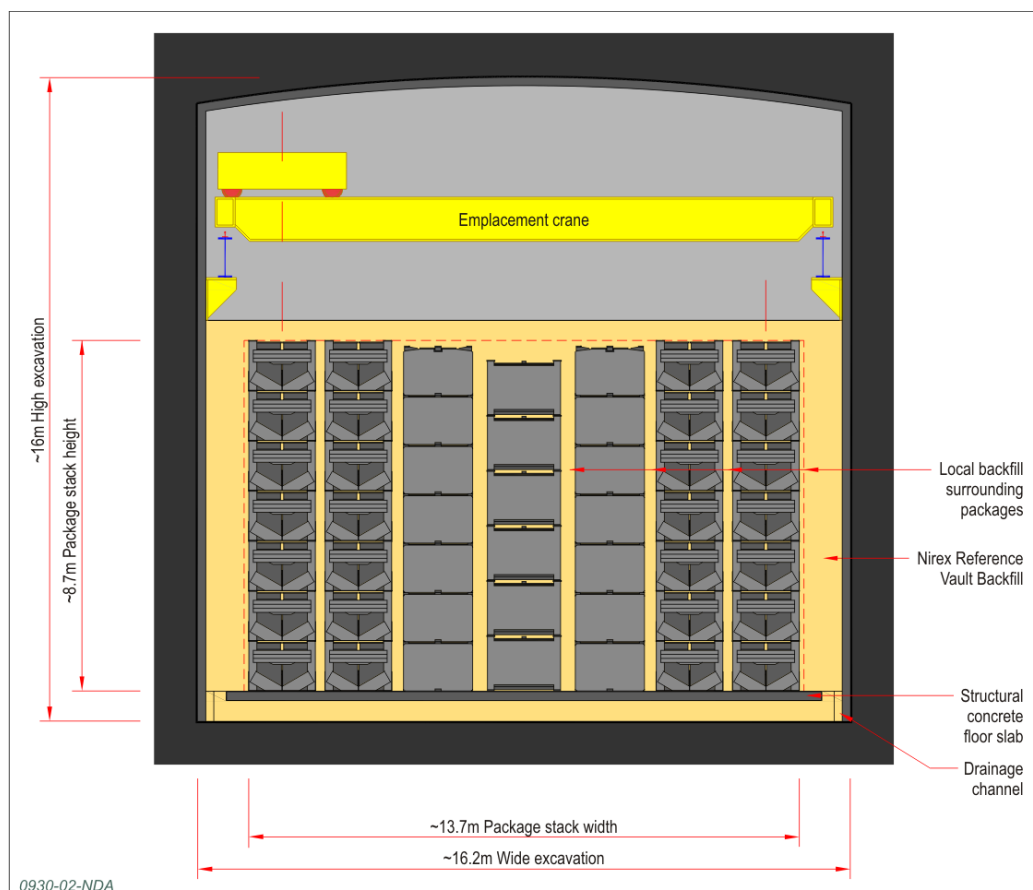
Figure 22 Schematic of UK disposal concept showing cross section through an unshielded-ILW vault in higher-strength rock (NDA, 2010b)

3.2 pH conditions

The pH conditions that organic wastes are subjected to during storage and final geological disposal is important to their chemical degradation behaviour, particularly in the case of condensation polymers including cellulose. Extreme alkaline pH will also limit the ability of microbial processes to metabolise organic degradation products. Due to the heterogeneous nature of many types of ILW and the complexity of the engineered barrier system, pH evolution is complex and will vary in space and time.

The cementitious materials used in the various parts of the engineered barrier system will result in the establishment of strongly alkaline conditions. The controls on pH buffering by cementitious materials in the context of radioactive waste disposal is well established (e.g. Atkinson *et al*, 1989; Berner, 1992). The alkaline buffering results from the presence of soluble alkali hydroxides present together with larger amounts of calcium hydroxide ($Ca(OH)_2$) and a wide range of Ca-containing silicates and aluminosilicates, of which calcium silicate hydrated gels (CSH) are most abundant and

important with regard to pH buffering. Leaching studies on cementitious materials and individual CSH phases reveal that the pH evolution progresses through a series of stages corresponding to buffering by a particular phase (Figure 23).

Initially (Stage I) pH is buffered at high values (pH >12.5) by the presence of Na and K hydroxide. As these hydroxides are highly soluble this stage is typically limited to leaching by the equivalent of a few pore volumes of water.

Stage II is characterised by the dissolution of $Ca(OH)_2$, which at 25˚C buffers pH at around 12.5. Calcium hydroxide has low solubility and so pH can be buffered at this high level for a considerable length of time depending on the amount of free $Ca(OH)_2$ present and the rate of water flow. The amount of $Ca(OH)_2$ present in a cement formulation can vary and some formulations such as the NRVB material developed in the UK contains additional lime to enhance the Stage II buffering. In other cases, a lower pH may be desirable such as to reduce the effects of pH on the dissolution of glass waste forms and here the formulation will be designed such that during curing there is no free Ca available that can form $Ca(OH)_2$.

Stage (III) begins once $Ca(OH)_2$ is completely dissolved and here CSH gel phases buffer pH. CSH gels have variable composition (Ca/Si ratio), with more Ca rich gels buffering at higher pH. Initially during Stage III, CSH dissolves incongruently with preferential release of Ca, consequently pH declines as the CSH gel becomes richer in Si. During the incongruent dissolution, Ca/Si ratio decreases from above 2 to below 1 until the gel dissolves congruently and pH is buffered at a constant pH of typically between pH 8 and 9. The exact point (Ca/Si and pH) at which congruent dissolution is attained will depend on the cement formulation and the interactions with other elements that are present in these gel phases.

Stage IV represents the attainment of chemical equilibrium, where the cement gel phases have dissolved or altered to be in equilibrium with the incoming water. Here calcite ($CaCO_3$) will be the predominant alteration mineral and will buffer pH at near neutral pH depending on carbonate concentration. Other phases formed by interaction with groundwater such as $Mg(OH)_2$ or Mg in wastes can buffer pH at higher values.
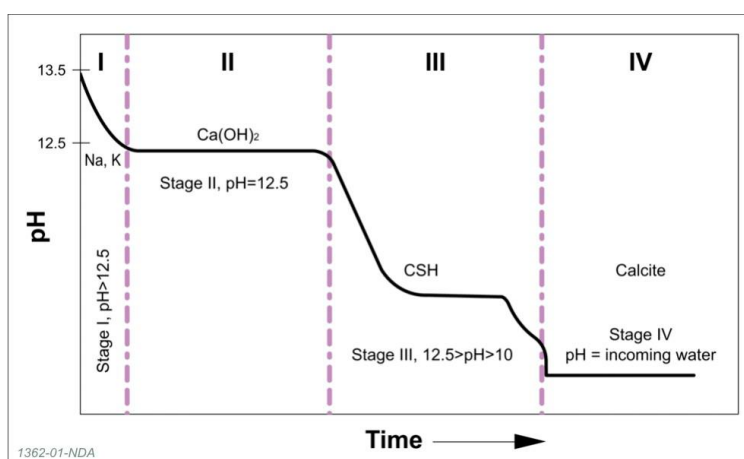
Figure 23 Schematic of the stages of pH buffering of cementitious materials present in ILW geological disposal (NDA, 2010c)

The above stages of pH evolution observed by experimental studies are expected to develop over long periods of time in a geological repository. The duration of the stages will depend on the amount of cement present and, in crystalline host rocks with advective water flow, the flow rate. In clay host

rocks, where the transport of chemical species occurs by diffusion, strongly alkaline (pH >12) conditions are expected to be maintained for over 100,000 years and over this time it is expected that the cement materials in the waste cell will degrade zonally and there will be some secondary alteration of the clay (Figure 24).
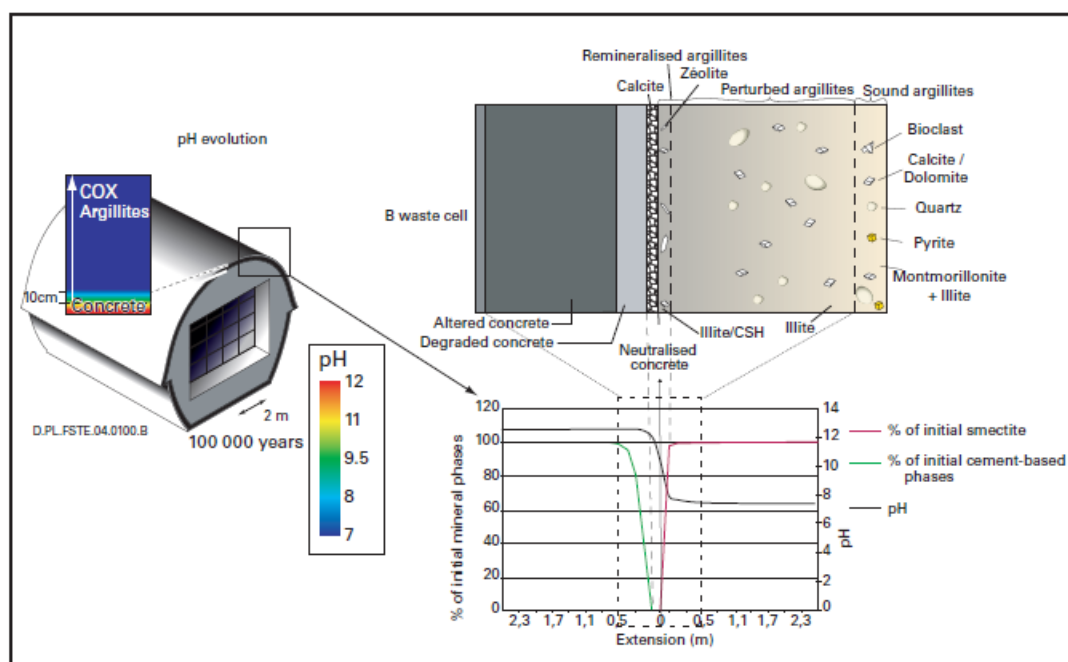
Scheme of alkaline perturbation in argillites around B waste cells and of lining concrete degradation at 100,000 years

Figure 24 Evolution of pH at the interface between concrete and clay host rock for the French concept for B waste cells (Andra, 2005).

In addition to the interactions between cement materials and groundwater, waste materials and their degradation products may also affect pH. In particular, organic wastes, which are a focus of MIND Work Package 1 may enhance the neutralisation of the alkaline pH through reactions with carbon dioxide that results from the degradation of organic wastes. The radiolysis of halogenated organic polymers also has the potential to release HCl which, being a strong acid could result in the establishment of low pH conditions in some waste packages, especially in compacted organic PCM wastes (e.g. Figure 19).

After backfill and closure, the repository near field will re-saturate with groundwater, but this will be controlled by the hydrogeological properties of the host rock. In addition, complete saturation will be affected by processes of gas generation and migration from some wastes and this may be a complex coupled process involving the reaction of water. Generally, repositories located in crystalline hard rock will saturate rapidly, whereas those located in indurated clay rocks, such as proposed in France, are anticipated to take 100,000 years to return to a state of hydrogeological equilibrium (Andra, 2005). Interestingly though, the Boom Clay formation, which is plastic, is expected to re-saturate at a much faster rate allowing water to saturate bituminised wastes after 50 years (Weetjens *et al*, 2010).

3.3   Redox conditions and electron acceptors

Redox conditions are also important to consider in designing the radiolysis and biodegradation experiments to be undertaken within MIND. Of key importance is the consideration of the presence of oxygen, since aerobic microbial processes yield significantly higher amounts of energy and will

proceed at faster rates than anaerobic processes. The presence of oxygen is also important in considering the radiolytic degradation of organic polymers and materials as it will promote the formation of more oxidised radicals and consequently different radiolysis products. For instance, oxalate is recognised as a radiolysis product formed under oxidising conditions (See Sections 4.1.1 and 4.3.1).

In the absence of oxygen, anaerobic microbial processes utilise other oxidised species as electron acceptors including; nitrate, ferric iron (Fe(III)), sulfate and carbonate. Processes utilising these species, together with electron donors such as organic carbon monomers (e.g. carboxylic acids) and hydrogen gas (H_2) are potentially important in mediating redox potential (Eh) and the speciation of some important multivalent radionuclides (e.g. Tc, Se, U, Np and Pu). The energy available from these terminal electron accepting processes decreases in the order nitrate reduction > Fe(III) reduction > sulfate reduction > fermentation > methanogenesis. The latter process effectively involving the reduction of carbonate.

Notwithstanding the role that microbial processes may have in mediating redox reactions in organic containing ILW, the corrosion of large quantities of metallic ILW, container and engineering construction materials is a key driver for developing reducing chemical conditions in a deep geological repository. The corrosion of reactive metal wastes present in ILW, including carbon steels, aluminium and magnesium alloys and uranium metal, is expected to consume oxygen quickly within wastepackages and will begin to generate H_2 by anaerobic corrosion. The corrosion process is affected by the alkaline pH of cementitious ILW, with carbon steel corrosion being passivated under high pH conditions, while aluminium and magnesium alloy corrosion will be enhanced at high pH. Polymeric organic wastes, such as PCM (Figure 19), are often compacted in carbon steel drums, which will consume oxygen by corrosion. Such packages are normally vented to permit the release of gas (e.g. H_2). Diffusion of oxygen into wastepackages during surface interim storage is unlikely due to the small area of such vents. It is expected then that oxygen will not be present in organic containing wastepackages.

In nitrate containing bituminised wastes, such as those present in the Belgian Eurobitum and French B2 wastes, nitrate salts provide an electron acceptor which could maintain positive Eh that could stabilise the more oxidised and mobile forms of some radionuclides (e.g. Tc, Se, U, Np and Pu). In these wastes water will slowly diffuse into the bitumen allowing nitrate to dissolve and diffuse out of the wastepackages. A significant amount of chemical energy is potentially available to microbial processes that are capable of reacting nitrate with the organic carbon that comprises the bitumen. Nitrate may also react abiotically with metal container materials (Truche *et al*, 2013). The consideration of nitrate as an electron acceptor is therefore of key importance to these wastes.

Following oxygen and nitrate as providing the highest amounts of energy for microbial processes are Fe(III) and sulfate. Ferric iron will be present in ILW as a corrosion product of steels formed under aerobic conditions. Some effluent treatment flocs contain significant quantities of Fe(III), but these are not expected to be closely associated with organic ILW. Sulfate is viewed as being of wider importance as an electron acceptor given its high solubility and presence in groundwater and its presence in cement materials. Additionally, some important organic ILW materials could release sulfate, such as soluble salts in bituminised wastes and sulfonyl groups in anion exchange resins, which are released as sulfate (Van Loon and Hummel, 1995).

Inorganic carbon present as dissolved CO_3^{2-}/HCO_3^- is ubiquitous in groundwater, and under cementitious conditions will be buffered by solid $CaCO_3$. Such oxidised carbon effectively forms an electron acceptor for methane gas generation, although methane may also be formed from acetic acid and other carboxylic acids that can form by fermentation and radiolysis.

3.4   Radiation dose considerations

Radiation dose is important to the biodegradation experiments that will be undertaken within the MIND project for two reasons:

1. In terms of the initial radiolytic degradation of anthropogenic organic materials that may generate degradation products that can be utilised by microbial processes, and

2. In potentially limiting the survival and growth of microorganisms in waste packages and the repository due to the effects of radiation on proteins, DNA and cell physiology.
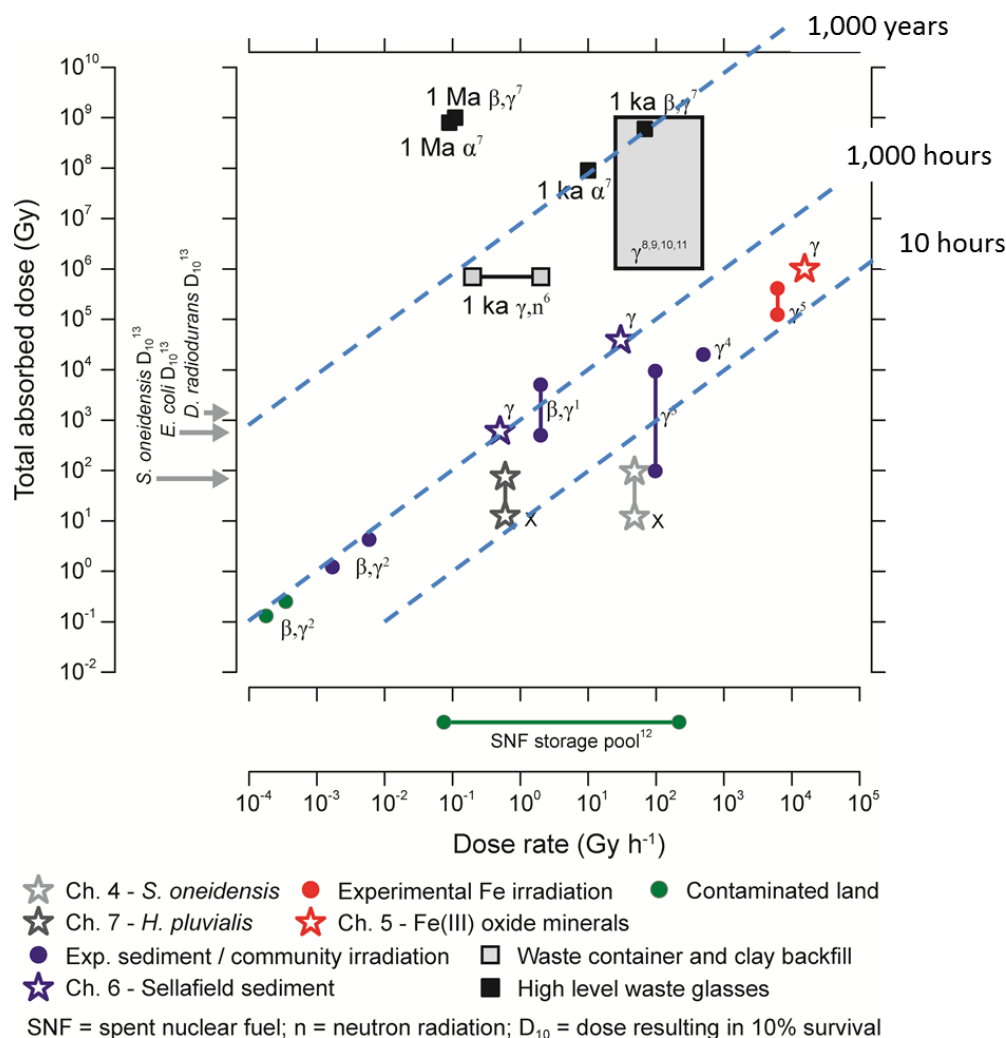
Evaluation of the effects of radiation on microbial processes in radioactive waste disposal is complicated because of the complex inventory of radionuclides with a wide range of half-lives, decay mode and emission energy and because of shielding effects. In the case of ILW, estimation of the total adsorbed dose and dose rate is complicated by the heterogeneity of radioactive waste, and wasteform materials. Brown (2014) has summarised the range of total adsorbed dose and dose rate of nuclear storage and disposal environments and compared them to conditions of experimental studies that examine microbial radiation tolerance (Figure 25).

Total adsorbed doses for nuclear disposal facilities range from around 1 MGy to 1,000 MGy (Figure 25). The majority of these studies have focussed on the disposal of high level vitrified waste and spent fuel and have considered the dose to which clay buffer materials are exposed after shielding by the waste canister. For instance, Plotze *et al* (2003, after Reed *et al* 1987) considered that the surface of a fuel canister would be exposed to a total dose (gamma and neutron ray) of 0.7 MGy after 1,000 years. After breach of the canister, when dose from migrating α emitting radionuclides is considered important a total absorbed α dose integrated over 10,000 years was about 140 MGy.

For ILW, the activity will generally be lower than for such heat generating vitrified waste and spent fuel, but for ILW the dose to which the waste materials are subject is of primary interest rather than the dose outside of the waste packages. For ion exchange resins and contaminated plastics the contaminating radionuclides are either present within the resin structure or on the surface of plastics. Consequently, the decay energy of the radionuclide inventory will be mainly absorbed by the waste and shielding effects of waste encapsulant and container materials will be less important. Studies of resin irradiation and PVC irradiation (see later section 3) have typically considered total adsorbed doses of between 0.1 and 10 MGy (e.g. Van Loon and Hummel, 1995; Shashoua, 2008; Dawson, 2013).

As well as the total adsorbed dose, the dose rate is an important consideration. High dose rates may have to be used in experimental studies as a compromise to achieve the total absorbed doses estimated for storage and disposal scenarios. Such high does may however induce different mechanisms of radiolytic degradation. Figure 25 includes dashed lines indicating the equivalent dose and dose rate achievable for given time periods. Stankovskiy (2011) has evaluated the dose rates relevant to the Belgian Eurobitum matrix that will be constantly exposed to radiation from its waste inventory (Table 10). For the first 100 years, the main contributors to the total radioactivity will be β-

and γ-emitters, while in the long term (up to 1 million years) α radiation becomes dominant. Between 100,000 and 1 million years, the nuclides belonging to the decay chain of ^{234}U and ^{206}Pb are predominantly present. Based on data from Stankovskiy (2011), the average dose rate for β/γ radiation will decrease from ~ 5 Gy h^{-1} after the first year to ~ 0.002 Gy h^{-1} after 100,000 years. For α radiation, the average dose rate will decrease from ~ 0.6 Gy h^{-1} after the first year to ~ 0.05 Gy h^{-1} after 100,000 years. Such dose rates will result in total adsorbed doses greater than 1 MGy after several thousand years.

References (1) Bruhn *et al* (2009); (2) Niedrée *et al* (2013); (3) Pitonzo *et al* (1999); (4) Bank *et al* (2008); (5) Daub *et al* (2011); (6) Plotze *et al* (2003) after Reed *et al* (1987); (7) Ewing *et al* (1995) after Weber (1991); (8) Allard and Calas (2009); (9) Allard *et al* (2012); (10) Stroes-Gascoyne *et al* (1994); (11) Noynaert *et al* (1998); (12) Rivasseau *et al* (2013); (13) Daly *et al* (2004). Ch. 4, 5, 6 and 7 refer to the chapters of the thesis (Brown, 2014) from which this figure was reproduced.

Figure 25 Total absorbed doses and dose rates relevant to the geodisposal of radioactive waste and bioremediation of radionuclide contaminated land (after, Brown, 2014)

Table 10 Evolution of the average dose rates in the course of time in Eurobitum containers with average and maximum activity, calculated from data of Stankovskiy (2011)

Time	Containers with average activity		Containers with maximum activity	
	Alpha Gy h^{-1}	**beta/gamma** Gy h^{-1}	**alpha** Gy h^{-1}	**beta/gamma** Gy h^{-1}
1 y	0.6	5	1.6	20
100 y	0.8	1	2.2	5.5
100 000 y	0.05	0.002	0.1	0.008

The time period over which organic containing ILW will be subject to significant dose rates will depend on the actual inventory of radionuclides and their half-lives. Example inventories of French plastic-containing wastes (Figure 9) and Swiss ion exchange resins (Figure 17) show some variability in the projected decay in activity. In the case of the French B3.1.2 waste, activity decreases by two orders of magnitude over a period of 1,000 years (Figure 9). In the case of the Swiss ion exchange wastes (BA-B-HP-F2-SMA) activity increases by over an order of magnitude during the first 100 years by in-growth and then slowly decays to just below initial values after 1,000 years (Figure 17).

Brown (2014) discussed and investigated the radiation tolerance of some anaerobic bacteria e.g. *Shewanella* spp that are capable of coupling the oxidation of organic matter to the reduction of a range of electron acceptors, including metals, anions and radionuclides (Nealson and Saffarini, 1994; Wade and DiChristina, 2000; Daulton *et al*, 2007). A dose tolerance of around 1 kGy is indicated by studies that have quantified the dose resulting in 10% survival of microorganisms (D_{10}, Figure 25). Further research undertaken by Brown (2014) has examined the cellular physiology in response to irradiation. The whole cell metabolism of *Shewanella oneidensis* was profiled via Fourier transform infrared (FT-IR) spectroscopy after exposure to acute X-radiation doses (12 to 95 Gy). Brown's results show an increase in lag time, suggesting that ionizing radiation inhibits the viability and growth of *S. oneidensis* cultures. Observed growth effects are likely controlled by both viability and metabolic changes; for example, alteration to lipid and protein metabolism throughout irradiation, which may also be preserved throughout multiple generations despite biomass recovery. These metabolic changes may have implications for microbial population dynamics in subsurface environments where doubling times are very long, in the order of years to decades (Brown (2014). Further work by Brown *et al* (2014, 2015) has shown that radiation induced changes to Fe(III) substrates at higher total adsorbed dose (~1 MGy, Figure 25), result in an increase in the bioavailable iron, which could compensate for the physiological effects of radiation.

3.5   Summary of conditions of interest

The preceding discussion of the effects of radiation is a useful starting point to consider the time periods of interest, which can then be used to constrain the physical and chemical evolution of the ILW concept. Considering the decay of activity of organic ILW, radiolytic degradation of organic ILW is likely to occur during storage and the first 1,000 years of disposal. Over this timescale organic wastes are likely to be subjected to a total adsorbed dose of the order of 1 MGy, although this total

dose and time period will be subject to considerable uncertainty. Such a 1 MGy total dose has been considered in previous irradiation studies of organic materials (See following Section4) and is likely to result in the generation of soluble organic degradation products that could fuel microbial metabolism. A 1 MGy dose would be achieved at an average dose rate of around 0.1 Gy h^{-1} over 1,000 years (Figure 25). Microbial activity is likely to be viable at this dose rate as shown by studies in the literature (Figure 25; Brown, 2014). Of course to achieve such a total adsorbed dose of 1 MGy in the laboratory will require the use of higher dose rates (e.g. 10 kGy h^{-1}), which will potentially sterilise the organic materials.

Over such a 1,000 year period the repository will, depending on the host rock, begin to or completely saturate with groundwater. Some ILW waste containers may begin to corrode allowing groundwater to begin the leaching of cementitious encapsulants and backfill. Radiolysis of some organic wastes may also liberate CO_2 and HCl, which will also neutralise the initial high pH of cement encapsulants. It is also possible that microbial degradation of compacted mixed organic wastes (e.g. PCM wastes, Figure 19) containing cellulose could generate acid fermentation products and CO_2. In such mixed organic wastes pH could range from weakly acidic to strongly alkaline (pH 12.5) buffered by $Ca(OH)_2$ and other cement phases present in the encapsulation grout.

In the case of ion exchange resins that are directly encapsulated in cementitious materials, it is perhaps less likely that microbial activity could develop given the better mixed nature of the wasteform which will initially result in uniform strongly alkaline conditions (pH > 12.5). Chemical and radiolytic degradation of ion exchange resins could result in the generation of acidity by the formation of CO_2 by radiolysis of organic carbon. The release of SO_4^{2-} by leaching of sulfonyl groups from acid ion exchange resins is also considered to generate acidity by the oxidation of sulfonyl to sulfate (Van Loon and Hummel, 1995; Section 4.1.1). However, the acidity generated by SO_4^{2-} release may not be as significant as that resulting from HCl release from halogenated plastics because SO_4^{2-} will be charge balanced by the release of exchangeable cations (e.g. Na^+) from the resin. Microbial activity could perhaps be initiated in lower pH regions by the utilisation of sulfonate/sulfate as electron acceptors and amines as electron donors that are present as functional groups on the resin structure (See following section 4.1). Radiolysis of the polystyrene resin structure will also provide dissolved organic carbon and a further electron donor. However, given the low oxygen content of resins compared to cellulose there is perhaps less potential for the generation of CO_2 and acidity to neutralise cement than in mixed organic wastes. In this case, microbial degradation of radiolysis products of resins may occur after they have migrated away from the waste package, or after longer periods of time where electron donors (e.g. sulfate) can be supplied by groundwater. Resins encapsulated in cement may therefore be expected to undergo radiolysis under mainly alkaline (Stage I pH conditions, Figure 23) conditions and only after extended periods of time (10,000 to 100,000 years) would lower pH (Stage II and III pH conditions, Figure 23) conditions be expected, by which time dose rates will have declined significantly.

In the case of bituminous wastes, including encapsulated resins and salt concentrates, the degradation processes will be dominated by the diffusion of water into bitumen and the diffusion of soluble species out of the resin. Diffusion of water into bitumen will induce swelling of the bitumen matrix (see later Section 4.3). The interaction of bitumen with alkaline water associated with concrete materials in the repository (Figure 21) will be clearly less important than for cement encapsulated waste. Radiolytic interactions between the bitumen and water that may lead to oxidation of the bitumen will be limited to the interface zone between the bitumen and water.

Because of the absence of void space and porosity (providing space for biomass) within the bitumen and the high salinity of the water phase that diffuses into the material (see later Section 4.3), it is unlikely that microbial activity could develop in the bitumen matrix. Conditions of interest are thus those at the interface of the bituminised waste canister and cement container /backfill material. Microbial activity utilising organic degradation products and soluble electron acceptors (nitrate, sulfate) as energy sources could develop outside of the bituminised waste packages under neutral or cement buffered pH conditions depending on the disposal concept design and its temporal evolution.

As discussed above (Section 3.3) anaerobic conditions are likely to prevail in organic containing ILW both during storage and disposal. Under these conditions sulfate present in wastes (e.g. resins and evaporated salts) and in groundwater will be an important electron acceptor. For bituminised wastes, nitrate will also provide a strong electron acceptor for microbial processes reacting with organic degradation products as well as H_2 generated by radiolysis and by anaerobic corrosion of metals. In the absence of sulfate or nitrate, fermentation and methanogenesis are predicted to develop, which is important in regard to gas generation from ILW.

4 Nature and degradation of organic materials of interest

In this section more detail is provided regarding the nature and degradation mechanisms of the three organic materials; ion exchange resins, halogenated polymers and bitumen that will be the focus of experimental studies within Work Package 1 of the MIND project. For each of these three materials the chemical structure and physical nature is described and then the current understanding of degradation processes is reviewed, including where appropriate chemical, radiolytic and biodegradation processes.

4.1 Ion exchange resins

Ion exchange resins used in the nuclear industry to reduce radioactivity in reactor coolant water and in the treatment of effluents are based on the divinyl benzene (DVB) styrene copolymer (Figure 26). DVB styrene is composed of polystyrene chains cross linked by DVB. The styrene aromatic ring can contain either a sulfonyl group (Figure 26a) which is negatively charged (strongly acidic) and can be balanced by an exchangeable cation e.g. Na^+. Alternatively, the styrene can contain a quaternary amine group (Figure 26b) and can act as a strong base balanced by an exchangeable anion e.g. Cl^-. The simple cation (or anion) present is easily exchanged by other cations (or anions) present in solution. In nuclear applications, sulfonyl cation resins are used to remove metallic radionuclides (e.g. $^{137}Cs^+$, $^{60}Co^{2+}$ and $^{90}Sr^{2+}$) while amine resins are used to remove anionic radionuclides (e.g. $H^{14}CO_3^-$, $^{36}Cl^-$). Such ion exchange resins may be regenerated after use by displacing the contaminant radionuclides by introducing a flow, either in the same direction or counter to the operational flow, of an acid solution for cation resins, or an alkali solution for anion resins (Dowex, 2000). Regeneration will yield a concentrated solution of radionuclides that can be further treated such as by evaporation.
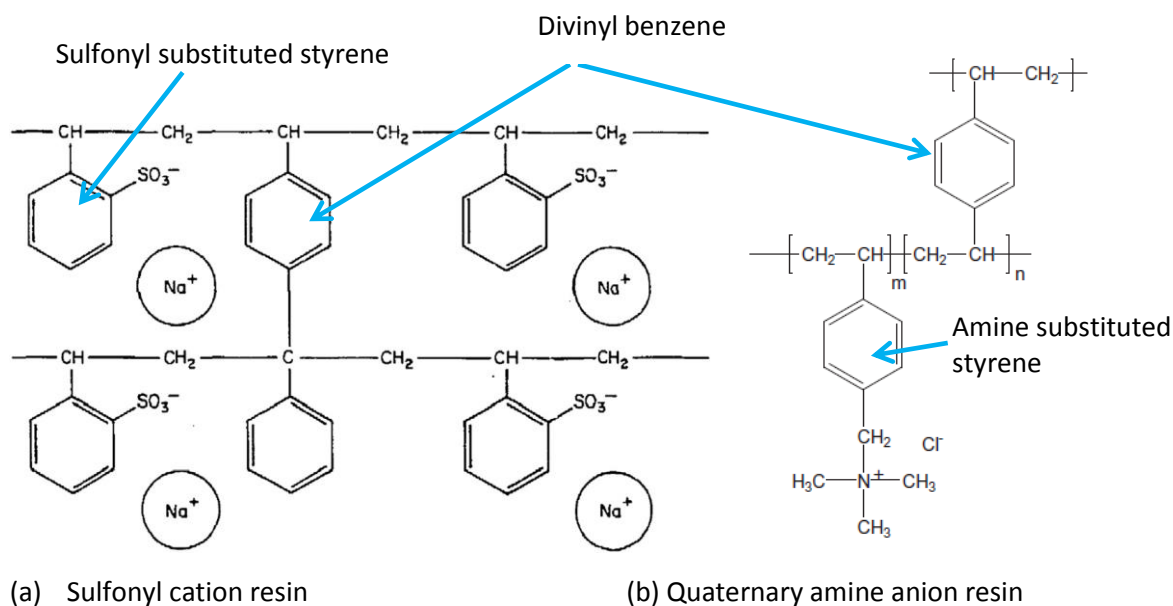
Figure 26 Structures of DVB-styrene resin with (a) sulfonyl and (b) quaternary amine functional groups (after Wang and Wan, 2015; Baidak and La Verne, 2010)

The rate of the ion exchange process is dependent on the surface area of the resin material. Resins are produced in both bead form and in powdered form. Powdered resin can have as much as 100 times more surface area than the equivalent weight of bead resin (Wang and Wan, 2015). Bead resins are normally used in columns and are more easily regenerated than powdered resin. Anion and cation resins can also be used together, either in series or in a mixed-bed. Mixed bed exchangers are the primary type of exchanger used in radionuclide waste treatment applications (Dowex, 2000). Regeneration of such mixed bed columns is however more difficult and as a result a number of treatment and disposal options have been examined for spent radioactive ion exchange resins (Wang and Wan, 2015). Wang and Wan (2015) discuss encapsulation methods using cement, bitumen and plastics, which are in operation in countries considered in this review (Section 2). As discussed by Wang and Wan (2015) DVB styrene copolymer is stable under radiation and a number of oxidation technologies have been considered to decompose spent resin materials.

4.1.1 Degradation of Ion Exchange Resins

The degradation of DVB styrene ion exchange resins has been studied mainly to examine its stability under operational conditions in the nuclear industry under radiation e.g. Baidak and La Verne (2010). Few studies have considered the degradation under disposal conditions for ILW, where the chemistry may be influenced by the cementitious materials used, and where pH is buffered by $Ca(OH)_2$ at around pH 12.5. Under these conditions, organic polymers may degrade by two main mechanisms: radiolytic and chemical (alkaline) degradation (Van Loon and Hummel, 1995). All organic polymers are susceptible to radiolytic degradation (Van Loon and Hummel, 1995; Baidak and La Verne, 2010). Condensation polymers, such as cellulose, are readily chemically degraded under alkaline conditions (Van Loon and Hummel, 1995). However, addition polymers such as DVB styrene are not susceptible to nucleophilic attack by the OH^- ion, because they do not contain carbon atoms with a partial positive charge. Radiolysis is therefore a key degradation mechanism of ion exchange resins during their operation, storage and final disposal. The microbial degradation of resins has not been studied in detail and remains uncertain (Van Loon and Hummel, 1995; Warthmann *et al*, 2013).

Ion-exchange resins for use in the nuclear industry are quite strongly resistant to radiation, and this is due to their aromatic nature (Van Loon and Hummel, 1995). Radiation tolerance depends on the type of resin; acidic ion exchange resins can tolerate a radiation dose between 1 and 10 MGy, while basic anion exchange resins have a lower tolerance between 0.1 and 1 MGy absorbed dose (Van Loon and Hummel, 1995). Irradiation of resins mainly causes the loss of sulfonyl or amine functional groups, which can also occur in the absence of radiation due to thermal degradation (Hall *et al*, 1970). Strong base anion exchange resins in the hydroxide form, may emit a characteristic "fish odour" which is a result of very low levels of trimethylamine release.

Van Loon and Hummel (1995, 1999a, b) examined the radiolytic and chemical degradation of acidic and basic ion exchange resins under alkaline conditions (NaOH buffered in range pH 10.2 – 12.9). Their experiments were designed to evaluate the formation of organic ligands that could affect radionuclide speciation and so affect transport properties from a geological repository. Experiments compared the effect of resin degradation with and without ^{60}Co ϒ irradiation at a total doe of 1.7 MGy at rate of 8.5 kGy h^{-1}. In the case of irradiated acidic resin water, the concentration of Na$^+$, SO$_4^{2-}$, dissolved organic carbon (DOC), inorganic carbon (IC) and oxalate were significantly higher than in a non-irradiated control experiment. The SO$_4^{2-}$ in the water results from release of the sulfonic acid groups, followed by oxidation of the SO$_3$ formed to form dissolved SO$_4^{2-}$. Van Loon and Hummel note that this reaction is similar to that observed in earlier work. Oxalate is a major identified soluble organic degradation product and is thought to form from •COO$^-$ radicals generated during radiolysis of resins, where two radicals join to form an oxalate molecule (Van Loon and Hummel, 1995). Oxalate is also observed as a radiolysis product of bitumen (Van Loon and Kopajtic, 1991). Van Loon and Hummel, (1995) measured concentrations of between 0.23 and 0.46 mM of oxalate from irradiated resins. Significantly higher concentrations of DOC and IC were measured, with 8.7 mM DOC and 13.3 mM IC formed from irradiation of Powdex™ resin at 2.17 MGy. The mole ratio of carbon to sulfate in the irradiated solutions was between 0.42 and 0.89 and indicates that radiolysis preferentially strips the sulfonyl groups from the resin, with less attack of the aromatic carbon structure. A drop in pH was observed due to formation of SO$_4^{2-}$ and CO$_3^{2-}$. Complexation studies with Cu^{2+} and Ni^{2+} showed that oxalate was the main complexing ligand present up to pH 7. But at higher pH an unknown ligand is increasingly important.

Van Loon and Hummel (1995) also examined the effect of radiation on strong basic resins (Powdex™ PAO and Lewatit™ M500) and a mixed bed resin (Amberlite™ MB1). These studies used an apparatus to separate and analyse volatile amine degradation products. The most important degradation products were ammonia (NH$_3$), methylamine (NH$_2$CH$_3$), dimethylamine (NH(CH$_3$)$_2$) and trimethylamine (N(CH$_3$)$_3$) (Table 11) as observed by previous workers (Hall and Streat, 1963; Ahmed *et al*, 1966). Trimethylamine is formed by the direct effect of radiation on the resin (Hall and Streat, 1963; Baidak and La Verne, 2010). Hall and Streat (1963) proposed several reaction mechanisms resulting in the formation of ammonia, methylamine and dimethylamine and involving interaction with water, which tends to lead to the formation of simpler nitrogen-containing products, i.e. (NH$_2$CH$_3$ and NH$_3$ (Baidak and La Verne, 2010). Ahmed *et al* (1966) showed that the reaction with water radiolysis products increased with water content and that under operating conditions half the deamination appears to be due to reactions resulting from the radiolysis of the water.

Table 11 Concentrations of amines, DOC and sulfate from irradiation of strong basic resins, and Amberlite™ mixed bed resin at 1.7 MGy total dose (Van Loon and Hummel, 1995)

Resin	pH	DOC (mM)	SO_4^{2-} (mM)	NH3 (mM)	NH_2CH_3 (mM)	$NH(CH_3)_2$ (mM)	$N(CH_3)_3$ (mM)
Powdex™ PAO	12.45 (12.70)	139 (3.2	0.29 (0.12)	21 (nd)	5.6 (nd)	11.1 (nd)	11.4 (nd)
Lewatit™ M500	12.66 (12.67)	268 (0.78)	0.08 0.08	18 (nd)	9.8 (nd)	19.0 (nd)	14.0 (nd)
Amberlite™ mixed resin MB1	12.92 (12.66)	20.5 (0.26)	0.12 (nd)	1.1 (nd)	0.23 (nd)	0.13 (nd)	0.04 (nd)

Values in parentheses indicate data from un-irradiated control experiments, nd indicates the species was not detected

Van Loon and Hummel measured oxalate in the basic and mixed bed resin experiments, but in contrast to the acid resins, oxalate was not detected in the solution after irradiation. Oxalate formation is a characteristic of irradiation under oxidising conditions. The basic and mixed bed irradiation experiments were undertaken under a N_2 atmosphere, which may not be conducive for the formation of $\bullet COO^-$ radicals leading to oxalate formation. It is also possible that any $\bullet COO^-$ radicals formed have reacted with the amines released from the basic resins. Deamination of basic resins also yields hydrogen, especially in water saturated systems (Baidak and La Verne, 2010), which might also prevent the formation of oxidised radicals that lead to oxalate. Higher levels of DOC were measured in the basic resins than for the same concentration of acid resins irradiated at the same dose. The DOC measured is in addition to that present in the methyl amines.

Van Loon and Hummel note that for the mixed bed resin the composition of the irradiated solution is not a simple addition of the SO_4^{2-} released from the acid resin with the amines released from the base resin. Both the SO_4^{2-} and amine concentrations are lower than expected. Other soluble sulfur compounds (perhaps organic) appear to be present since the total dissolved sulfur concentration after irradiation was 37.5 mM of which the measured SO_4^{2-} concentration represents just 0.1%.

Baidak and La Verne (2010) have examined the decomposition of anion exchange resins by ϒ ^{60}Co radiation. Their research focused on the formation of molecular hydrogen (H_2) during the ϒ-radiolysis of water slurries of quaternary ammonium resins with varying water content. Irradiations with 5 MeV ^{4}He ions were used to simulate the effects of α-particles. The degradation of the strongly basic anion exchange resin Amberlite™ IRA400 in NO_3^- Cl^- and OH^- forms was examined. The radiolysis of Cl^- and OH^- forms, with high water content led to enhanced levels of H_2 production. Studies with various electron acceptors (NO_3^-, N_2O, O_2) show the role that the solvated electron plays in H_2 formation. H_2 production results from the leaching of trimethylamine and dimethylamine from the resin. Studies with ^{4}He ions (α-particles) were found to be similar to that for ϒ-radiolysis showing increased H_2 yields at higher water content. The yields of H_2 expressed as G values (molecules of H_2 / 100 eV) were however higher for ^{4}He irradiation than for ϒ ^{60}Co radiation.

Dhiman and La Verne (2013) have examined the generation of gaseous H_2 and methane (CH_4) from quaternary ammonium salt components of Amberlite™ basic ion exchange resin. G values were determined for dry methylammonium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride and benzyl trimethylammonium chloride under ϒ ^{60}Co

radiation and 5 MeV helium ions. The highest G values for H_2 formation result from trimethylamine and the polyethylene components which have G values of 4.43 and 3.3 molecules H_2 /100 eV respectively. The aromatic components of the resin have lower H_2 yields. Yields of CH_4 are generally negligible except for trimethylammonium chloride and tetramethylammonium chloride, with G values of 0.26 and 0.02 molecules per 100 eV, respectively. Traboulsi *et al* (2013) examined gas generation from basic resins irradiated by ϒ ^{60}Co at doses between 0.1 and 4 MGy under anaerobic, anaerobic with liquid water, and aerobic conditions. Their results confirmed the formation of soluble amines with gaseous trimethylamine and H_2 formed under all conditions. Carbon dioxide gas (CO_2) was formed under aerobic conditions due to the oxidation of trimethylamine and other organic degradation products. Rebufa *et al* (2015) have further investigated the formation of gases during irradiation of nuclear grade mixed bed ion exchange resin and its pure degradation products under different irradiation conditions. Irradiation was undertaken using two ^{60}Co irradiators at dose rates of around 0.4 or 4 kGy/h and total doses between 0.1 and 4 MGy. H_2 gas production from Amberlite™ IRA400 resin in OH form and mixed bed resin Microionex MB400 was decreased under aerobic conditions. The presence of water increased the H_2 yield for Amberlite™ IRA400 in H^+ form, consistent with the findings of Baidak and La Verne (2010). However, a decrease in H_2 yield with increasing water content was found for mixed bed resin MB400.

4.1.2   Potential for biodegradation

There is little direct evidence that ion exchange resins can be subject to biodegradation processes directly. Van Loon and Hummel (1995) commented that the potential exists for microbial processes to operate under cement buffered pH conditions, which could affect the stability of the potential complexing agents generated by radiolytic degradation. More recently, Warthmann *et al*, (2013) reviewed the potential for direct microbial degradation of organic polymers including ion exchange resins and concluded there were no clear indications in the literature that the polymer structure of synthetic polymers is biodegraded under anoxic conditions. However, functional groups of ion exchangers (and plasticisers in plastics) are considered to be readily available and biodegradable. A key step in the biodegradation of ion exchange resins is the depolymerisation process to produce labile small molecules that can be metabolised. Warthmann *et al*, (2013) calculated that the thermodynamic energy yield that could be obtained from polystyrene is so low under repository conditions that it is unlikely that the usable energy for microorganisms would barely be sufficient to breakdown ion exchange resins.

The stability of polystyrene and its slow biodegradation is an environmental concern known as so-called "white pollution" (Shang *et al*, 2003). Rates of mineralisation of polystyrene are slow (around 1% over 2–3 months of incubation) under aerobic composting conditions and subject to UV radiation, but are accelerated to around 2–5% over 2–3 months of incubation where oxo-biodegradable forms are considered (Ojeda *et al*, 2009). Under anaerobic conditions and, as noted by Warthmann *et al*, (2013) in the presence of H_2, the rates of polystyrene biodegradation will be slow or zero due to the lower energy obtainable.

Such arguments do not however consider the energy input from radiation present either in UV light radiation in the case of white pollution or in the case of ILW alpha/beta/gamma radiation which for ion exchange resins may be concentrated in the resin material itself. Radiolysis studies have shown that release of functional sulfonyl or amine groups is enhanced under ϒ and heavy ion radiation, which could provide a source of electron acceptor and electron donor to fuel microbial metabolism.

Significant (100 mM) concentrations of DOC are generated, particularly from basic resins which might provide a carbon and energy source for microbial activity. Anaerobic conditions and water saturated conditions promote the formation of H_2 gas from radiolysis of basic quaternary amine resins, which can provide a readily utilised electron donor for microbial processes.

Methylamines released from basic ion exchange resins are naturally occurring compounds that are readily metabolised by microbial processes and are recognized as an important substrate for methanogenesis (Purwantini *et al*, 2014). Enhanced biodegradation treatment methods to treat methylamines, including trimethylamine have been developed e.g. (Yang *et al*, 2013).

Apart from the methylamines formed from basic resins and oxalate formed from radiolysis under oxidizing conditions (Van Loon and Hummel, 1995), the DOC content resulting from radiolysis of the DVB styrene structure is poorly characterized and it is currently not known what proportion of the DOC can be metabolised by terminal electron accepting processes, such as Fe(III) and sulfate reduction and fermentation and methanogenic microbial processes. This knowledge gap will be targeted by research within Work Package 1 of the MIND project.

4.2   Halogenated polymers

These are polymers with structures that contain fluorine, chlorine and, in rare cases, bromine and iodine. Commonly available plastics in this category include polyvinylchloride (PVC), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), ethylene tetrafluoroethylene (ETFE) and chlorinated polyethylene (Dawson and Magalhaes, 2012). Also important in the nuclear industry are Hypalon™ (chlorosulfonated polyethylene) and neoprene (polychloroprene).

PVC is however of prime importance as it is one of the most widely used synthetic polymers in the nuclear industry, being used extensively as a glove box posting bagging material, as well as cable insulation, soft tubing etc. As such, it comprises around 95% of the halogenated polymer inventory in the UK. Fluorinated polymers such as PTFE are used for their resistance to most chemicals and high temperatures and make up the majority of the remainder of the halogenated polymer inventory.

4.2.1   Polyvinylchloride (PVC)

PVC (shown in Figure 27) is formed from the polymerisation of the vinyl chloride monomer. The large chlorine atom in the polymer chain causes a restriction in chain mobility and consequently, unaltered PVC is a rigid, mainly amorphous material with little flexibility.
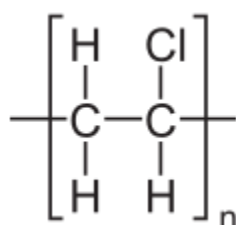
Figure 27 Polyvinyl chloride (PVC)

PVC is commonly used to manufacture glove box posting bags. As well as the respective base polymer, it contains a mixture of additives such as plasticisers, stabilisers, antioxidants and fillers, as shown in Table 12. Plasticisers impart flexibility to the otherwise rigid PVC polymer. Stabilisers are added to the polymer in order to prevent degradation by heat and light. Different types of stabilisers

are used and their content in the final product varies according to the technical requirements of the intended application.

Table 12 Common PVC Additives (Smith et al, 2013)

Additive Function	Range of % by volume in PVC	Generic Additives Used
Plasticisers	30 – 50	Esters (phthalates, adipates, azelates, phosphates) Epoxies Trimellitates
Stabilisers	1 – 5	Lead compounds Cadmium compounds Organotins Barium/zinc compounds Calcium/zinc compounds
Fillers	10 – 20	Silicates Barium/calcium sulfate Calcium carbonate
Pigments	1 – 3	Metal oxides Organic dyes
Flame retardants	0 – 5	Chlorinated or brominated organics Antimony oxide

The bulk of PVC in the UK national inventory is expected to be flexible films which have been used as glove box posting bags, protective suits and sheeting. Such PVC films have a particularly high plasticiser content of around 40 % by weight.

The most common plasticisers in PVC compounds are phthalate esters, or phthalic acid esters (PAEs). In 1997, 93% of the PVC plasticisers were phthalates (European Commission, 2000), including: DEHP (di-ethylhexyl phthalate), sometimes referred to as di-octyl phthalate (DOP), DINP (di-isononyl phthalate) and DIDP (di-isodecyl phthalate) (NDA, 2012a), which are shown in Figure 28. These are selected due to their compatibility with the polymer, ease of manufacture and low cost. They have similar chemical structures to one another, the differences being the nature and size of the aliphatic groups connected to the phenol group via two ester linkages.
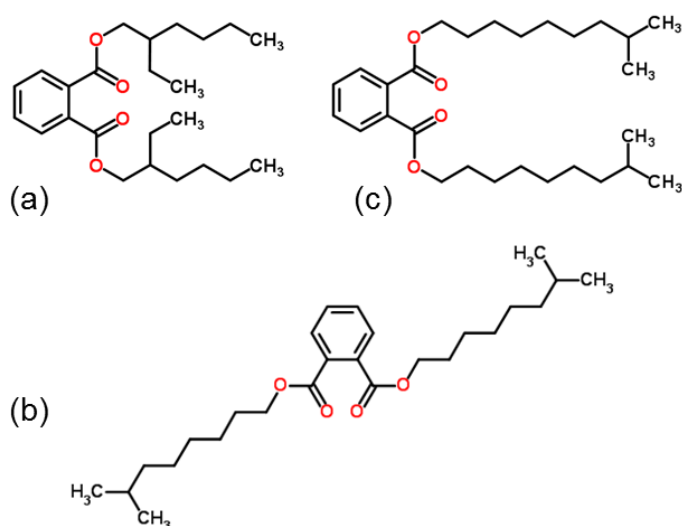
Figure 28 Structures of common phthalate esters (a) DEHP, (b) DINP, (c) DIDP

The increased concern related to the human health effects of phthalates has led to their decreased usage as plasticisers since the late 1990's. Since 2005, European legislation has restricted the use of the phthalate compounds DEHP, dibutyl phthalate (DBP) and benzyl butyl phthalate (BBP) in toys and childcare products (European Parliament, 2005). DINP, DIDP and di-n-octyl phthalate (DNOP) were also restricted to a lesser extent.

Due to regulatory pressures, PVC materials are increasingly being manufactured with alternative, non-phthalate plasticisers, such as diesters of terephthalic acid, e.g. dioctyl terephthalate (DOTP) (shown in Figure 29), aliphatic carboxylic esters, adipates, epoxides, phosphates, polyesters and cyclohexyls. It is not expected that PVC materials containing these non-phthalate plasticisers will exist in significant quantities in current radioactive waste inventories, however. It should be recognised that the chemical nature of PVC polymers has varied with time and that PVC waste materials will contain a range of additives of interest.
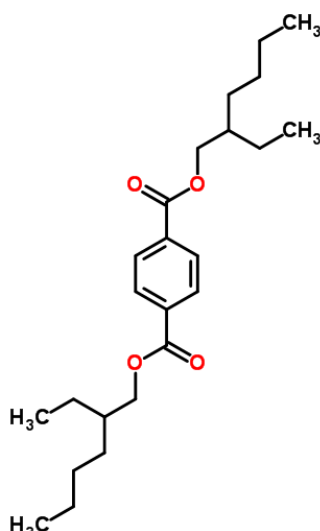
Figure 29 Structure of non-phthalate plasticiser dioctlyl terephthalate (DOTP), or Bis(2-ethylhexyl) terephthalate

4.2.2 Degradation of PVC and Plasticisers

Wypych (2015) gives a good review of PVC degradation including the effects of different types of radiation. Unlike UV radiation, the energy of γ-rays is much higher than the energy necessary for any organic bond to be dissociated, which leads to a direct formation of double radicals. Because of the high energy of this kind of radiation, the whole volume of the polymer is affected. Irradiated PVC generates HCl at higher temperatures. Under inert-gas atmosphere, alkyl radicals are formed, transforming to peroxyradicals, when the sample is exposed to air. In presence of air, more chain scissions are observed due to γ-radiation, which facilitates crosslinking. The molecular weight of a polymer does not change during irradiation. This is a consequence of crosslinking and chain scission occurring simultaneously. Irradiation of plasticised PVC may lead to the formation of monoesters of certain plasticisers. β-irradiation of PVC results mainly in the generation of HCl.

A study by Colombani *et al* (2009) shows that plasticised PVC released 100 times more organic compounds than pure PVC, concluding that the influence on the degradation of PVC macromolecules due to γ-irradiation is not significant. The majority of leaching compounds in case of plasticised PVC consists of leached additives and their degradation products. The longer the irradiation time the lower is the leached species concentration, due to grafting reactions. Leaching products are mainly composed of phthalic ions resulting from hydrolysis of phthalate esters.

In a review of literature on PVC additives, particularly those used in the UK nuclear industry (Smith *et al*, 2013), it was concluded that the PVC base polymer itself and stabilisers and fillers are unlikely to degrade significantly under repository conditions. However, phthalate plasticisers could diffuse from the PVC under conditions of heat, radiation or high pH (Watson, 2004). These could then potentially act as complexants for radionuclides, substrates for microbial activity or form non aqueous phase liquids (NAPLs).

As detailed above, the most common PVC plasticisers are phthalic acid esters (PAEs) including: DEHP (di-ethylhexyl phthalate), sometimes referred to as di-octyl phthalate (DOP), DINP (di-isononyl phthalate) and DIDP (di-isodecyl phthalate).

Chemical Degradation

An ageing experiment (Baston and Dawson, 2012) carried out on PVC material stored in deionised water (pH 7) and $Ca(OH)_2$ solution (pH 12) observed around 2 % mass loss of the PVC in the pH 7 solution and around 30 % loss in the pH 12 solution, indicating a strong pH effect and evidence of alkaline hydrolysis and leaching of the plasticiser present.

Studies on the alkaline degradation of phthalate ester plasticisers show that aliphatic alcohols and phthalic acid (1,2-benzenedicarboxylic acid, Figure 30), or phthalates, are generated. The mechanism is assumed to be alkaline hydrolysis of the ester linkages.
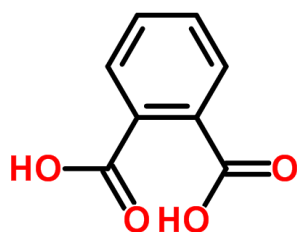
Figure 30 Phthalic acid

In a disposal environment, calcium phthalate might be expected, which is water soluble under these conditions (Baston and Dawson, 2012). In the case of DEHP, the expected alcohol is ethylhexanol. This has low solubility in water and could form a discrete, buoyant NAPL. However, there is some disagreement in the literature about the nature of the phthalic degradation products from DEHP hydrolysis.

Radiolytic Degradation

Irradiation studies of PVC in contact with aqueous solution have observed the release of hydrochloric acid (HCl) from the polymer. Irradiation at 10 MGy (at 4 kGy/hr for 2500 hrs) under aqueous conditions observed the pH of solution decreasing from 7 to 2.2 (Dawson, 2013). However, in systems of PVC in $Ca(OH)_2$ solutions, the pH remained at 12.4 following irradiation, presumably due to HCl buffering by excess $Ca(OH)_2$. The release of chloride from PVC under irradiation has been observed via ion chromatography (Sims and Walters, 1996).

Following irradiation, the PVC systems showed an increase in solution total organic carbon (TOC) content. Gas chromatography mass spectrometry (GC-MS) showed that in the PVC aqueous systems a wide range of organic degradation products were released into the solution and gas headspace. These included aliphatic and aromatic hydrocarbons, ketones, carboxylic acids, alcohols and aldehydes (Dawson, 2013).

Smith *et al* (2013) report the results of irradiation experiments on dry PVC components at ambient temperatures, up to 1 MGy (Shashoua, 2008) and up to 10 MGy (Dawson, 2013), which showed evidence of a sticky residue on the surface, indicating the mobility of plasticisers that readily diffuse from the PVC. However, the radiolytic stability of the plasticisers themselves is unclear. Whilst the common PAEs contain aromatic groups that might be expected to infer stabilisation under ionising radiation, the ester linkages might be susceptible to enhanced hydrolysis in the presence of both high pH solution and radiation. However, the reactions will be complex and there is limited data to draw further conclusions.

Thermal Degradation

Experiments on unirradiated PVC cable components (Dawson and Schneider, 2002, reported in Smith *et al*, 2013) aged at 70 – 110 ^{0}C observed weight losses of around 17 %, accompanied by loss of flexibility and increased brittleness. This was attributed to the loss of plasticiser, rather than thermally induced degradation of the PVC itself.

Thermal ageing of PVC is thought to occur via two simultaneous processes (NDA, 2012a):

- Plasticiser loss – where the plasticiser migrates out of the PVC and causes the polymer to become hard, rigid and brittle;

- Thermal degradation – a complex, not fully understood process where attack of the PVC polymer chains occurs, resulting in the release of HCl and unsaturation (polyene formation) via an unzipping mechanism.

At temperatures below ~80°C, plasticiser loss dominates, whilst above this temperature, thermal degradation usually dominates. However, the diffusion of plasticiser out of the polymer is also dependent on the molecular structure of the PVC (NDA, 2012a).

Microbial Degradation

Studies on PVC under landfill conditions (which, whilst different to the conditions of geological disposal, have some relevance) show that the PVC polymer itself is stable, but released plasticisers could be subject to microbial degradation. Under both aerobic and anaerobic conditions, PAE plasticisers undergo hydrolysis of the phthalates to form diesters, various alcohols and monoester intermediates before finally forming phthalic acid (Mersiowsky, 2001). The alcohols are metabolised to methane and CO_2. The fate of phthalic acid is more dependent on the conditions, being converted under aerobic conditions to key intermediates in common biochemical pathways and under anaerobic conditions to benzoate and ultimately to hydrogen gas, CO_2 and acetates (Mersiowsky *et al*, 2001). Nalli *et al* (2006) report the degradation of DEHP and another plasticiser di-2-ethylhexyl adipate (DEHA) to the alcohol 2-ethylhexanol and 2-ethylhexanoic acid by a single species culture by the soil microbe *Rhodococcus rhodochrous* suggesting that complete degradation may be difficult even under aerobic conditions. 2-ethylhexanoic acid has also been found in trench leachate samples collected from commercially operated low-level radioactive waste disposal sites (Francis *et al*, 1980).

There is evidence that the length of the alcohol chain of the diester can affect the rate at which the monoester is formed; those with long hydrophobic side chains degrade more slowly, which is thought to be due to increased hindrance to the binding of microbial enzymes that catalyse the reactions (Ejlertsson et al, 1997, reported in Smith et al, 2013).

There is evidence that microbial degradation of PAEs occurs primarily during the methanogenic phase of landfill evolution, in which the bacterial populations utilise the plasticisers as they diffuse out of the PVC. High levels of phthalic acid have been observed in landfill leachates, indicating that the phthalic diesters and monoester intermediates are readily hydrolysed to phthalic acid, but that further microbial conversion to terminal products (methane and CO_2) occurs much less readily (Smith *et al*, 2013). Whilst a number of the mechanistic stages in PAE degradation may be kinetically hindered and slow to take place, it is recognised that a stable mature landfill microflora appears to be capable of the complete biodegradation of phthalates into biogas (Mersiowsky, 2001). The biodegradation of phthalates is however complicated by ecotoxicological effects in soil and compost environments (Kapanen *et al*, 2007).

Whilst the conditions of a GDF will be considerably different to those of landfill (e.g. the highly alkaline conditions will hinder microbial growth), areas of lower pH will evolve over time and these microbial degradation mechanisms could be significant.

4.2.3 NAPLs derived from halogenated polymers

Degradation studies of PVC and other organic polymers in the UK have generally focused on the production of non-aqueous phase liquids (NAPLs). If produced from polymer degradation, over long timescales, NAPLs may accumulate to form a separate phase. Those that have a specific gravity of less than one could become mobile under buoyancy forces and rise towards the surface. This could potentially accelerate radionuclide release from the near field and could also affect sorption properties of the backfill and rocks (NDA, 2012a; Smith et al, 2013).

Under aqueous conditions, no NAPL was detected following irradiation of PVC at a dose of 10 MGy. Under dry conditions, however, a separate liquid phase was released, which was attributed to the plasticiser, rather than radiolysis of the polymeric component itself (Dawson, 2013). Phthalate-based NAPLs are viscous, not especially buoyant and are not expected to be particularly mobile (Watson et al, 2012).

Any NAPLs that do form from the degradation of PVC in a repository environment may themselves be degraded by chemical, radiolytic or microbial mechanisms. A review by the Nuclear Decommissioning Authority (NDA, 2012a) concluded that the formation of NAPLs from the degradation of parent polymers is likely to be very low. Phthalate ester plasticisers appear to break down to water-soluble species and also form a denser insoluble phase on gamma irradiation. They are also expected to hydrolyse in contact with alkaline water (Watson et al, 2012). It further concludes that radionuclides present in the aqueous phase as ions or stable charged complexes are likely to be excluded from the NAPL phase, especially in the presence of complexing species in the aqueous phase.

In summary, as phthalate plasticisers diffuse from PVC under repository conditions, they are expected to be chemically and radiolytically unstable. They will come into contact with a combination of some or all of: a highly alkaline aqueous environment, ionising radiation, elevated temperatures and possible microbial attack. Each of these will contribute to decomposition of the plasticiser into phthalic acid (or calcium phthalate), which is not a NAPL and alcohols, which could exist as NAPLs, especially those C8-C10 alcohols from the most common plasticisers DEHP, DINP and DIDP. However, these alcohols may themselves under go further degradation, e.g. via radiolysis (Smith *et al*, 2013). The eventual fate of phthalic acid depends on the environment. Under aerobic conditions, it is oxidized to 4,5- or 3,4-dihydroxyphthalate before being converted to key intermediates in common biological pathways. Under anaerobic conditions, phthalic acid is decarboxylated to benzoate, with further degradation to hydrogen gas, carbon dioxide and acetates (NDA, 2012a).

The UK programme has also examined the radiolytic degradation of some other halogenated polymers.

Hypalon™ (chlorosulfonated polyethylene)

No NAPLs were observed above the aqueous solutions following irradiation (NDA, 2012a). The highest TOC measured in solution was approximately 150 ppm following 150 kGy irradiation. It was lower at 10 MGy, suggesting radiolytic degradation of the dissolved organic species. The pH of the water decreased to approximately 2 at 10 MGy, attributed to the release of chloride.

Neoprene (polychloroprene)

There was no evidence for the presence of a non-aqueous phase in any of the irradiated neoprene experiments (NDA, 2012a). There was no trend of pH change with radiation dose. There was no

change in the pH of the Ca(OH)$_2$ solution experiments. Relatively small increases in TOC occurred after irradiation, though the concentrations decreased at the higher accumulated doses. There were no changes in the polymer's appearance following irradiation, though the flexibility decreased in all environments.

4.3   Bitumen

Bitumen is obtained by partial distillation of crude petroleum and consists mainly of a complex mixture of high molecular weight hydrocarbons and a minor amount of structurally analogous heterocyclic species and functional groups containing nitrogen, sulfur and oxygen atoms. It also contains trace amounts of metals such as vanadium, nickel, iron, magnesium and calcium present in the form of inorganic salts and oxides or in porphyrin structures (Read and Witheok, 2003). The precise composition depends on the source of the crude oil from which the bitumen originates and on the modifications induced during the further production process and is therefore extremely complex. However, four broad chemical groups can be identified in bitumen, namely asphaltenes (5-25 % wt), saturates (5 - 20 % wt), resins (10 - 25 % wt) and aromatics (40 - 65 % wt). Typical chemical structures are presented in Figure 31.

There are two different types of bituminised waste used in the nuclear industry. One type is conditioned in a matrix of distilled bitumen i.e. soft bitumen, while the other part is conditioned in a matrix of blown bitumen i.e. hard bitumen (Ondraf/Niras, 2001). This latter 'hard' Eurobitum bituminised waste is the most significant fraction (± 80 %) used in Belgium and has been primarily studied in its application to immobilise radioactive soluble salts recovered by evaporation of liquid wastes. In France a similar process uses soft bitumen. Chemically the two types of bitumen are similar, although the processes whereby the harder physical properties of Eurobitum are produced is a result of partial oxidation where air is passed through bitumen at elevated temperature (Eurobitum, 2011). The chemical changes occurring during air blowing of bitumen have been examined by UV and nuclear magnetic resonance (NMR) spectroscopy (Quddas *et al*, 1995) which indicate the conversion of aliphatic straight chain hydrocarbons (e.g. Figure 31 structure (c))to increased amounts of aromatic hydrocarbons. The process is catalysed by the addition of transition metal salts leading to the blown product becoming more complex and condensed and with an increase in molecular weight (Quddas *et al*, 1995). This oxidation process is also relevant to the long term stability of bituminised waste during storage, which is discussed below. In the remainder of this section the discussion of bitumen composition focusses on the Eurobitum used in Belgium, but the processes are relevant to bituminised waste in France and other applications such as the encapsulation of ion exchange resins.

a)

b)

c)
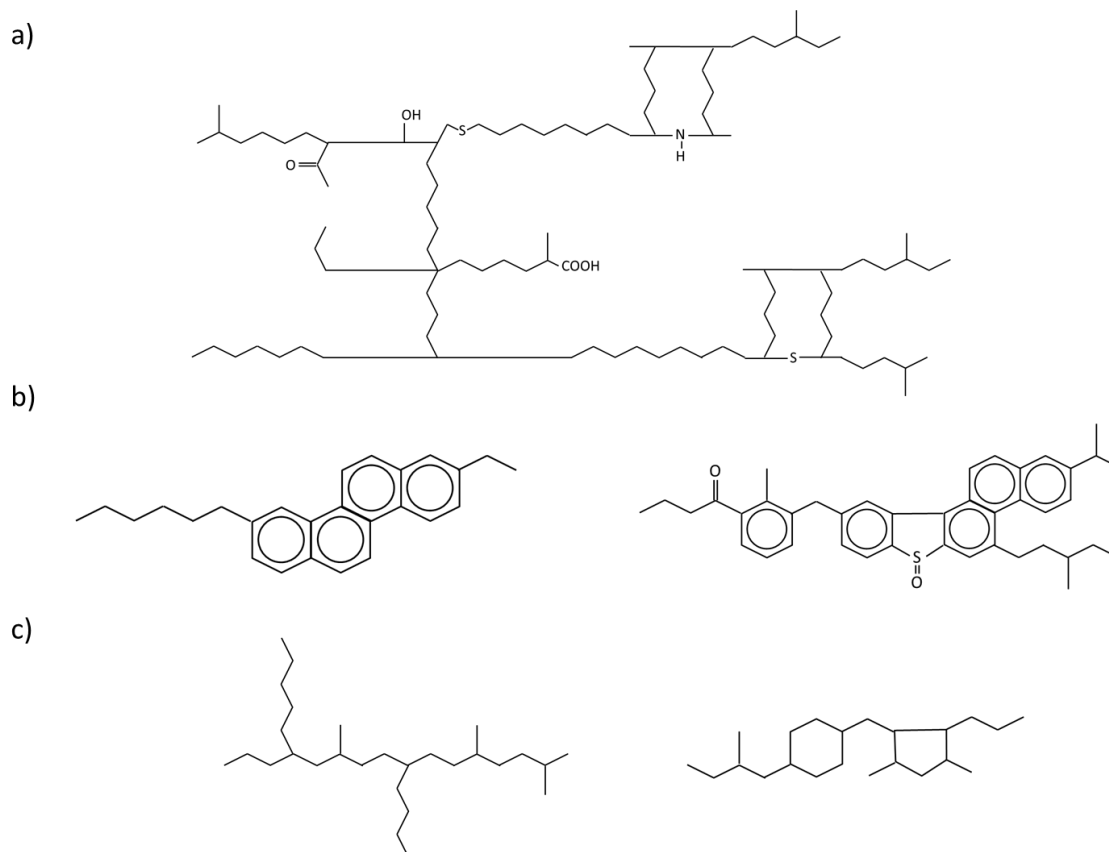
Figure 31: Types of organic compounds found in bitumen a) asphaltene structure, b) aromatic structures, c) saturated structures based on Read and Witheok, (2003)

Eurobitum used to encapsulate evaporator salts contains 60 % bitumen Mexphalt R85/40 and 40 % waste containing soluble and insoluble salts (Table 13). It contains 20 - 30 wt % $NaNO_3$, 4 - 6 wt % $CaSO_4$, and small amounts of CaF_2, $Ca_3(PO_4)_2$, $Ni_2[(Fe,Mn)(CN)_6]$, and (hydr)oxides of Fe, Zr, and Al. The residual amount of water present is between 0.5 - 1 %. The total radionuclides inventory (U and Pu isotopes, [241]Am, [244]Cm, ^{60}Co, ^{90}Sr, ^{137}Cs, ...) counts for 0.4 wt % for drums with an average activity but can be up to 1.15 wt % for drums with higher activities (Stankovskiy, 2011).

Table 13 Composition of the reference Eurobitum waste (Stankovskiy, 2011)

	Parameter	Value (wt %)
Bitumen **60.6 %**	Carbon	50
	Hydrogen	5.45
	Sulfur	3.64
	Oxygen	0.91
	Nitrogen	0.61
Waste **39.4 %** homogenously distributed in the bitumen	$NaNO_3$	29.5
	$CaSO_4$	5.6
	CaF_2	1.5
	$Zr(OH)_4$	0.95
	$Fe(OH)_3$	0.9
	Other insoluble salts	0.75
	Radionuclides	0.4

4.3.1 Chemical and radiolytic degradation of bituminised waste

To ensure a safe geological disposal of the waste, a good understanding of the long-term behaviour of bituminised waste and its influence on the host rock (Boom Clay) is of paramount importance. Under disposal conditions, the following processes need to be considered (Valcke *et al*, 2009):

- Uptake of pore water by hygroscopic salts embedded in the waste and gas production by anaerobic corrosion of steel drums, radiolysis and microbial activity can lead to an increase of the pressure in and around the waste.
- The leaching of large amounts of $NaNO_3$ and other soluble salts in the host rock can influence the geochemistry in the vicinity of the near field and influence the migration of radionuclides.
- Radiolysis, chemical- and biodegradation will entail the production of water-soluble organic complexing agents that can modify the speciation and mobility of radionuclides.

The extent of some of these processes will be affected by the continuous evolution of the rheological properties of the bitumen. This so called ageing results in harder bitumen, which tends to lose its binding capacity and becomes increasingly brittle. Details on this ageing process are beyond the scope of this review, but briefly, the most important ageing process is oxidation, particularly when the bitumen is heated and/or irradiated in the presence of oxygen, which is most relevant to the storage of bituminised waste prior to disposal. Oxidation results in an increase of the number of C=O and C=C groups together with an increase of the asphaltene content, a decrease of the saturates and aromatics, while the amount of resins remains constant. In addition, starting from the surface, oxidation causes the formation of (micro) fissures in the bitumen through which oxygen can subsequently infiltrate deeper in the waste and further deteriorate the structure. Furthermore,

asphaltenes contain more hydrophilic groups, which results, together with the expansion of (micro) fissures caused by ageing, in an increased affinity for water (Read and Witheok, 2003). These changing properties have important consequences during geological disposal, when the bitumen gradually takes up pore water from the host rock.

The organic compounds in the bituminised waste will be prone to radiation and highly active free radicals $^\bullet COO^-$, $R\text{-}H^\bullet$, $H^\bullet$, $O^{\bullet-}$, $O^{\bullet 2-}$, $OH^\bullet$, $HO_2^\bullet$, $NO_3^{\bullet 2-}$, $NO_2^\bullet$, $N_2O_4^\bullet$ will be formed. In the absence of oxygen (deeper inside the bituminised waste), the radicals are involved in cross-linking reactions with molecules and will lead to the production of gases, with H_2 making up approximately 95% of the total volume of gas produced. Other radiolytically produced gases are N_2, CH_4 and small hydrocarbons (1 - 4 C atoms) (Eschrich, 1980; Walczak, 2000). As already stated, due to the fissures that appear in time, oxygen can infiltrate deeper in the waste and consequently the type of radiolytically generated gases will change. The amount of small hydrocarbons will decrease, while in addition to H_2, N_2 and CH_4, H_2O_2, CO and CO_2 are produced as well (Eschrich, 1980; Walczak, 2000). The presence of oxygen will inhibit cross-linking reactions but favour oxidation reactions resulting in the formation of oxidised polar groups such as ketones, sulfoxides, carboxylic acids and alcohols (Walczak, 2000). Although still under discussion, another putative source of oxygen deeper inside the waste, is the oxygen produced by the irradiation of the $NaNO_3$ crystals. Different studies have shown that there is an additional excitation (heating, dissolution in water) of the $NaNO_3$ crystals necessary to release the oxygen after γ irradiation (Walczak, 2000; Valcke et al, 2009). However, a study by Hochanadel (1962) showed that α irradiation of $NaNO_3$ resulted in the production of oxygen levels that were 5 times higher compared to those after ϒ irradiation and still slightly higher compared to produced levels after γ irradiation at increased temperature. Nevertheless, the most obvious effect of the radio-oxidation is the earlier explained hardening of the bitumen. This was also observed in a 25 year old radioactive Eurobitum sample. When cutting the upper ~ 10 mm of the sample with a firmly stretched steel wire, the loaded part of the sample disintegrated nearly completely into small crumbs. The upper 5 cm was highly oxidised and the oxidation process took place until a depth of at least 25 cm (total height is about 75 cm). It is likely that with time this oxidation will extend deeper into the waste matrix (Valcke et al, 2009). Here, the source of oxygen radicals deeper in the waste can be explained by the diffusion of oxygen due to fissures or putatively by the irradiation of $NaNO_3$.

During disposal conditions, the bituminised waste will be gradually saturated with pore water resulting in the leaching of soluble salts and radionuclides. Although in time anoxic conditions will be achieved, radiolysis of water will occur, and this can result in the production of oxygen bearing radicals which in turn may promote oxidative ageing. Experimental work showed that the leaching rate is influenced by temperature, leachate composition and the physical characteristics of the bitumen matrix (Sneyers and Van Iseghem, 1998). Moreover, it showed that the amount of leaching products is dependent on several factors, such as the presence or absence of oxygen (Kagawa et al, 2000), the quantity of the bitumen and the surface area/volume ratio (Walczak, 2000). In addition, the pH and ionic strength of the leachate are indicated as important factors. The amount of leached dissolved organic carbon (DOC) increases strongly as a function of the pH of the leachate. When a slightly alkaline solution of pH 8, reflecting Boom Clay host rock conditions, is used as leachate for 8 weeks, the DOC was 5 times higher compared to ultra-pure water conditions. An increase in pH to 13.5 to reflect the near field conditions (i.e. the cementitious backfill) further increases the DOC 8 times (Walczak, 2000). When leaching experiments (70 hours) were performed with Eurobitum, the

amount of DOC was also 2 times higher when cement-equilibrated clay water (pH 12.5) was used as leachate compared to synthetic Boom Clay water (pH 8.5) (Valcke *et al*, 2000). The observed differences can be explained by the higher solubility of certain types of organic molecules and on the chemical attack of the bitumen matrix at alkaline pH (Walczak, 2000).

Due to the heterogeneity in experimental setups and the consequent variable results, it is difficult to predict the real concentrations of soluble compounds specifically relevant for Eurobitum. Nevertheless, next to the high amount of salts (mainly $NaNO_3$) the following groups of molecules have been identified after leaching experiments of bitumen and bituminised waste in alkaline conditions (Walczak, 2000; Kagawa *et al*, 2000):

- Carboxylic acids, comprising lower linear acids, such as formic acid and acetic acids but also longer mono-carboxylic acids such as propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid and octanoic acid.
- Polycarboxylic acids such as oxalic acid and malonic acid.
- Glycol, essentially ethylene glycol
- Aromatic compounds such as naphthalene, alkyl substituted naphthalene and polysubstituted phenol
- Oxidised compounds such as
  - Linear alcohols with between 8 and 19 aliphatic carbon atoms
  - Linear carbonyls with between 7 and 13 aliphatic carbon atoms
  - Aromatics
- Sulfur compounds
- Nitrogen compounds

Combined chemical degradation and radiolytic degradation experiments have also been performed. Here, it is again difficult to predict the real concentrations of the soluble compounds. Moreover, most experiments study non-radioactive bitumen and irradiate it with an external gamma source, while in the real scenario the dose absorbed by alpha radiation will be more significant. In addition, the dose rates used are in most cases much higher than the real dose rates to obtain realistic total absorbed doses within a reasonable time frame. The amount and nature of degradation products depends on whether oxygen and/or water are present during the irradiation. Nevertheless, from the performed experiments, it seems that the defined soluble compounds are in general very similar in nature and in quantity to those found in the case of purely chemical degradation. Additionally identified compounds are ketones and phenols (Walczak, 2000; Valcke *et al*, 2000) and other types of carboxylic acids (Valcke *et al*, 2000). Another compound worth mentioning is oxalate as in some experiments it is found, while other researchers cannot detect it. Oxalate is often found when carboxylic acids are irradiated as a consequence of the reaction of two •COO$^-$ radicals. It is expected that oxalate will only be produced in the presence of oxygen (Van Loon and Kopajtic, 1991; Valcke *et al*, 2000).

Walczak *et al* (2001) analysed the water-soluble organic matter in bitumen leachates under different conditions. At a pH of 8 they identified the following components: carboxylic acids, alcohols, linear carbonyls, and aromatics. There are some studies investigating the radiolytic degradation of bitumen under alkaline conditions (Kopajtic and van Loon, 1989; Kagawa *et al*, 2000; Libert, and Walczak, 2000). The main water soluble degradation products were linear carboxylic acids (lower than butanoic acid), phthalic acid (and its dibutylester), oxalic acid, aromatics (e.g. naphthalene), and

oxidised compounds (alcohols, linear carbonyls, glycols, and nitrogen compounds). Bruno *et al* (2013) revealed that bitumen colloids occur in cementitious environments, but complexation of radionuclides is expected to be low.

These chemically and radiolytically produced degradation products may form complexes with the radionuclides present in the waste and influence their solubility (See Section 5). Moreover, most of the degradation products are theoretically degradable by microorganisms if proper growth conditions are attained.

4.3.2 Microbial degradation of bitumen

The possible degradation of bitumen by microorganisms is already known and studied since at least 1935 (Hundeshagen, 1935). Biodegradation rates depend on the chemical composition of the bitumen substrate, the metabolic character of the microorganisms involved and various biological and physico-chemical parameters (Ait-Langomazino *et al*, 1991). In aerobic conditions biodegradation rates are much higher compared to anaerobic conditions (Wolf and Bachofen, 1991a,b; Jacquot *et al*, 1997). Wolf and Bachofen (1991a, b) calculated on the basis of their experimental results that after 1000 years under oxic conditions 25-70% of bitumen matrix and under anoxic conditions 0.3-0.8% will be degraded. Roffey and Norqvist (1991) investigated the biodegradation of bitumen (conditions: aerobic, anaerobic, pH=7-11.5) using different model-compounds for bitumen (decane, hexadecane, cyclohexyldodecane, pristane, naphthalene and anthracene). These compounds were degraded under all conditions. In a long term study, Libert *et al* (1997) revealed that microorganisms are able to degrade not only water soluble hydrocarbons but also hydrocarbons from the bitumen matrix. The main degradation products were CO_2, N_2, and linear carboxylic acids (C_5-C_{10}). The biochemical mechanisms involved in anaerobic degradation of hydrocarbons are completely different and more diverse, compared to those involved in aerobic degradation. In addition, organisms capable of anaerobic hydrocarbon degradation described until now belong to different genera than the aerobic degraders (Heider, and Schühle, 2013; Rosenberg, 2013). The most frequently isolated organisms capable of aerobic degradation of hydrocarbons belong to the genera *Pseudomonas, Acinetobacter*, *Flavobacterium*, *Corynebacterium*, *Alcanivorax* and *Arthrobacter*, all common soil or freshwater bacteria, but a wide range of other genera has been identified (Rosenberg, 2013). The anaerobic hydrocarbon-degrading bacteria comprise among many others the genera *Thauera*, *Azoarcus*, *Aromatoleum, Georgfuchsia*, *Geobacter, Desulfobacula* and *Desulfococcus (*Heider, and Schühle, 2013). Therefore, the low degradation rates observed in anaerobic conditions in these experiments can putatively be explained by the cultures used in the degradation experiments. Nevertheless, also in anaerobic conditions a distinct production of N_2 and CO_2 was observed after one year and all short strain carboxylic acids (C_5-C_{10}) leached from the bitumen were degraded by microorganisms, showing a clear activity of microorganisms (Jacquot *et al,* 1997). In addition, in aerobic as well as anaerobic growth conditions, biofilm formation on the bitumen was often observed (Ait-Langomazino *et al*, 1991; Wolf and Bachofen, 1991; Springael *et al*, 1997). It was shown that blown 'hard' bitumen is more sensitive to biodegradation compared to a distilled 'soft' bitumen, comprising a lower amount of saturates (Ait-Langomazino *et al*, 1991). This is in agreement with the fact that the resins and asphaltenes are much more resistant to biological degradation compared to the saturates, although organisms able to use asphaltenes as carbon source are reported several times (Pineda-Flores *et al*, 2004; Ali *et al*, 2012; Tavassoli *et al*, 2012).

In conclusion, the biodegradation of the bitumen itself can occur, although the biodegradation rates will probably be low. However, as already mentioned above, the chemically and radiolytically produced degradation products can be used by microorganisms as a carbon source.

4.4   Factors affecting microbial degradation of bitumen in the repository

The understanding of the potential microbial processes relevant to the geological disposal of bituminised waste is generally more advanced than that of organic polymers. In this subsection a number of environmental factors affecting microbial activity are discussed. This understanding has been driven mainly by studies in countries considering disposal of bituminised waste in clay formations. The information is however of wider interest to the potential microbial processes fuelled by degradation products of organic polymers (e.g. PVC and ion exchange resins) and under a wider range of geological conditions.

4.4.1   Presence of microorganisms in the repository

Microorganisms will be ubiquitous in the repository, either as autochthonous species that are already present in the host formation or as species brought into the repository during its construction or putatively via the waste monolith. Although the conditions are far from optimal, the necessary components for metabolic activity are present. The occurrence of viable indigenous microorganisms in clay formations has already been shown for different clay formations studied in the context of nuclear waste disposal (e.g. Opalinus Clay, Bentonite, Boom Clay) (Boivin-Jahns *et al*, 1996; Stroes-Gascoyne *et al*, 2007;Lopez-Fernandez *et al*, 2015). Moreover, borehole water samples from different layers within the Boom Clay have been shown to comprise a highly diverse bacterial community of which a large fraction is active (Wouters *et al*, 2013). The latter study shows that, although at least part of this community is probably introduced during the installation of the piezometers, the community can survive and be metabolically active and therefore has to be considered when radioactive waste will be disposed. Importantly, species belonging to different genera that are known to be able to degrade hydrocarbons in aerobic conditions (*Acinetobacter, Pseudomonas*) and in anaerobic conditions (*Azoarcus, Desulfotomaculum*) were found in Boom Clay (Boivin-Jahns *et al*, 1996).

4.4.2   Stress induced by salt conditions

In the case of the Boom Clay, within 50 years after closure of the repository gallery, all pores and voids would be expected to be filled with cement equilibrated Boom Clay pore water. Water will gradually infiltrate into the Eurobitum and consequently large amounts of $NaNO_3$ will be released. In the case of disposal in indurated Jurassic Callovian Oxfordian or Opalinus Clay considered in France and Switzerland much longer periods of re-saturation are expected, of quite saline groundwater of marine origin (Andra, 2005; Wersin *et al*, 2011) Such anticipated saline conditions associated with bituminised waste will induce an osmotic pressure on the microbial and archaeal communities present. Scoping calculations indicate that for the Boom Clay during the first ~300 to ~1400 years, the $NaNO_3$ concentration within the monolith will remain above 1 M and 0.5 M, respectively (Weetjens *et al*, 2010). Closer to the waste drums, the concentrations are estimated to reach up to a few molar (Weetjens *et al*, 2010). Recently, reviews have been published with an overview of the

widespread occurrence of halotolerant[2] and halophilic[3] bacteria and archaea (Uratani *et al*, 2014). In addition, organisms that can degrade hydrocarbons in environments with up to 6 M of NaCl (Fathepure, 2014) and halotolerant organisms able to use aphaltenes as sole carbon are identified (Ali *et al*, 2012). Moreover, it is known that bacteria can adapt to osmotic stress. Some of the adaptation mechanisms haven been studied in detail (Kramer, 2010). Consequently, it is not a requirement for survival of the indigenous or introduced species to be already halotolerant.

4.4.3   Stress induced by highly alkaline pH

Another stress factor that the microbial community will encounter in repository conditions will be the high alkaline pH (> 12) originating from the pore water from the concrete lining of the waste monolith and the cementitious backfill material. Although aerobic and anaerobic microbial metabolism is expected to be largely inhibited at a pH of about 12 (Sorokin, 2005; Rizoulis *et al*, 2012), the pH will gradually drop to pH 10 over prolonged periods of time (ca. 10^5 year) (Berner, 1992, Section 3.2). In addition, several processes are expected to lower the pH on a shorter time span.

First of all, it is not known how much CO_2, will be produced in geological conditions, thus decreasing the pH of the contacting solution. As discussed in a previous section (4.3.1), CO_2 will be produced as one of the radiolytically generated gases in the presence of oxygen. Moreover, CO_2 is also produced as result of abiotic decarboxylation of fatty acids which are abundantly present in bitumen. A consequent decrease of the pH was also observed by Valcke *et al* (2000), where the pH of irradiated bitumen leached in equilibrated cement dropped from pH 12.3 to pH 9.1. The total absorbed dose of gamma irradiation of the bitumen in this experiment was 4.8 ± 1.2 MGy corresponding with a predicted total alpha-dose that will be absorbed by the bituminised waste within about $1×10^4$ to $1×10^5$ years, depending on the specific activity of the waste (Valcke *et al,* 2000). Another source of CO_2 production was observed after growth of microorganisms on Isosaccharinic acid (ISA) (Bassil *et al*, 2015). ISA is the main alkaline degradation product of cellulose and is able to complex a number of metals and radionuclides making them potentially more mobile (Van Loon *et al*, 1997). Recent studies have shown that alkaliphilic microorganisms isolated from an analogous site for an ILW repository were able to use ISA as sole carbon source at pH 10 both in aerobic and anaerobic conditions (Rout *et al*, 2015). Moreover, microcosms established from neutral, near-surface sediments demonstrated complete ISA degradation under methanogenic conditions up to pH 10, showing the ability to quickly adapt to a higher pH (Rout *et al*, 2015).

Due to the excavation and operation of the disposal gallery, a small layer of Boom Clay surrounding the concrete liner will be partially oxidised, resulting in higher sulfate and thiosulfate contents, which typically leads to the generation of the pore waters rich in sulfates and a concomitant decrease of the pH (De Caen *et al*, 2004). Furthermore, when the cement equilibrated pore water comes into contact with the Boom Clay, some primary minerals of the Boom Clay tend to dissolve, forming new secondary minerals. A common feature of most of these reactions is the consumption of OH^- hence leading again to a decrease of pH (Wang *et al*, 2007). All these pH-lowering processes are expected to lead to niches where growth of microorganisms will be possible. Finally, microbial influenced

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[2] Microbes not needing salt to grow, but which can tolerate the presence of high amounts of salt
[3] Microbes that require salt for growth

degradation of concrete has been observed ubiquitously in the environment (Wei *et al*, 2013). When microorganisms colonise concrete, they produce either organic or inorganic acids that can dissolve and disintegrate the concrete matrix. This will lead to a local decrease of the pH which will in turn promote colonisation by other microorganisms (Wei *et al*, 2013).

4.4.4   Stress induced by radiation

Microorganisms present in the repository will be constantly exposed to radiation. However, as mentioned in the previous Section (3.4) and shown in Table 10, the average dose rates are limited and β/γ emitters are only predominant during the first 100 years. Afterwards, radiation will mainly originate from α-emitters and actinide toxicity is mainly chemical, rather than radiological (Ruggiero *et al*, 2005). Microcosms exposed to 0.5 Gy/h and 30 Gy/h of γ-irradiation during 56 days have been shown to suffer no significant effects and to remain active, still catalysing biogeochemical processes (Brown *et al*, 2015). In addition, laboratory directed evolution experiments showed that relatively radiosensitive bacteria were able to adapt to extreme radiation exposures (Davies and Sinskey, 1973; Harris *et al*, 2009; Parisi and Antoine, 1974). Therefore, the radiation conditions present in the repository are probably not sufficient to completely inhibit microbial activity.

5   Radionuclide complexation studies

Whilst Section 4 details the degradation mechanisms and the expected products arising from organic waste degradation, this section reviews previous literature concerning radionuclide complexation by the water-soluble degradation products of the main anthropogenic polymers and materials. Complexation of radionuclides by organic degradation products may enhance their migration out of a repository by increasing the aqueous solubility of the metal ions and/or limiting their sorption to surfaces of the engineering barrier system employed or mineral surfaces in the geosphere.

Radionuclides may also be associated with solid organic residues representing the residual organic matter, but also potentially including microbial biomass. These interactions with solid organic materials could provide a mechanism to transport or retard radionuclides depending on the potential colloidal nature of such solid degradation products.

Work Package 1 of the MIND project includes spectroscopic[4] and microscopic[5] studies undertaken by HZDR (Germany) and UGR (Spain) that will examine the complexation and association of radionuclides (actinides and lanthanide analogues) with organic radiolysis and biodegradation products. As part of this research this section compiles information regarding the complexation of radionuclides with known organic degradation products, which are typically small water soluble organic species. This section includes experiments performed on bitumen degradation products, ion-exchange resin degradation products (mixtures of species), as well as individual organic acids that could be representative of a range of waste degradation products.

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[4] UV-visible, time resolved laser fluorescence spectroscopy (TRLFS), infra red (IR), X-ray absorption spectroscopy (XAS)
[5] Scanning Transmission Electron Microscopy High Angle Annular Dark Field (STEM/HAADF), element mapping, Electron Energy Loss Spectroscopy (EELS), Field Emission Scanning Electron Microscopy (SFESEM), Environmental Scanning electron Microscopy (ESM)

It should be noted that there is considerable uncertainty as to the specific molecules that will be released from the organic waste materials during radiolysis and biodegradation that may act as complexants. Characterisation of degradation products is not always comprehensive, due to the difficulties of identifying specific organic acids in solution. Leachate from radiolysis and biodegradation experiments undertaken within the MIND project will be analysed using gas chromatography mass spectroscopy (GC-MS) and ion chromatography (IC) in order to characterise the DOC.

This part of the review provides an overview of previous experiments carried out on a range of relevant elements and then considers those complexing ligands that may have a significant effect on radionuclide migration.

Overview of radionuclide complexation studies

A detailed review of complexation studies of radionuclides (U, Np, Pu, Am, Tc, Se, Ni and Zr) with different low molecular weight organic compounds; oxalate, citrate, ethylenediaminetetraacetic acid (EDTA), and isosaccharinate (ISA) is published by Hummel *et al.*(2005). However, the complexation potential of other small organic compounds, which are more common radiolysis and fermentation products, such as formate, acetate, propionate, and butyrate towards actinides and lanthanides was not highlighted.

The interaction of uranyl (UO_2^{2+}) with a wide range of organic ligands is reported in the literature and relevant studies are presented here. In addition, a range of studies of neptunium complexation are reported.

It is well known that plutonium is a redox sensitive element and can coexist in several oxidation states (III, IV, V, VI) in environmental waters. Hence complexation studies with small organic acids are challenging due to their reducing properties. In a recent review (Kersting, 2013) important aspects of the plutonium transport in the environment are discussed. The ability of colloids to facilitate the migration of strongly sorbing contaminants like Pu could be demonstrated. It is stated that very little is known about the molecular-scale geochemical and biochemical mechanisms controlling Pu transport. Among other processes, interactions of Pu with organic matter was summarised with a focus on humic substances. Pu was found to bind to humic colloids, enhancing the transport of Pu in groundwater. The ability of microbes to influence the fate of plutonium in the environment by complex interaction mechanisms was pointed out. Among other actions they can produce organic acids which than can contribute to a solubilisation of plutonium. The role of small organic acids/organic compounds complexing Pu was not described. A number of studies exist in the grey literature concerning the effect of organic degradation products on plutonium solubility and sorption.

A review of experimental data obtained by TRLFS on the speciation of curium(III) were compiled by Edelstein *et al* (2006). Compared to studies involving polyamino acids (e.g. DTPA, EDTA), α-hydroxyacetate (glycolate), and humic substances, little is known about the direct speciation of curium(III) with small organic acids.

Europium is a representative of Ln(III), providing excellent luminescence properties. It is commonly assumed that Ln(III) mimic An(III) and can be used as suitable non-radioactive chemical analogue. Data was found on its complexation with phthalic acid, acetate, propionate using calorimetric methods. Less information could be found describing the complexation of Eu(III) with formic,

propionic, and butyric acid with direct speciation methods (e.g., TRLFS in combination with factor analysis). Hence more experimental work is required to improve the understanding in this area.

5.1   Organic Polymer Degradation Products

The effect of organic polymer degradation products on the solubility of a number of key radionuclides (thorium, uranium plutonium, americium, and neptunium) has been examined as part of previous UK geological disposal research programmes (Bradshaw *et al*, 1986; 1987; Sims and Walters, 1996; Greenfield *et al*, 1997; 2000; Brownsword *et al* 1999a). These studies have focused on the effects in PCM wastes that arise in the UK (Section 2.2.9). They included studies of chemical degradation under cement buffered alkaline conditions and α and γ irradiation studies. The α irradiation studies were undertaken using reactor grade Pu, ^{238}Pu and ^{241}Am (Bradshaw *et al*, 1986; 1987) and using a particle accelerator (Sims and Walters, 1996) in order to achieve a full lifetime dose in a repository (up to 800 MGy). Some long term experiments examining the irradiation by PuO_2 within cement matrices are also reported (Greenfield *et al*, 2000). The materials examined included cellulosic materials and a number of organic polymers e.g. PVC, Hypalon™, neoprene, polystyrene, polythene, nylon.

These studies adopted an empirical approach that compared the solubility of plutonium (predominantly Pu(IV)) and uranium (IV and VI) in solutions following irradiation with control experiments in the absence of organic degradation products. The results show that cellulose degradation products complex strongly with plutonium and other radioelements, including americium, thorium and neptunium, to give increases in solubility of up to a factor of 10^5, from 10% loadings of cellulose materials in cements (Greenfield *et al*, 1997; 2000). In contrast, the degradation of other organic materials including PVC and polystyrene, increased Pu solubility to a much lesser extent (up to 1 order of magnitude) than the degradation of cellulosic materials. This was despite the presence of high concentrations of DOC (around 0.1 M) resulting from the chemical degradation of PVC and other anthropogenic polymers (Greenfield *et al*, 2000). Most of these studies were undertaken under nominal aerobic conditions, although in most cases Pu(IV) solubility is inferred. Some α-irradiation studies of organic materials were undertaken in an inert atmosphere which gave plutonium solubility values that were lower than those obtained in air (Greenfield et al, 2000). Studies included long-term α-irradiation experiments, in which organic materials were coated with plutonium oxide powder within cement blocks, at a 10% loading of organic material, stored in water at ambient temperature for around eight years (reported in Greenfield *et al*, 2000). Measurements of the solution concentrations of the plutonium leached from the cement blocks indicate that, for organic materials other than cellulose, extended α-radiolysis of organic materials and exposure to aqueous alkaline conditions did not lead to any significant increase in plutonium solubility.

Brownsword *et al* (1999b) examined the effect of organic degradation products on the sorption of plutonium and uranium. The degradation products from cellulose can decrease distribution ratios for plutonium by a factor of around 100 and for uranium (VI) by a factor of around ten. The degradation products from the majority of the anthropogenic organic polymers investigated had little effect on sorption behaviour. Degradation products from nylon cause a slight decrease in the sorption of plutonium, which may be related to the release of amines.

Studies were also undertaken to examine the effect of the chemical degradation products of ion exchange resins including DVB polystyrene materials. (Biddle *et al*, 2002; Heath and Williams, 2005). These experiments did not show any significant increase in plutonium solubility.

Overall the conclusion from these studies is that the complexation effects of chemical and radiolytic degradation of organic polymers is low compared to that observed for cellulose degradation products. Degradation of most of the more common non-cellulosic polymers is unlikely to form strong complexants. (Heath and Williams, 2005).

5.2   Bitumen degradation products

Kopajtic and van Loon (1989) reported the interaction behaviour of uranyl with the radiolytic degradation products of bitumen. The radiolytic degradation of bitumen was studied under conditions most likely occurring in the near field of a cementitious radioactive waste repository. The major bitumen degradation products in solution were monocarboxylic acids (acetic acid, acetylacetic acid, formic acid, myristic acid, stearic acid), dicarboxylic acids (oxalic acid, phthalic acid) and carbonates. In general 1:1 complexes with UO_2^{2+}, with log K values of 6.1 were measured at an ionic strength of 0.1 M in bitumen water. The experimental technique used was an ion exchange method. The bitumen degradation product oxalate was identified to have the highest potential to form stable complexes with uranyl.

The complexation studies with oxalate and bitumen waters were performed at pH 5. As a result, at pH values ≤ 7 uranyl complexes with the carboxylic acids dominate. However at higher pH their influence decreased with increasing influence of ternary carbonate and hydroxide ion complexation. The possibility of ternary species involving the carboxylic acids was not discussed. Therefore, more experimental studies to bridge the gap between slightly acidic pH values and alkaline pH values should be conducted. The authors conclude that the radionuclide speciation in the near field of a cementitious repository should be less influenced by bitumen degradation products. The picture is different in the far field, where lower pH values dominate. Under such conditions, an increased influence of bitumen degradation products on the actinide/lanthanide speciation could occur.

5.3   Oxalic acid
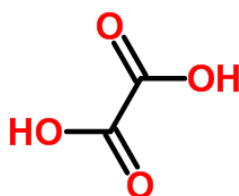
Figure 32 Oxalic acid

As noted previously, oxalic acid (Figure 32) is a radiolytic product of bitumen under oxidizing conditions and has also been reported from irradiation of ion exchange resins (Section 4.1.1). The oxalate ligand is used in process and separation strategies for recovery of radionuclides (e.g. Pu) by oxalate precipitation because of their low solubility in acidic solutions (Wick *et al* 1980). Consequently, oxalate –radionuclide complexation is quite well documented in the literature.

Hummel *et al* (2005) have reviewed in detail the thermodynamics of oxalate (ox) radionuclide complexation and recommend data for the following aqueous complexes: Ni(ox)(aq), Ni(ox)$_2$$^{2-}$, Am(ox)$^+$, Am(ox)$_2$$^-$, Am(ox)$_3$$^{3-}$, NpO$_2ox^-$, NpO$_2(ox)_2$$^{3-}$, UO$_2$ox(aq), UO$_2(ox)_2$$^{2-}$, UO$_2(ox)_3$$^{4-}$. Hummel *et al* also define solubility products for uranyl oxalate solids and further data for aqueous and solid Ca, Mg oxalates and solubility and dissociation constants for oxalic acid. Hummel *et al* provide an extensive

compilation of literature concerning plutonium oxalate solid phases and aqueous species for the main Pu oxidation states. However Hummel *et al* do not recommend any thermodynamic data for Pu oxalate complexation from their critical review of these studies and experimental data.

In a recent study Brunel *et al* (2015) reported results on the complexation of various actinides (U(VI), Np(V), Pu(V), and Am(III)) with oxalate investigated by capillary electrophoresis (ICPMS detection) in 0.1 M NaClO$_4$ at various temperatures (15, 25, 35, 45 and 55 °C). The formation of 1:1, 1:2 and 1:3 complexes for U(VI) and Am(III); the formation of the 1:1 and 1:2 complexes for Np(V) and the formation of only 1 complex for Pu(V) could be confirmed. The corresponding stability constants are reported. The extrapolation to infinite dilution was done using the specific ion interaction theory (SIT).

For the first time, Günther *et al* (2011) investigated the interaction of uranyl with oxalic acid using time-resolved laser-induced fluorescence spectroscopy (TRLFS) at pH 2 and 4. By using cryo-TRLFS, emission signals of the various complex species were detected. The spectroscopic data obtained were used to calculate the corresponding complex stability constants applying factor analysis software.

Several works described the interaction mechanisms of Np with oxalic acid using a combination of X-ray diffraction (for solids), Vis/NIR and IR spectrocopy (Bean *et al* 2004, Andreev *et al* 2008, Arab-Chapelet *et al* 2008).

Thakur and Van Luik (2014) studied the complex formation of NpO$_2^+$ with a wide range of organic ligands, including oxalate. The results obtained indicated the formation of only the 1:1 NpO$_2^+$/complex with the ligands studied. However, Rao and Tian (2010) did observe both 1:1 and 1:2 Np(V) complexes with oxalate. It was found that NpO$_2^+$ is coordinated to this ligand in a monodentate, bidentate, and/or bridging mode via its equatorial plane.

Tian and Rao (2012) determined the thermodynamic parameters including the equilibrium constants and enthalpy of complexation of Np(V) with oxalate at variable temperatures ranging from 283K to 343 K using a combination of spectrophotometric and microcalorimetric titrations. Thermodynamic data (stability constants, enthalpy and entropy complexation) must be determined in order to predict the fate and behavior of Np(V) in the repository and surrounding environment. The results indicate that the complexation of Np(V) with oxalate is moderately strong and becomes weaker at higher temperatures. The authors related the effect of temperature on the complexation in terms of the energetics of ion solvation and hydrogen bonding involved in the complexation.

Bean *et al* (2004) investigated the interaction of Np(V) with oxalic acid in the presence of calcium chloride and sodium hydroxide under hydrothermal conditions and at pH 12. CaCl$_2$.2H$_2$O was added as a reactant due to its implication in oxalate precipitation conditions for processing Pu solutions. Under these alkaline conditions, brilliant green hexagonal hexagonal-shaped single crystals of Np(V) oxalate, Na$_2$NpO$_2$(C$_2$O$_4$)OH.H$_2$O, were produced. It was the first Np(V) oxalate produced under alkaline conditions.

Studies of europium sorption onto α-alumina (Alliot, *et al*, 2006) observed that both oxalate and acetate reduced sorption, with a greater effect for oxalate. The authors found evidence for a synergistic sorption mechanism of cationic europium-ligand complexes onto alumina. 1:1, 1:2 and 1:3 complexes were reported for both ligands, with stability constants ranging from logK = 5.7 to 12.45 for oxalate.

The application of cryo-TRLFS would be very helpful for a complete understanding of the spectroscopic properties of the uranyl-oxalato species by extending the existing TRLFS data sets (pH 2 to 4) up to pH 6 and higher.

Hummel *et al* (2005) in their review of oxalate complexation note there is very little information in the literature concerning the compounds and aqueous complexes of technetium, although a few solid phases have been identified. Xia *et al* (2006) have however determined the stability constants of Tc(IV) oxalate complexes as a function of ionic strength (NaCl solutions ranging in concentration from 0.5 and 2 M).

Technetium complexation with oxalate has also been examined in the context of the Purex process. Seifert *et al* (1992) reported the preparation, characterisation and crystal structure of a mixed ligand complex of Tc with DPPE and oxalic acid: oxalate-bis(1,2-bis(diphenylphosphino)ethane)technetium(II). Under these conditions, the reduction of pertechnetate leads to the formation of a mixed ligand complex with DPPE and oxalic acid. The crystal structure of the paramagnetic oxalate-bis(1,2-bis(diphenylphosphino)ethan)technetium(II) was determined. In this complex, oxalic acid is coordinated to Tc in a bidendate binding mode. Melentev *et al* (2011) studied the effect of oxalic acid on the extraction-chemical behaviour of Tc, as applied to the reductive splitting of U and Pu in the system TBP-$N_2H_5NO_3$-HNO_3 within the framework of the purex process. The results obtained indicated that oxalic acid added to the Tc- $N_2H_5NO_3$-HNO_3 system exerts a stronger protective effect on the both the reduced Tc and hydrazine ($N_2H_5NO_3$). The reduction of Tc and the decomposition of $N_2H_5NO_3$ were both decelerated in the presence of oxalic acid: The oxidation of the reduced Tc either is insignificant or is not observed at all.
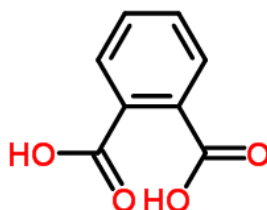
5.4   Phthalic acid

Figure 33 Phthalic acid

As discussed in Section 4.2 phthalic acid (Figure 33) is a degradation product of plasticisers used in PVC materials. Vazquez *et al* (2008) showed that phthalates can form soluble stable complexes with uranium. Potentiometric titrations confirmed the formation of a 1:1 U/phthalic acid complex where one uranyl ion is bonded to both carboxylate groups of phthalic acid. ESI-MS analysis revealed the formation of both 1:1 and 1:2 U/phthalic acid complexes. EXAFS studies confirmed the mononuclear bi-ligand 1:2 U/phthalic acid complex as the predominant form. On the basis of the potentiometric titrations the stability constant (log K) for the 1:1 complex was calculated to be 4.81 (0.1 M $NaClO_4$).

Further work (Vazquez *et al*, 2009) confirmed the predominance of the 1:2 complex and investigated the effects of biotransformation by *Clostridium* sp. In the absence of phthalate, the uranyl was reduced to U(IV), which precipitated. However, the U(VI)/phthalate complex underwent bioreduction to U(IV)-phthalate, which remained in solution as a polymeric colloid. This indicates that phthalate can cause U(IV) to remain in solution and not precipitate, which is contrary to its usual behaviour. The persistence of U(IV) in solution when complexed could have implications for migration.

The interaction of phthalic acid and Cm(III) by application of the direct speciation technique, TRLFS were investigated by Panak *et al* (1995). Based on the peak de-convolution of the emission data, it could be concluded that phthalic acid forms a moderately strong 1:1 complex with Cm(III), log $\text{ß}_{1:1}$ = 3.62 (0.1 M NaClO$_4$). The spectroscopic properties of the complexed Cm(III) species (excitation, emission and lifetime) are reported.

Jain *et al* (2009) explored the complexation of Eu(III) with phthalic acid (amongst other ligands) by TRLFS. The emission spectra were recorded in the range of 550 and 650 nm. The experiments were carried out at varying ratios of ligand to metal ion concentration. The ratio of the intensities of the 616 and 592 nm peaks was used to determine the corresponding stability constants. For the model compounds including phthalic acid, the luminescence lifetime was found to increase with increasing ligand to metal ratio indicating the decrease in quenching of the luminescence by coordinated water molecules with increasing complexation. Eu(III) forms 1:1 and 1:2 complexes with the model ligands. For phthalic acid the following stability constants were reported: $\log\text{ß}_1$ = 3.7 ± 0.3 and $\log\text{ß}_2$ = 5.8 ± 0.3 (I=0.1M NaClO$_4$).

Zhou et al (2004) synthesized europium complexes with aromatic acids, including phthalic acid, and studied their composition by elemental analyses. Results concerning the UV spectra, the IR characteristics and the luminescence properties are also reported. With phthalic acid, a compound having the following stoichiometry was synthesized: (Eu)$_2$(o-Phth)$_3$·3H$_2$O.

Further studies could explore the spectroscopic properties of the U/phthalic acid complexes using absorption spectroscopy, TRLFS and ATR-FTIR. This spectroscopic approach could help to determine the stability constant of the 1:2 complex, which is still missing.

5.5 Monocarboxylic acids

The simple carboxylic acids (C1 to C4) are reported as degradation products of bitumen and are likely to be a common radiolytic product of organic polymers. These carboxylic acids are likely to be readily consumed by microbiological processes, where they can act as an electron donor. However, in the absence of strong electron acceptors (e.g. nitrate, Fe(III), sulfate), higher carbon number carboxylic acids may also form by fermentation processes. It is thus feasible that concentrations of these simple carboxylic acids could be preserved under strongly reducing conditions and this may warrant further study of their complexation properties. In general though, these monodentate ligands will form weaker complexes than the bidentate oxalate and phthalate species. There is evidence that the bioreduction/biodegradation of metal-organic complexes is affected by the metal and the ligand. Ganesh *et al* (1997) report that reduction of U(VI) complexed by organic ligands (acetate, oxalate, malonate, citrate) by sulfate and Fe(III) reducing bacteria varies by species, with some preferentially consuming simple monocarboxylic acid complexed U, while a *Shewanella* sp preferentially consumed multidentate complexes rather than monodentate acetate. Further studies (Francis, 2003; Renalla *et al,* 2004) indicate that certain metal complexes are more resistant to biodegradation. Study of the complexation of radionuclides and other major elements (Fe, Ca, Mg) and heavy metals present in ILW with monocarboxylic acids is therefore relevant to understanding how these major degradation products may be metabolised.
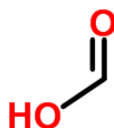
5.5.1 Formic acid

Figure 34 Formic acid

Lucks *et al* (2013) summarised the current knowledge of complex formation between uranyl(VI) and formic acid (Figure 34). Infrared absorption (IR), EXAFS and DFT calculations were applied for a structural and photochemical characterisation. The formate ion binds to uranyl(VI) in a unidentate fashion. The investigations were performed in aqueous solution within a pH range of 0 to 4.5 at relatively high uranyl concentrations of 0.05 M (1 M formic acid). In the uranyl formate system, 1:1, 1:2 and 1:3 species are known.

Wei *et al* (1999) reported results developing a rapid elution method of tetravalent plutonium from anion exchanger for purification. In concentrated nitric acid solution, Pu(IV) forms anionic nitrate-complexes which adsorb onto anion exchangers. Using formic acid as eluent, a rapid elution of Pu(IV) was observed. The authors stated that formate has negligibly weak complex-forming ability with Pu(IV) and cannot form anionic Pu(IV) complexes. However, formic acid must be strong enough to provoke the dissociation of Pu(IV) nitrato-complexes.

Further experiments could focus on the TRLFS characterization of the complexes at low uranyl concentrations and at a higher pH range.
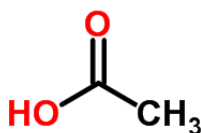
5.5.2 Acetic acid

Figure 35 Acetic acid

Meinrath *et al* (2014) characterised the uranyl complex formed with acetic acid (Figure 35) at high uranyl concentrations (≥ 1mM) between pH 1.9 and 3.4 using conventional UV-vis spectroscopy. They characterized the 1:1 complex in terms of the single component spectrum, the extinction coefficient and the corresponding stability constant (log $\beta_{1:1}$ = 2.8±0.3). The absorption spectra were evaluated using a factor analysis procedure.

Sladkov (2014a) investigated the U(VI)-acetic acid system in aqueous solution at pH 2 in the temperature range from 15 to 55 °C by affinity capillary electrophoresis (ACE). The ionic strength was fixed at 0.05 M (NaClO$_4$-HClO$_4$). The formation of two complex species, $UO_2CH_3COO^+$ and $UO_2(CH_3COO)_2$, was observed. A review of the interaction of uranyl with acetic acid at room temperature was published by Sladkov (2013). The focus was again on the application of ACE at pH 2.0 and 2.5.

The aqueous U(VI) complexes with acetic and succinic acid, their speciation and structure were revisited by Lucks *et al* (2012). DFT calculations, UV-vis spectroscopy, ATR-FTIR analysed with iterative transformation factor analysis (ITFA) was employed to determine the structures and the pH-speciation of aqueous acetate U(VI) complexes. A relatively high uranyl concentration of 0.05 M was

used. The acetate concentration was 1 M and a pH range of 0.86 to 3.77 was covered. The 1:1, 1:2 and 1:3 complex could be characterised. In contrast, the EXAFS data resulted in only 3 different components (including the free uranyl ion). The 1:1 and the 1:3 complex could be isolated directly whereas the 1:2 complex was only reproducible by a linear combination of the spectra of the 1:1 and 1:3 complexes.

In a recent study TRLFS was used to study uranyl speciation in an acetate solution (Sladkov, 2014b). The uranyl concentration was 1×10^{-4} M and the acetic acid concentration was varied between 0 and 0.6 M at pH-values of 1.5, 2.0 and 2.5 in perchloric acid. Under these conditions the acetate ion was responsible for the quenching (static and dynamic quenching) of the uranyl luminescence. Hence the 1:1 complex ($UO_2CH_3COO^+$) emits no luminescence light at room temperature. The authors found an indication that the 1:2 complex might emit luminescence light. At an ionic strength of 0.1 M the stability constant of the 1:1 complex was calculated to be 2.67 ± 0.15. Using the SIT theory the stability constant was extrapolated to infinite dilution log $\beta_{1:1}$ = 2.95 ± 0.08.

Pu(IV) in aqueous acetic acid solutions exhibits irreversible polymerisation to form colloidal aggregates (Alei *et al*, 1967). UV-vis-NIR spectra of plutonium (+3, +4, +6) in pure acetic acid and in 0.5 M $HClO_4$-AcOH solution are reported and discussed. However no information is given concerning soluble aqueous plutonium acetate complexes.

Grenthe (1963) investigated curium acetate complexes by using a special cation-exchange method. Two Cm(III) acetate species were identified and the corresponding stability constants were calculated (log β_1 = 2.06 and log β_2 = 3.1) at an ionic strength of 0.5 M $NaClO_4$.

In Plancque *et al* (2005) ESI-MS and TRLFS have been used to obtain stoichiometries and complexation constants between acetic, glycolic and 4-hydroxyphenylacetic acids and europium(III). Also in this paper is a brief overview on different techniques used to extract Eu(III) stability constants with acetic acid, which are spectrophotometry, ion exchange, and electrochemistry. Using TRLFS the 1:1 complex of Eu(III) with acetate was observed having a stability constant log β_1 of 2.2 (I=0.1 M). However, with ESI-MS, 1:1, 1:2 and 1:3 complexes of Eu(III) with acetate were found with stability constants log β of 2.8, 5.9 and 8.0, respectively (I=10^{-3}M).

Potentiometric and micro-calorimetric titration techniques were applied (Kitano *et al*, 2006) to determine the thermodynamic quantities including the stability constants between Eu(III) and carboxylic acids (acetic, glycolic, malonic and malic acids). At 1 M $NaClO_4$ the stability constants of the 1:1, 1:2 and 1:3 complexes of Eu(III) with acetate were calculated to be 1.97, 3.38, and 3.98, respectively. The investigated complexation is mainly entropy driven. TRLFS was used to support the discussion of the thermodynamic quantities by measuring the hydration numbers of Eu(III) in the complexes after excitation at 394 nm. A confirmation of, for instance, the stability constants by applying the direct speciation technique TRLFS was not performed. Spectroscopic properties of the formed species besides the lifetimes were not reported.

In another study (Alliot, *et al*, 2006) the effect of acetic and oxalic acids on the adsorption of europium onto α-alumina was investigated. Decreased sorption of Eu(III) onto alumina was observed with increasing concentrations of the ligands, with the effect of acetate less than that of oxalate. Stability constants of the complexes were determined and in both cases the 1:1, 1:2 and 1:3 complexes were reported with stability constants ranging from 1.75 to 5.5 for acetate.

Further studies should focus on TRLFS measurements at low temperatures to measure the luminescence emission of at best all U(VI)-acetato-complexes (cryo TRLFS), TRLFS experiments at higher pH and acetate concentrations, and on characterization of the luminescence emission of acetate by application of femto-TRLFS.
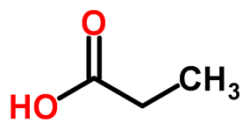
5.5.3 Propionic acid

Figure 36 Propionic acid

Kirishima *et al* (2007) determined the thermodynamic quantities of uranium(VI)-carboxylate complexes, including those of formate, acetate, glycolate, and propionate (Figure 36) by potentiometric and microcalorimetric titrations. The experiments were performed in the uranyl concentration range of 1 to 5 mM with ligand concentrations between 0.05 and 0.4 M in 1 M NaClO$_4$ at 25 °C. The stability constants of the 1:1 and the 1:2 complexes between uranyl and propionate are reported. The structures of the formed species are not discussed in detail.

There are ongoing studies by HZDR/IRE on the complexation of uranyl with propionic acid by a combination of continuous wave (CW) laser spectroscopy, UV-vis spectroscopy, TRLFS, ATR-FTIR with parallel factor (PARAFAC) analyses of the spectral data including density functional theory (DFT) calculations (Schmeide *et al*, 2015). The focus was also to extend the database to higher ionic strength. The experimental parameters were: [U(VI)] 5×10^{-4} M, [Prop] 0.005 to 0.5 M, I$_m$ = 0.75 to 4 M (NaClO$_4$/NaCl) and [H$^+$] 1.3×10^{-4} M. 1:1, 1:2 and 1:3 complexes of uranyl with propionic acid could be isolated and the log ß values were calculated. These studies are currently ongoing.

Free-energy, enthalpy (measured calorimetrically) and entropy changes from the formation of europium(III) complexes from propionate and other ligands at an ionic strength of 2 M (NaClO$_4$) are reported by Aziz *et al* (1971). For the propionate system, the equilibrium constants were studied potentiometrically. The formation of three Eu(III)-propionate species was observed, presumably with the stoichiometry 1:1, 1:2, and 1:3. However, the values of the stability constants were not reported.

5.5.4 Butyric acid
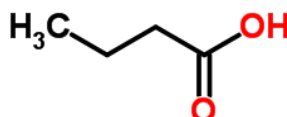
Figure 37 Butyric acid

The knowledge concerning the complexation of uranyl with butyric acid (Figure 37) in aqueous solution is very limited. Ramamoorthy *et al* (1969) reported a first insight in the system by applying potentiometric titrations. The measurements were performed in 0.1 M NaClO$_4$ at [U(VI)] 0.005 M and [HBut] 0.05 M within a pH range of 1.5 to 3.5. Two complex species were determined with the corresponding stability constants log ß$_{1:1}$ = 2.91 and log ß$_{1:2}$ = 4.53. Possible further work studying this system is the validation of the results with another technique and the application of

spectroscopic techniques (UV-vis, TRLFS, ATR-FTIR, NMR, EXAFS) in combination with DFT calculations.

Recently, Skerencak-Frech *et al* (2015) presented results on the complexation of trivalent actinides (Cm, Am) and lanthanides (Nd) with clay-organic ligands at T = 20 − 90 °C. The authors investigated the thermodynamics and structure of complexes of Cm(III) and Am(III) with different small clay-organic ligands (formate, acetate, propionate, lactate, oxalate) by TRLFS, EXAFS and quantum-chemical calculations. The conditional stability constants of the different Cm(III) ligand complexes were determined as a function of the ligand concentration and the ionic strength (I = 0.5 − 4.0 with $NaClO_4$, NaCl and $CaCl_2$). The results showed that all simple carboxylic ligands, which lack a functional group in the α-position (formate, acetate, propionate), coordinated in a bidentate mode via the two oxygen atoms to the metal ion ("end-on").

However, the knowledge is still scarce concerning direct speciation studies exploring the complexation of Cm(III) with other small organic ligands (for instance butyric acid). Therefore more experiments are needed to bridge this identified gap, especially with butyric acid.

5.6   Amines

Amines (ammonia, methylamine, dimethylamine, trimethylamine) are degradation products of organic ion exchange resins and may be released from the resin structure as a result of thermal or radiolytic degradation. Amines may be subject to biodegradation, acting as an electron donor.

Ammonia forms strong complexes with soft cations such as Ni, Cu, Ag, Hg, and Pd. The affinity to hard cations such as Ca, Mg, and actinides is relatively weak. Ammonia and methylamine show nearly the same affinity towards complex formation. The stabilities of the bulkier amine complexes decrease significantly with increasing numbers of methyl groups. The stability constants show the following relation: ammonia ≈ methylamine > dimethylamine > trimethylamine. In the study of Van Loon and Hummel (1999) only the metals Ni, Ag, and Pd were considered. There were no investigations with actinides or lanthanides.

Wang *et al* (2007,2008) undertook experiments and calculations with Th and U reacting with NH_3 affected by laser-ablation in excess argon. But these reactions are not relevant for considerations concerning repository conditions. Otherwise, it is hard to find stability constants or parameters for ammonia and methylamine-actinide complexes. This is possibly due to the fact that complexes with a hard actinide central-atom and nitrogen-containing ligands are very weak (e.g., compared to hydroxide- or carbonate species). Nevertheless it would be interesting to investigate the impact of NH_3 (and methylamine) on the speciation of actinides at higher pH regions, where NH_3 is not protonated.

5.7   Complexation Summary

Compared to alkaline cellulose degradation products (e.g. ISA) the degradation products of anthropogenic organic materials such as bitumen, ion exchange resins and PVC are weaker complexants. Experimental studies that adopt an empirical approach that compare the solubility and sorption of radionuclides in the presence or absence of degradation products indicate only moderate (generally within one order of magnitude) increases in solubility or reduction in sorption distribution coefficient in the presence of chemical and radiolytic degradation products of PVC and polystyrene resin materials. Such studies are however complicated and difficult to interpret without more

fundamental understanding of the complexation processes. The soluble organics formed by chemical and radiolytic degradation of these polymers and bitumen are only partially characterised.

The most significant complexants identified to date are di-carboxylic acids such as oxalate and phthalate, which can act as strong bi-dentate ligands. Phthalate is recognised as being of significance forming by hydrolysis of PVC plasticisers that can be leached from the PVC polymer materials. However, little is known about the interaction of actinides and lanthanides with degradation products of plasticised PVC. On the one hand, there are no degradation products from the PVC polymer itself having the potential to be a complexant and on the other hand the degradation products of plasticisers (with the exception of phthalate) are quite insoluble in water, which is a challenge for speciation studies. A further interesting point, which should be investigated, is the interaction of actinides and lanthanides with un-degraded or partially degraded, plasticised PVC.

Oxalate is a well-known radiolysis product of organic polymers and bitumen, formed by the reaction of carboxyl radicals. However, oxalate is typically formed under oxidising conditions and so it may mainly be formed during storage of ILW when exposed to aerobic conditions.

Amines released from ion-exchange resins may also act as effective complexants for radionuclides. Current studies of amine complexation are focused on mono and divalent metals (e.g Ni^{2+}) and there is scope to examine interactions with lanthanides and actinides.

Monocarboxylic acids (formic, acetic, propionic, butyric) are expected to form following chemical and radiolytic degradation of polymers and may also be generated or modified by subsequent fermentation processes. These simple organic acids will be less significant in terms of their effect on radionuclide complexation, however their complexation with other metals present in the ILW system such as Fe, Ca and Mg could affect how these electron donors are metabolised. However, the influence of less investigated monocarboxylic acids (e.g., butyric acid) on their potential to change the radionuclide speciation will be investigated using a range of direct speciation techniques including UV-vis, TRLFS, IR, XAS, and NMR.

Subsequent complexation studies within the MIND project will be driven by the IC and GC-MS analyses of the chemical and radiolytic degradation products of PVC, ion exchange resins and current knowledge concerning bitumen degradation (Section 4.3.1). Complexation studies will also be linked to the cellulose degradation studies within the MIND project and will examine a) the radionuclide speciation with model compounds, in the supernatant and on the biomass by different spectroscopic techniques (e.g., UV-vis, TRLFS, IR, and XAS) and b) the solid phase complexation of biomass materials from the biodegradation experiments using a range of techniques available, including STEM/HAADF, element mapping, EELS, FESEM and ESM.

6   Summary and Outlook

Work Package 1 of the MIND project addresses remaining key issues for the geological disposal of ILW concerning the long-term behaviour, fate and consequences of organic materials in the waste along with H_2 generated by corrosion and radiolysis. This review begins this work by collating information concerning the inventory and nature of organic materials present in ILW and some LLW that requires geological disposal. The review has then considered the physical and chemical conditions that the organic materials will be subjected to during storage and geological disposal. Using this information, the experimental work within Work Package 1 will be targeted on the most

relevant organic materials and conditions. The review then provides a summary description of the physical and chemical nature of the main organic materials present in ILW and their known chemical and radiolytic degradation behaviour. The effect of the organic degradation products on radionuclide speciation, which could affect how some radionuclides are transported in groundwater, is then considered to focus subsequent work in this field.

Inventory information concerning the distribution of the different types of organic material present in ILW and some LLW is collated from published sources. The information includes inventories of current near surface repositories (SFR repository (Sweden), VLJ repository (Finland) and repositories in the Czech Republic) as well inventories of countries which are at various stages of planning for deep geological disposal of ILW (Belgium, France, Spain, Switzerland, The Netherlands, UK). A wide range of organic materials are present in ILW and LLW requiring geological disposal, including:

- Bitumen, used to condition and encapsulate ILW in most countries

- Organic ion exchange resins

- Halogenated polymers (mainly comprising PVC, but including other Cl containing polymers and fluorinated polymers)

- Non-halogenated polymers (e.g. polyethylene, polypropylene)

- Cellulose materials

- Other polymers (including rubber, polyurethane, polyamides, nylon, epoxy resins)

The proportion of these materials varies between countries depending on the nuclear power generation, industry and research activities. Ion exchange resins form a high proportion of the inventory of countries with light water reactors, while larger quantities of mixed polymeric wastes and cellulose wastes arise in France and the UK from reprocessing and research.

The review has confirmed that bitumen, organic ion exchange resins and halogenated polymers (PVC) are present in significant amounts in the national inventories. These three main organic materials were selected when the proposal for the MIND project was developed, taking account of the views of waste management organisations. In addition, further work will be undertaken within MIND on cellulose, given its importance compared to other organic materials due to the strong radionuclide complexation effects of its hydrolysis products formed under alkaline (cementitious) conditions. It should be noted that due to the more established knowledge and existing reviews cellulose has not been considered in detail by this review.

Bitumen, resins and PVC together with cellulose provide a major source of organic carbon that has the potential, following initial chemical and radiolytic degradation, to fuel anaerobic microbial processes including methane gas generation in a geological repository, but which may also consume H_2 gas (e.g. from corrosion) and biodegrade organic complexants. The three anthropogenic organic materials selected for study are of differing physical and chemical nature and structure and their degradation will involve a range of different processes e.g.

- Ion exchange resins are comprised of an aromatic (polystyrene) structure with attached functional sulfonyl or amine groups. The functional groups being released more easily leaving the aromatic structure that will be more resistant to radiolysis and biodegradation. Released

sulfate and amines (NH_3, NH_2CH_3, $NH(CH_3)_2$, $N(CH_3)_3$) provide potential energy sources for microbial activity including methanogenesis in the case of the amines.

- The PVC polymer is aliphatic and may be less resistant to radiolysis than resins and its radiolysis products might be more readily biodegraded. Radiolysis of PVC will liberate the strong acid HCl, which may be significant to pH buffering. PVC materials commonly include a variety of organic additives, such as plasticisers, which are not bound to the polymer and so may be easily leached and biodegraded.
- Bitumen degradation will firstly involve the diffusion of water into the complex mixture of aromatic and aliphatic compounds, with the leaching of a water soluble fraction. Complex radiolytic interactions will occur in the original and partially hydrated bitumen. Biodegradation is more likely to occur at the bitumen-water interface.

The degradation products of the three anthropogenic organic materials studied by MIND also have the potential to complex with radionuclides and affect radionuclide sorption and solubility. However, previous work examining the presence or absence of chemical and radiolytic degradation products on radionuclide solubility and sorption suggests that they are weaker than ISA and other cellulose degradation products formed by alkaline hydrolysis. Oxalate and phthalate are perhaps the most significant degradation products identified in terms of their potential to form metal complexes. Oxalate is a radiolysis product generally formed under oxidising conditions, while phthalate results from hydrolysis of plasticisers used in PVC materials. Amines released from basic ion exchange resins may also act as complexants. Simple monocarboxylic acids (e.g. formic, acetic, propionic, butyric) are also likely to form by radiolytic degradation of the organic polymers and may also form by microbial fermentation processes. These soluble species form weaker metal complexes and have less potential to significantly enhance radionuclide mobility. Complexation of the species by Fe, Ca and Mg and other metals present in ILW may however influence their utilisation by microbial processes.

Reviews of the inventory information from a range of European countries, including details of waste conditioning, waste packaging and design concepts for the geological disposal of ILW have been used to consider the range of physical and chemical conditions to which the organic ILW will be exposed. Considering the half-lives of radionuclides typically present in organic ILW, radiolytic degradation of organic ILW is likely to occur during storage and the first 1,000 years of disposal. Over this timescale organic wastes are likely to be subjected to a total adsorbed dose of the order of 1 MGy although this total dose and time period will be subject to considerable uncertainty. A 1 MGy dose would be achieved at an average dose rate of around 0.1 Gy h^{-1} over 1,000 years. Microbial activity is likely to be viable at this dose rate as shown by studies in the literature. Of course to achieve a total adsorbed dose of 1 MGy in the laboratory will require the use of higher dose rates (e.g. 10 kGy h^{-1}), which will sterilise the organic materials, so products from radiolysis experiments will require inoculation by relevant microbes.

Over such a nominal 1,000 year period the repository will, depending on the host rock, begin to or completely saturate with groundwater. Some ILW waste containers may begin to corrode allowing groundwater to begin the leaching of cementitious encapsulants and backfill. Radiolytic degradation of the organic ILW is also likely to generate acidity that may neutralise the alkaline pH of the cementitious encapsulants used. A range of pH conditions from neutral, representing accumulations of organic-rich waste, to strongly alkaline (pH 12.5) buffered by $Ca(OH)_2$ (Stage II cement leaching) are therefore relevant to the irradiation and biodegradation experiments that will be performed. Anaerobic conditions are likely to prevail in organic containing ILW both during storage and disposal.

Under these conditions sulfate present in wastes and in groundwater will be an important electron acceptor. For bituminised wastes nitrate will also provide a strong electron acceptor for microbial processes reacting with organic degradation products, as well as H_2 generated by radiolysis and by anaerobic corrosion of metals. In the absence of sulfate or nitrate, fermentation and methanogenesis conditions are predicted to develop, which is important in regard to gas generation from ILW.

In the next phase of the MIND project, ion exchange resin, PVC, bitumen and cellulose materials will be irradiated using ^{60}Co γ radiation at a range of dose rates up to around 10 kGy h^{-1}, to give a total adsorbed dose of up to 1 MGy. These first irradiation experiments will be undertaken under a range of pH conditions with air and inert gas headspace. The aim of these experiments will be to represent storage and disposal conditions and ensure that sufficient soluble organic material is produced in order to characterise the compounds present (using GC-MS and IC) and to use the leachate in subsequent biodegradation experiments. Subsequently, depending on the outcome of the first experiments, irradiation studies may be undertaken at lower dose rates and/or durations to give lower total adsorbed doses (around 1 kGy).

The biodegradation experiments will be inoculated by various cultures, including consortia adapted to high pH conditions and indigenous microbes sampled from underground rock laboratories. The biodegradation experiments will consider the main anaerobic electron acceptors (nitrate, Fe(III), sulfate) depending on the waste material. For instance, nitrate will be a focus of the bitumen degradation experiments, while the resin studies will focus on sulfate present in the resins and in groundwater. In the case of bitumen and PVC studies, biodegradation experiments will be undertaken on known degradation or leachable products, such oxalate and phthalates. The biodegradation studies will also explore the process of methane generation under cement buffered ILW conditions. The bioreduction of multivalent radionuclides such as Tc, Se, U, Np and Pu by the organic degradation products will also be studied. The soluble organic species will be characterised before and after biodegradation to identify compounds for complexation studies and to draw conclusions regarding the degradation of known complexants such as the cellulose degradation product ISA. The solid residues and biomass materials will also be utilised for microscopy studies including interactions with radionuclides.

The information collated in this review is of prime importance to the design of experimental work undertaken in Task 1.2 of Work Package 1 of the MIND project. The review will also provide a basis of Task 1.3 that examines processes under *in situ* waste form and repository conditions and modelling and integration of WP 1 in Task 1.4 and wider integration and dissemination through MIND Work Package 3.

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