Radioactive Waste Management

Geological Disposal:

Guidance on the use of organic polymers for the packaging of low heat generating wastes

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WASTE PACKAGE SPECIFICATION AND GUIDANCE DOCUMENTATION
WPS/901 GUIDANCE ON THE USE OF ORGANIC POLYMERS FOR THE PACKAGING OF LOW HEAT GENERATING WASTE

Executive Summary

This document forms part of the Waste Package Specification and Guidance Documentation (WPSGD), a suite of documents prepared and issued by Radioactive Waste Management Ltd (RWM). The WPSGD is intended to provide a 'user-level' interpretation of the RWM packaging specifications, and other aspects of geological disposal, to assist UK waste packagers in the development of plans for the packaging of higher activity waste in a manner suitable for geological disposal.

Key documents in the WPSGD are the *Waste Package Specifications* (WPS) which define the requirements for the transport and geological disposal of waste packages manufactured using standardised designs of waste container. The WPS are based on the high level requirements for all waste packages as defined by the *Generic Waste Package Specification* (GWPS) and are derived from the bounding requirements for waste packages containing a specific category of waste, as defined by the relevant *Generic Specification*.

This document provides guidance on the potential use of organic polymers for the packaging of ILW, and other low heat generating wastes, in such a form as to render them suitable for geological disposal.

The WPSGD is subject to periodic enhancement and revision. Users should refer to RWM website to confirm that they are in possession of the latest version of any documentation used.

WPSGD DOCUMENT NUMBER WPS/901 - VERSION HISTORY		
VERSION	**DATE**	**COMMENTS**
WPS/901	December 2005	Based on Nirex PGRC and Nirex Report No. N/104
WPS/901/02	March 2015	Based on 2010 DSSC and NDA Report No. NDA/RWMD/068.

List of Contents

Abbreviations and acronyms used in this document

ALARP	as low as reasonably practicable
DSSC	Disposal System Safety Case
DSTS	Disposal System Technical Specification
EBS	engineered barrier system
GDF	geological disposal facility
GWPS	Generic Waste Package Specification
IAEA	International Atomic Energy Agency
ILW	intermediate level waste
LHGW	low heat generating waste
LLW	low level waste
LoC	Letter of Compliance
MRWS	Managing Radioactive Waste Safely
NDA	Nuclear Decommissioning Authority
ONR	Office for Nuclear Regulation
RWM	Radioactive Waste Management Limited
SCRU	submersible caesium removal units
VES	vinyl ester styrene
WAC	waste acceptance criteria
WPS	Waste Package Specification
WPSGD	Waste Package Specification and Guidance Documentation

1   Introduction

The Nuclear Decommissioning Authority (NDA), through Radioactive Waste Management Ltd (RWM), is responsible for implementing UK Government policy for long-term management of higher activity radioactive wastes, as set out in the *Implementing Geological Disposal* White Paper [1]. The White Paper outlines a framework for managing higher activity radioactive waste in the long term through geological disposal, which will be implemented alongside the ongoing interim storage of waste packages and supporting research.

RWM produce packaging specifications as a means of providing a baseline against which the suitability of plans to package higher activity waste for geological disposal can be assessed. In this way RWM assist the holders of radioactive waste in the development and implementation of such plans, by defining the requirements for waste packages which would be compatible with the anticipated needs for transport to and disposal in a geological disposal facility (GDF).

The packaging specifications form a hierarchy which comprises three levels:

- The *Generic Waste Package Specification* (GWPS) [2]; which defines the requirements for all waste packages which are destined for geological disposal;

- *Generic Specifications;* which apply the high-level packaging requirements defined by the GWPS to waste packages containing a specific type of waste; and

- *Waste Package Specifications* (WPS); which apply the general requirements defined by a Generic Specification to waste packages manufactured using standardised designs of waste container.

As a means of making the full range of RWM packaging specifications available to waste producers and other stakeholders, a suite of documentation known as the Waste Package Specification and Guidance Documentation (WPSGD) is published and maintained for ready access via the RWM website.

The WPSGD includes a range of WPS for different waste package types together with explanatory material and guidance that users will find helpful when it comes to application of the WPS to practical packaging projects. For further information on the extent and the role of the WPSGD, reference should be made to the *Introduction to the RWM Waste Package Specification and Guidance Documentation* [3].

The requirements for waste packages containing intermediate waste (ILW), and wastes with similar radiological properties, are defined by the *Generic specification for waste packages containing low heat generating waste* [4]. These requirements are applied to the waste packages that can be manufactured using the current range of standardised waste containers (as identified in the *Disposal System Technical Specification* (DSTS) [5]) in the WPS that make up the WPS/300 Series of documents that form part of the WPSGD.

This guidance has been produced to provide advice on the potential use of organic polymers for the packaging of low heat generating wastes (LHGW), in order to assist waste packagers in the development of packaging strategies. Its principal aims are to identify the types of organic polymers that have been used and that are proposed for use worldwide, to provide information on them and discuss their relative merits and limitations with respect to their practicality of use, performance and properties, and to examine the consequences of the use of such materials, in particular their evolution and degradation, on the post-closure performance of a GDF.

The remainder of this document is structured in the following manner:

- Section 2 provides background information on the manner in which RWM defines the requirements for waste packages, and the role that packaging specifications play in assessing the suitability of proposed waste packages for geological disposal.

- Section 3 provides a brief introduction to relevant aspects of the science and technology of organic polymers.

- Section 4 identifies the most common types of organic polymers that have been used, or proposed for use, in the conditioning of LHGW. Separate sub-sections on each of the identified organic polymers describe their production, chemical and physical composition, practicality and use, performance and properties, and evolution and degradation.

- Section 5 discusses Research and Development (R&D) that has been undertaken across the industry on the use of polymers for waste conditioning, and collates the key outcomes of the R&D using the same sub-section headings used in Section 4.

- Section 6 discusses assessments of disposability that RWM has undertaken that proposed the use of organic polymers, and collates the key outcomes of those assessments.

2 Background

2.1 The definition and purpose of packaging specifications

When radioactive waste is disposed of in an operational GDF it must be compliant with the waste acceptance criteria (WAC) defined for that facility. WAC would be expected to be produced by the facility operator, overseen by the relevant regulatory authorities, and would be based on the safety cases produced for the operational and post-closure periods of the facility.

In the UK, plans for the geological disposal of higher activity radioactive waste are still at an early stage, so the information necessary to develop WAC is not available. However, in order that wastes can be converted into passively safe and disposable forms, as soon as is reasonably practicable, RWM produce packaging specifications. These specifications define the standard features and performance requirements for waste packages which will be compatible with the anticipated systems and safety cases for transport to and disposal in a GDF. In this way they play an important part in the assessing the suitability of waste packages for geological disposal and may thus be considered as the *preliminary* WAC for a future GDF.

RWM have established the *Disposability Assessment Process* [6] to support those responsible for the packaging of higher activity wastes by demonstrating that the waste packages they propose to produce will be passively safe and disposable, and in line with regulatory expectations for the long term management of the waste [7]. In this manner RWM also demonstrate that waste packages will be capable of providing the barrier to the release of radionuclides and other hazardous materials that is required of them as part of a multiple barrier geological disposal system. A *Letter of Compliance* (LoC) is issued for each specific design of waste package which has been shown to be disposable by way of the Disposability Assessment Process.

The Disposability Assessment Process also plays an important role in underpinning the generic Disposal System Safety Case (DSSC) [8] by demonstrating that the geological disposal concepts considered therein will be appropriate for the actual wastes they will be expected to cover. The process also serves to identify wastes that could challenge the disposal concepts currently assumed for particular categories of waste and thereby allow early consideration of what changes may be required to these concepts to permit such wastes to be accommodated. RWM have produced guidance on the manner by which waste packagers should prepare submissions for the disposability assessment of their proposals to package waste [9].

With waste packages being manufactured at many sites throughout the UK, and by a number of different organisations, the needs of ensuring cost-effectiveness, safety and environmental protection in the long-term are promoted by the adoption of common approaches to waste packaging. In support of these needs, RWM have defined a range of waste containers with standardised features (e.g. dimensions, handling/stacking arrangements) which can be used to produce waste packages. The definition of waste containers in this way will help to ensure a high level of confidence that all waste packages manufactured according to the requirements set out in the WPSGD will be compatible with future transport and GDF infrastructure and facilities.

RWM consider that the existing range of standardised waste containers will be suitable for use in the packaging of the majority of the ILW[1] predicted to arise in the UK. However, RWM acknowledge that these waste containers may not suit all of the needs of individual

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[1] These containers may also be suitable for use in the packaging of a wider range of LHGW, as discussed in the Generic Specification [4].

waste producers, and that additional designs may be required for the packaging of particular wastes. RWM use the Disposability Assessment Process to consider the suitability of alternative designs of waste container to produce disposable waste packages, by way of a demonstration of compliance of the proposed design with the relevant Generic Specification. If such compliance can be shown RWM can then use the concept change control management process to ensure that the waste packages that would result from the use of the new container design would be compatible with all aspects of RWM's plans for disposal concept. If this can be shown to be the case, the container will be added to those identified by the DSTS, and a WPS produced for the waste packages it could be used to manufacture.

2.2   The role of the waste package in geological disposal

The waste package provides the most immediate barrier to the release of radionuclides and other hazardous materials from the waste it contains during interim storage, transport and when it forms part of a multiple barrier geological disposal system. It can also play a role in protecting individuals from the radiation emitted by the radionuclides it contains during interim storage, transport and the GDF operational period.

The barrier provided by a waste package can be considered to comprise two components, each of which can act as a barrier in its own right:

- The waste container, which provides a physical barrier and also enables the waste to be handled safely during and following waste package manufacture. Containers can be manufactured from a range of materials with designs selected to suit the requirements for the packaging, transport and disposal of the wastes they contain.

- The wasteform, which can be designed to provide a significant degree of physical and/or chemical containment of the radionuclides and other hazardous materials associated with the waste. The wasteform may comprise waste which has been 'immobilised' (e.g. by the use of an encapsulating material) or that which may have received more limited pre-treatment prior to packaging (e.g. size reduction and/or drying).

It is the performance of the barrier(s) provided by the waste package that packaging specifications seek to address, as well as defining requirements for waste packages which take into account the other needs of the long-term management of waste packages, notably their transport.

In the DSTS [5] the concept of *safety functions* is developed as a means of defining the roles played by each of the barriers in the post-closure period of a GDF. This concept is further developed in the DSSC in which the safety functions that are required of waste packages during transport and the GDF operational period are also considered [10]. The GWPS identifies the safety functions specific to waste packages which will be required during transport and the period up to the time when a GDF is backfilled, and in the time following backfilling; the GDF post-closure period. The safety functions required in these periods can be summarised as:

- During transport and the GDF operational period:
  - Provide containment of radionuclides and other hazardous materials during normal operations and under accident conditions;
  - Limit radiation dose[2] to workers and members of the public;
  - Preclude criticality;
 - Provide the means of safe handling; and

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[2]   In this context radiation dose is that which could result from exposure to direct radiation from the surface of the waste package.

- o Withstand internal and external loads.
- During the GDF post-closure period:
    - o Provide containment of radionuclides and other hazardous materials;
    - o Contribute to the overall performance of the engineered barrier system (EBS);
    - o Contribute to ensuring that, following GDF closure, a criticality event is not a significant concern; and
    - o Withstand internal and external loads.

Both the waste container and the wasteform can contribute to the achievement of the required performance of the waste packages, the relative importance of each generally depending on the robustness of the former. This is illustrated in Figure 1 which shows in stylised form how the use of a more robust waste container can reduce the required contribution of the wasteform to overall waste package performance.

Figure 1 also shows that for all waste packages both the waste container and the wasteform will be required to play some role. It should also be noted that it is the overall performance of the waste package, rather than that of its two components, that is the governing factor in judging its disposability.

Figure 1   Relative contributions of the waste container and the wasteform to waste package performance
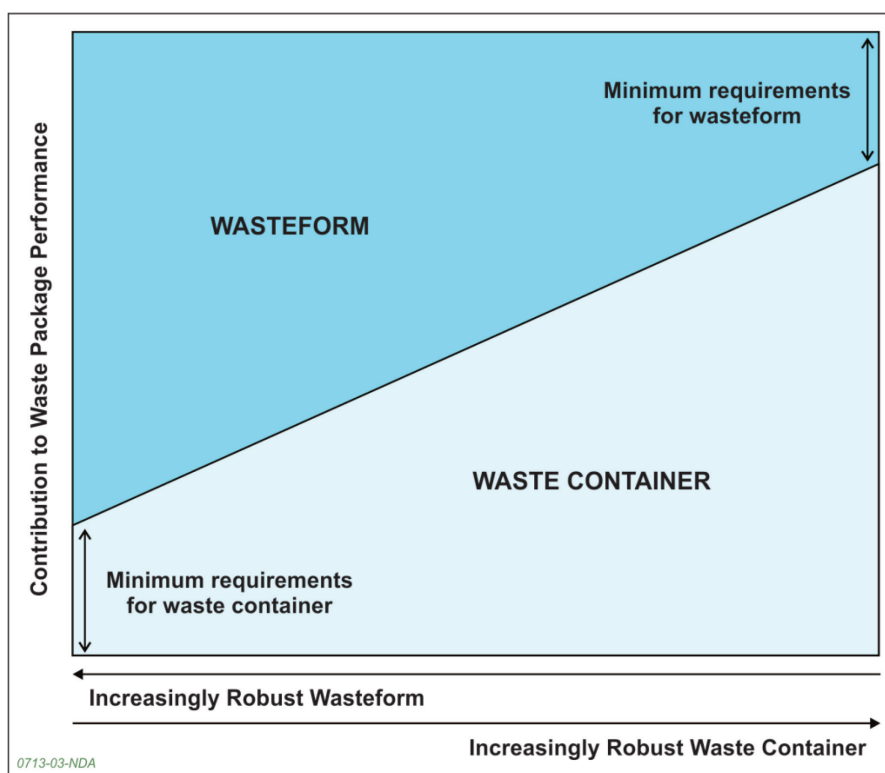
2.3   The definition of waste package types

A variety of waste container designs have been proposed for the packaging of LHGW for geological disposal. These designs can be grouped into three basic types, on the basis of the general nature of the waste packages they are used to produce:

- For use with wastes with low specific activity, such as would not generally require the extensive use of remote handling techniques, waste containers incorporating

integral radiation shielding[3] can be used to create *shielded waste packages.* Such waste packages would generally be expected to be capable of being transported through the public domain without additional protection and would therefore qualify as transport packages in their own right.

- For LHGW with higher activities, such as would generally require the use of remote handling techniques, relatively thin-walled (i.e. a few mm) metal containers can be used to create *unshielded waste packages.* Because of their high external radiation dose rate, or requirements for the containment of their contents, such waste packages would be expected to be transported through the public domain in reusable shielded transport containers.

- For all types of LHGW, thick-walled (i.e. many 10's of mm thick) waste containers can be used to provide both radiation shielding and physical containment of their contents, and to create *robust shielded waste packages.* Such waste packages are capable of being stored, transported and disposed of without the need for remote handling techniques or for additional shielding or containment.

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[3] If needed, to ensure that external radiation dose rates do not exceed the regulatory limits for transport.

3 The science and technology of organic polymers

This section provides a brief and basic introduction to the aspects of the science and technology of organic polymers that are relevant to their use in the immobilisation of radioactive waste by describing, in the following sub-sections, materials and processes that are commonly encountered when researching the subject. A more thorough understanding of the basics of polymer science and technology can be gleaned from standard textbooks such as [11] and [12].

3.1 Addition and condensation polymers

All organic polymers can be classified as either addition or condensation polymers. An addition polymer is one in which the molecular formula of the repeating structural unit is identical to that of the monomer. Examples of addition polymers include polystyrene and polyethylene. A condensation polymer is one in which the repeating structural unit contains fewer atoms than that of the monomer, or monomers, because of the loss of water or some other molecule during the condensation reaction. Examples of condensation polymers include polyesters and polycarbonates.

3.2 Thermoplastic and thermosetting polymers

An alternative way of classifying organic polymers, and one that is frequently employed when discussing their potential use as immobilisation materials for radioactive wastes, is as either thermoplastic or thermosetting polymers. Thermoplastic polymers such as polyethylene consist of tightly packed polymer chains held together by Van der Waals forces. At high temperatures, these rigid polymers become liquids that revert to their original solid form on cooling. Thermosetting polymers such as urea formaldehyde, on the other hand, have cross-linked polymer chains and set at room or elevated temperature to form rigid solids that cannot be remelted or reformed. For polymerisation, thermosetting polymers require additional constituents such as initiators and promoters.

3.3 Cross-linking

It is possible to link the linear chains of organic polymers together with strong chemical bonds through the use of cross-linking agents. Cross-linking agents are polyfunctional compounds capable of simultaneously taking part in two separate addition reactions to form three-dimensional network polymers. In certain applications, cross-linking results in improved mechanical and chemical properties such as thermal stability. A typical example of a cross-linked polymer is styrene-divinylbenzene.

3.4 Initiators (Catalysts)

The polymerisation of unsaturated monomers, such as styrene, is typically a chain reaction that can be initiated by the action of a free radical on a monomer molecule. Free radicals can be formed by the decomposition of an unstable molecule called an initiator or catalyst. Decomposition of the initiator can be effected by, for example, heating or exposure to UV light. The two most common types of initiators are organic peroxides and azo compounds.

3.5 Promoters (Accelerators)

Promoters (also known as accelerators) are chemical compounds that can induce the decomposition of an initiator, thereby removing the need for heating or exposure to radiation. An example of a promoter-initiator combination is dimethyl aniline and benzoyl peroxide. Special care must be taken when using promoters and initiators, as the reactions between the two components can be extremely vigorous and exothermic.

3.6   Inhibitors

Most monomers are stabilised with inhibitors prior to shipping. Inhibitors are chemical compounds that act as free radical scavengers, thereby preventing premature polymerisation from occurring as a result of reactions between monomer molecules and free radicals formed when the monomer is contaminated with oxidation products or with peroxides generated from oxygen in the air during handling and storage. A commonly used monomer-inhibitor combination is methyl methacrylate and hydroquinone.

4   The use of organic polymers for the packaging of LHGW

During all stages in the long-term management of radioactive waste (i.e. interim storage, transport and the operational and post-closure periods of a GDF) safety is predicated on the containment of the radionuclides present in the wastes by multiple barriers, one of which could be provided by an encapsulating material used to 'immobilise' the radionuclides. The demands placed on the properties and performance of such a material during the various stages of the management of the waste are various. For example, during transport and GDF operations, it will help to ensure that the waste packages are physically robust and able to survive credible accident scenarios (e.g. fires or impacts) without unacceptable releases of radioactivity. During the GDF post-closure period, it may be required provide a physical barrier to the release of radionuclides from the waste package and should contribute to, or at least not unduly undermine, the chemical containment of radionuclides within the EBS, notably the GDF vault backfill.

To date, the materials most used for the encapsulation of LHGW in the UK have been traditional inorganic cements[4]. In addition to being relatively cheap and readily available, cements have many desirable properties when used for this purpose. They have excellent mechanical, physical and thermal stability and are tolerant of a wide range of incorporated materials. The high pH buffering capacity of many cements allows them to contribute to the chemical containment function of the EBS and they are generally chemically compatible with cementitious backfill materials.

The beneficial properties of cements in the context of the packaging of LHGW do not, however, rule out the use of alternative encapsulants; indeed, there may be instances where the use of an alternative may be necessary to achieve adequate long-term performance of waste packages. A particular example is in the packaging of wastes containing significant quantities of 'reactive metals' (e.g. uranium, Magnox, aluminium etc.) where the use of a cementitious materials could exacerbate corrosion of the waste and cause problems such as wasteform expansion and/or excessive heat and gas generation. For these and other waste types, organic polymers can represent a potential alternative to cements.

To date, organic polymers have not been widely used in the packaging of ILW in the UK although, in the past decade a number of waste packagers have considered their use and there are a number of ongoing research programmes aimed at investigating the properties and performance of specific polymers and establishing their suitability for packaging certain wastes, particularly for 'niche' applications. A summary of the five organic polymers[5] that have been most extensively investigated and used in the immobilisation of radioactive wastes is presented below. These comprise:

a) *Thermoplastic* polymers: Bitumen, polyethylene
b) *Thermosetting* polymers: Epoxy resins, polyester resins, urea-formaldehyde

Information is provided on their production, chemical and physical composition, and their relative pros and cons with respect to practicality and use, performance and properties, and evolution and degradation.

Information that is available in the open literature on the subject of organic polymers in the conditioning of LHGW has been drawn on, and references to the source documents are provided where appropriate. In addition to the specific references that have been

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[4]   These are referred to generically as 'cement' for the remainder of this guidance

[5]   In addition to these, a number of other organic polymers (e.g. styrene-divinyl benzene, polyvinyl chloride, polymethyl methacrylate, polyurethanes) have been investigated to a lesser extent.

consulted, there are a few particularly significant documents that provide an important general overview.

The state of the art in the worldwide application of organic polymers to the packaging of ILW, and the then current research and development in the field, were reviewed in an International Atomic Energy Agency (IAEA) Technical Report published in 1988 [13]. Although it is now somewhat dated, the IAEA Technical Report provides a wealth of useful information and is extensively drawn upon below. Other reviews of the potential use of organic polymers for the packaging of ILW [14, 15] have also been considered.

4.1 Bitumen

4.1.1 Production

Natural bitumen, or pitch, has been used by mankind for millennia in a diverse range of applications such as waterproofing and construction. Today, however, virtually all bitumen is synthetically produced as a by-product of refining crude oil. A schematic of the process is shown in Figure 2.

Figure 2   Bitumen production from crude oil refining
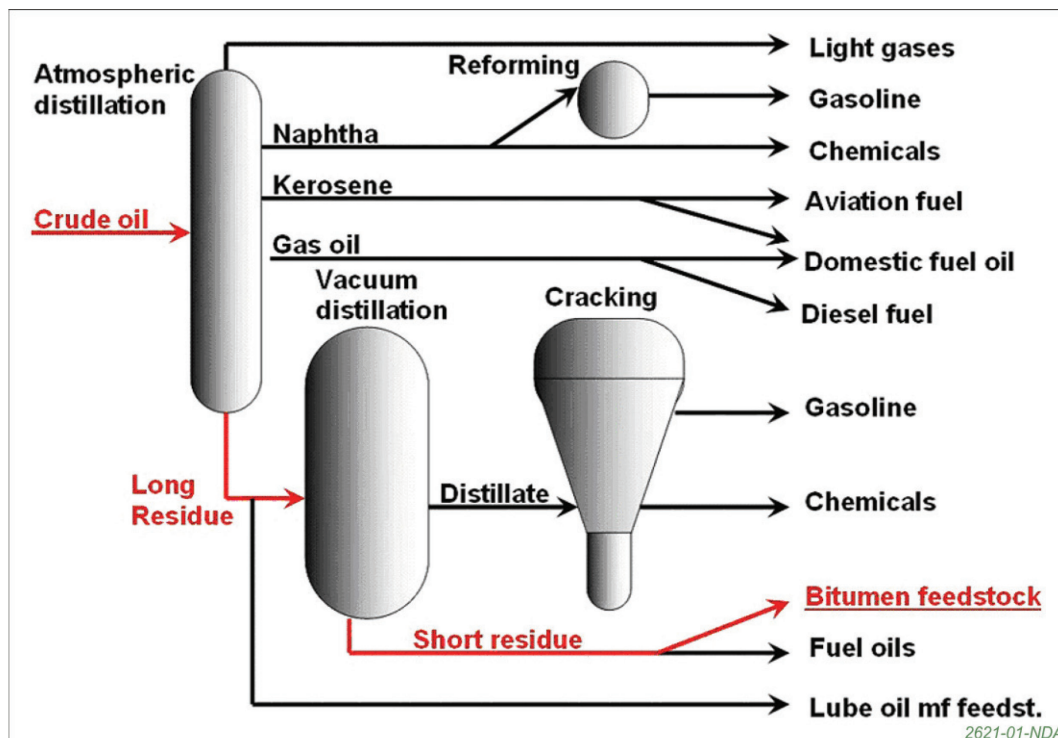
Three main types of bitumen exist: distilled, air-blown and emulsion bitumen. The first two have been extensively examined as immobilising materials for radioactive wastes. Distilled bitumen is the direct product of crude oil refining, and is modified to produce the other two types. Heating distilled bitumen in air at ~250°C produces the harder, less plastic type of air-blown bitumen. Emulsion bitumen is a dispersion of bitumen in water that is prepared in a variety of ways using surfactants as emulsifying agents. Diverse ranges of other, specially modified types of bitumen have been produced with properties specifically tailored to certain applications.

4.1.2 Chemical and physical composition

The chemical composition of bitumen is extremely complex and rather poorly understood, and varies considerably depending on the source of the parent crude oil and the details of the refining process. The principal components of bitumen have been classified as saturates, aromatics, resins and asphaltenes. Saturates comprise low molecular weight,

open-chain and cyclic alkanes. Aromatics, resins and asphaltenes are aromatic compounds with increasing molecular weight and polarity.

Physically, bitumen is a complex colloidal system in which micelles of the more polar constituents (resins and asphaltenes) are dispersed in a medium that mostly comprises the lower molecular weight components (saturates and aromatics).

4.1.3 Practicality and use

Bitumen is cheap, and is readily available commercially in large quantities in a wide variety of forms that can be tailored to provide desirable properties for specific applications. It is also relatively simple to use. However bitumen does possess some significant drawbacks which can severely limit its potential for the packaging of wastes, notably its chemical toxicity, flammability of the material and the requirement for high temperatures during its use.

Bitumen is able to incorporate wastes with widely differing chemical and physical properties, although incompatibilities have been reported with wastes containing iron and aluminium salts [15], and oils have a tendency to emulsify bitumen and are typically limited to <1% of the waste mass in bituminisation processes [14]. Solid wastes can generally be incorporated into bitumen to as high a level as the processing equipment can mix, and waste loadings as high as 50% are typically achieved. Bitumen, as a thermoplastic material, has the advantage that immobilised waste could be recovered, if desired, by re-melting the bitumen.

Bitumen has been extensively researched and applied in the packaging of radioactive waste and industrial-scale processes using bitumen have been operated in a number of countries including France, Japan, the USA and Russia. Wastes as diverse as evaporator concentrates, ion exchange resins and spent filter cartridges have been successfully immobilised in bitumen. Accumulated worldwide experience in the use of bituminisation techniques for the packaging of radioactive wastes was reviewed by the IAEA in 1993 [16].

In a typical bituminisation process (shown schematically Figure 3) [17], liquid bitumen (at ~120°C) and wet solid waste are pumped into a heated extruder (at ~200°C), where the components are spread, by screws, onto the heated surface of the extruder barrel. The high processing temperatures result in essentially complete evaporation of water from the waste, and provide homogeneous mixing of the waste solids with the bitumen. The bitumen-waste mixture is discharged from the extruder directly into a container, where it is allowed to cool and solidify. Because the mixture shrinks on cooling, each container is normally filled at least twice to enable better volume utilisation.

Figure 3   Schematic of typical bituminisation process
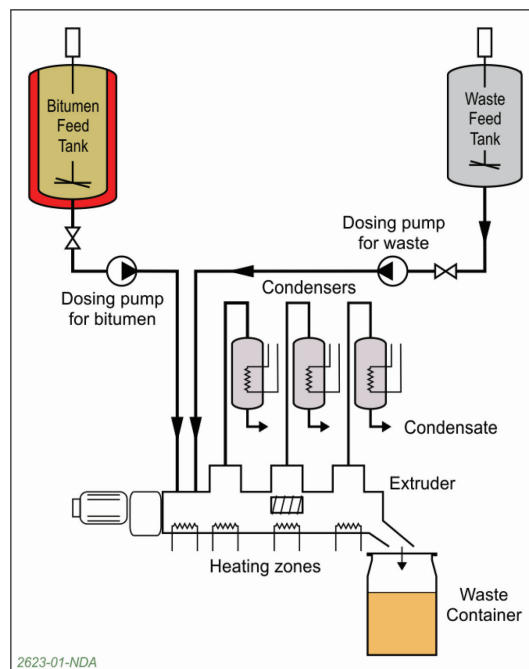
4.1.4 Properties and performance

Bitumen is a thermoplastic material that shows temperature dependent rheological properties, and can be classified as either a semi-solid or a solid. Bitumen can usually be softened at temperatures above about 70°C [18]. Molten bitumen characteristically has a rather high viscosity, although modified grades (with a higher proportion of saturates and aromatics) can have viscosities as low as 0.1 Pa.s at 165°C [19].

Once cooled and set, bitumen-based wasteforms are typically homogeneous (although some settling of waste components can occur during cooling of the wasteform immediately after its production), monolithic and have no associated freestanding water. They have relatively low compressive strengths with values in the range 0.3 to 8 MPa being reported [14]. The wasteforms have a tendency to creep and deform under applied loads at ambient temperatures, and have self-healing properties with respect to any cracks that might be formed as a result of, for example, thermal cycling.

Bituminous wasteforms are usually flammable, particularly when the waste contains oxidising agents such as nitrate. Grades of bitumen with relatively high flash-points (up to 300°C [15]) are typically employed for radioactive waste immobilisation. Thermal decomposition products of bitumen have been reported as mixtures of volatile hydrocarbons and involatile oils [20].

Leach rates from bituminised wastes are generally low, even for waste components and radionuclides (e.g. Sr-90 and Cs-137) with high aqueous solubilities, due to the low water permeability of bitumen. Leaching of toxic and carcinogenic organics (such as polycyclic aromatic compounds) from bitumen has been reported as being relatively insignificant [21].

4.1.5 Evolution and degradation

Radiolysis of bitumen wasteforms to total absorbed doses of 10^7Gy has been shown to result in little deterioration in wasteform properties and performance (e.g. compressive strength) [14]. Total doses >10^7Gy result in swelling and structural break down [14]. Radiolysis of bitumen-based wasteforms results in gas evolution (mainly H_2, but also CH_4, CO_2 and C_2H_2). Modest $G(H_2)$ and G(total gas) values of 0.07 and 0.1 have been reported for the radiolysis of bitumen to a total dose of 10^5 Gy [16]. Very high dose rates (e.g. in accelerated irradiation tests) can lead to swelling in bitumen-based wasteforms, due to the rate of hydrogen production exceeding that at which the gas can diffuse out of the matrix.

A study has concluded that the radiolytic degradation products of bitumen would have no influence on radionuclide speciation in the near field of a cementitious GDF and, as such, need not be considered in safety case assessments [22].

Bitumen-based wasteforms generally show good resistance to high pH aqueous solutions such as a cementitious repository pore-water. Bitumen-based wasteforms containing waste components such as hygroscopic salts (e.g. sodium sulphate) and ion exchange resins can, however, show a tendency to break-up when contacted with aqueous media, as a result of expansive rehydration reactions [16].

Microbial degradation of bitumen is possible under conditions replicating those in a deep waste repository. This degradation occurs either aerobically or anaerobically, although degradation is favoured under aerobic conditions. Degradation rates are, however, typically low, and the effects on the physical and mechanical properties of the wasteform are reported to be minimal [14].

4.2   Polyethylene

4.2.1 Production

Polyethylene is probably the most commonly encountered plastic in the world, and has been used in an enormous variety of applications. Polyethylene is produced by the addition polymerisation of ethylene.

Polyethylene is usually classified into two main types, Low Density Polyethylene (LDPE) and High Density Polyethylene (HDPE). LDPE is made by the high temperature (~200°C) and pressure (up to 4000atm) process of free radical polymerisation, in which ethane and an initiator (*e.g.* benzoyl peroxide) are injected into a reactor. HDPE is made by the more complicated, but much lower temperature and pressure, process of Ziegler-Natta polymerisation, which employs catalysts such as $TiCl_3–(C_2H_5)_2AlCl$.

4.2.2 Chemical and physical composition

All types of polyethylene have the same chemical composition, being made up of repeated methylene ($–CH_2–$) units. HDPE is a highly crystalline solid that consists of linear molecules with molecular weights in the range 200,000 to 500,000, while LDPE has a much lower degree of crystallinity and is comprised of branched chain molecules. The detailed molecular structure of polyethylenes can be designed and controlled to produce materials with properties tailored to specific applications.

4.2.3 Practicality and use

Polyethylene shares many of the same benefits as bitumen with respect to practicality in use as an immobilisation medium for radioactive wastes. Polyethylene is readily available commercially in a wide range of grades with specifically tailored properties, but is more expensive than bitumen. Polyethylene is less flammable than bitumen, but does still need to be used at elevated temperatures. Like bitumen, polyethylene is highly versatile in terms of tolerable waste types and loadings due to the lack of chemical interactions between waste and polymer. Polyethylene performs well in the immobilisation of some 'problem' wastes such as nitrate salts and ion exchange resins. Polyethylene is, however, incompatible with organic solvents such as lubricating oils. Immobilised waste can be recovered from polyethylene by simply remelting the polymer.

Mainly because of its relative ease of use (*e.g.* lower melt temperature), LDPE is generally preferred to HDPE for the immobilisation of radioactive wastes. Polyethylene has been widely studied as an immobilisation medium for radioactive waste, and a number of industrial scale processes have been operated, immobilising liquid concentrates, sludges and ion exchange resins in countries such as the Netherlands, Argentina and Japan.

The Brookhaven National Laboratory (BNL) in the USA actively markets polyethylene immobilisation processes and has a full-scale demonstration facility for a polymer-waste mixing and extrusion process, a schematic of which is shown in Figure 4.

Figure 4   Schematic of BNL polyethylene immobilisation process
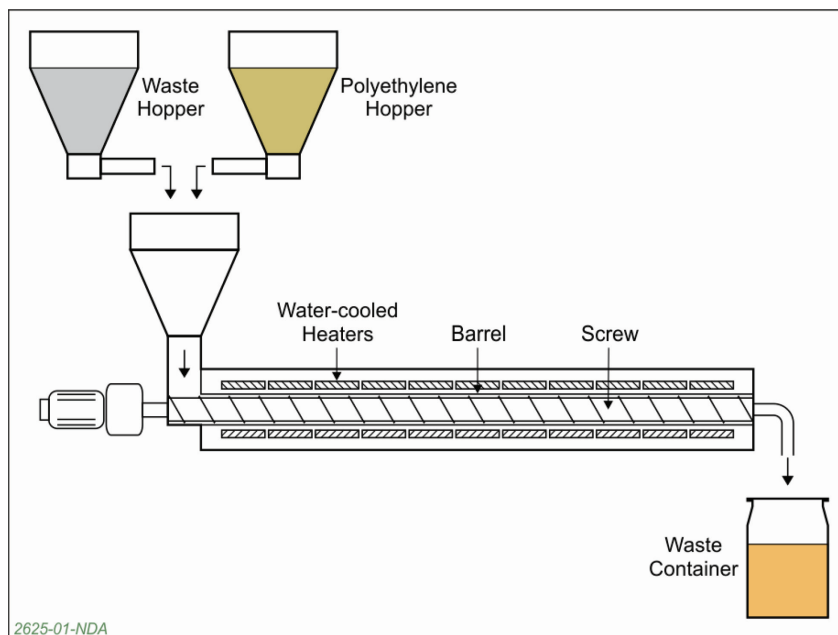
The process involves feeding dried waste and LDPE into a heated screw extruder, where distributive mixing produces a homogeneous molten mixture that is extruded directly into a waste container. The molten mixture is then allowed to cool to form a solid monolithic wasteform. The process has been used to immobilise a wide range of radioactive wastes, including nitrate salts, ion exchange resins and depleted uranium oxide powder.

BNL has also developed a 'macro-encapsulation' process for immobilising large items of waste in-situ. The polyethylene macro-encapsulation process utilises a single-screw extruder to melt, convey and pump molten polyethylene through a die and into a wasteform container in which waste materials have either been suspended or supported. Commercial application of polyethylene macro-encapsulation has recently been initiated, and the US Environmental Protection Agency has identified polymer macro-encapsulation as the Best Demonstrated Available Technology for immobilising radioactive lead solids and mixed waste debris.

4.2.4 Properties and performance

Polyethylene is a thermoplastic material that becomes fluid above about 85°C, and reverts to its original solid form on cooling. Variations in the processes used to produce polyethylene yields commercial products with a very wide range of physical and chemical properties, from soft waxes to extremely tough plastics. The viscosity of molten polyethylene is typically high (6 Pa.s at 160°C [23]) due to the high molecular weight of the polymer. Polyethylene-based wasteforms typically exhibit modest compressive strengths in the range 13 to 33 MPa [13], and have a tendency to deform rather than break under applied loads.

Polyethylene is slightly flammable and is self-extinguishing below its flash point, which can be as high as 465°C [14]. The immobilisation of wastes containing high concentrations of oxidising agents can, however, lower the flash point to 365°C [14]. Methods of retarding the flammability of polyethylene are well understood. Thermal decomposition of LDPE has been reported to commence at 260°C [24]. Decomposition in an oxygen bearing atmosphere would be expected to yield CO_2. Pyrolysis (degradation at high temperature in a non-oxidising atmosphere) products of LDPE have been reported to be mixtures of saturated and unsaturated aliphatic hydrocarbons [25].

The low water permeability of polyethylene means that leach rates of water-soluble radionuclides such as ruthenium-106 and caesium-137 are typically very low from polyethylene-based wasteforms.

Because of its chemical structure, polyethylene is very resistant to chemical attack and is unaffected by most acids, alkalis and aqueous solutions.

4.2.5 Evolution and degradation

Results from experiments involving the irradiation of polyethylene-based wasteforms can be somewhat contradictory, as radiolysis of polyethylene can lead to both bond scission (which tends to weaken the polymer) and cross-linking (which tends to strengthen the material). The consensus seems to be that polyethylene-based wasteforms are largely unaffected by total absorbed doses up to 10^6 Gy, and that doses of that order can actually result in increased strength, lower permeability and leachability, and better chemical resistance.

Radiolysis of polyethylene produces considerable quantities of gas. In the absence of oxygen, hydrogen is the main radiolysis gas produced ($G(H_2)$ of 4.0 reported [24]) together with small quantities of gaseous aliphatic hydrocarbons (methane *etc.*). Radiolysis of polyethylene in air results in consumption of oxygen and generation of carbon dioxide ($G(CO_2)$ of 2.7 reported [24]) in addition to hydrogen.

Polyethylene-based wasteforms do not appear to be susceptible to biodegradation.

4.3   Epoxy resins

4.3.1 Production

Epoxy resins are extremely versatile materials that have been employed as adhesives, high performance coatings and encapsulating materials. The most commonly encountered epoxy resins are prepared from the condensation polymerisation of epichlorohydrin and bisphenol A, in the presence of a sodium hydroxide catalyst, to produce the diglycidyl ether of bisphenol-A (DGEBA).

The resins are manufactured with a wide range of molecular weights, *i.e.* with a varying number of repeating units, *n*, in the polymer structure. A high proportion of epichlorohydrin to bisphenol A in the reaction mixture yields a low molecular weight, low viscosity liquid product. Conversely, a high ratio of bisphenol A to epichlorohydrin gives high molecular weight polymers that are typically high melting point solids.

Epoxy resins are cured using cross-linking agents known as hardeners, or by catalysts that promote self-polymerisation. Curing can take place over a wide temperature range (typically 5-150°C), depending on the system involved. The selection of curing agent for a given application depends on system requirements with respect to viscosity and temperature. Di-amines are frequently used as curing agents for epoxy resins based on bisphenol A.

4.3.2 Chemical and physical composition

A typical cross-linked structure of a di-amine cured, bisphenol based epoxy resin provides a high degree of cross-linking gives the polymer a very rigid structure.

4.3.3 Practicality and use

Epoxy resins with a very wide range of tailored properties are readily available commercially. This makes them very versatile as potential immobilisation agents for radioactive wastes, but also means that care needs to be taken in selecting a material with the right properties. In making such a selection, factors such as viscosity, working time and exothermicity of the curing reaction need to be considered. Achieving the correct ratio of epoxy to hardener in the curing reaction is very important (any unreacted resin or hardener remains within the matrix, affecting the final properties after cure). These complexities, together with their relatively high cost, have meant that epoxy resins have not been extensively employed in the immobilisation of radioactive waste.

Epoxy resins can tolerate the presence of some water in the waste, but can be sensitive to the chemical composition of the waste (*e.g.* the pH). As with most organic polymer

immobilising agents, epoxy resins can incorporate relatively high waste loadings (up to 50%w/w).

The French company Socodei currently operate mobile epoxy resin immobilisation plants that are used to condition ion exchange resins from the primary circuits of nuclear power stations. Since 1996, the immobilisation plants have completed conditioning campaigns at several reactors, and have processed a total of 400t of ion exchange resins. The basic epoxy resin immobilisation process has also been tested on evaporator concentrates, filters and dismantled reactor components. A schematic diagram of the process is shown in Figure 5. Ion exchange resin, the epoxy monomer and the hardening agent are metered into the waste container, where they are mixed by means of a sacrificial paddle. Following the mixing sequence, waste packages are transferred to a temporary storage area where curing of the resin takes place.

An epoxy resin based immobilisation process was also developed by the CEGB for conditioning Magnox fuel element debris. In the process, dried Magnox debris was compacted into waste containers, which were then infilled with an epoxy-hardener mixture. In recent years, there has been renewed interest in using epoxy resins for conditioning ILW and an appreciable amount of R&D work has been undertaken (Section 4.6).

Figure 5   Schematic of Socodei epoxy resin immobilisation process
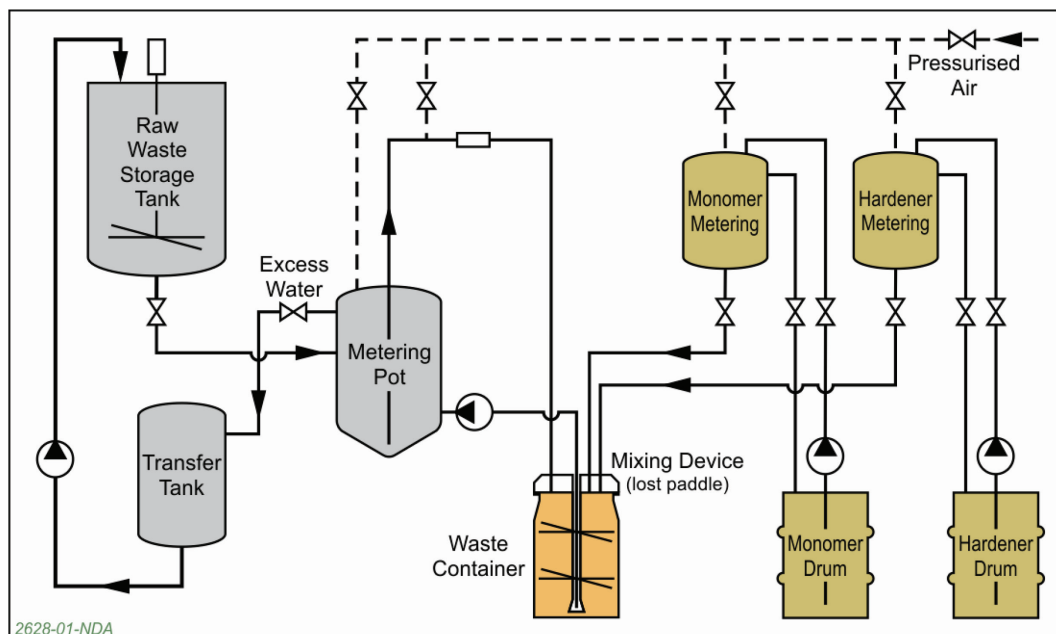
4.3.4 Properties and performance

Different types of uncured epoxy resin have a very wide range of viscosities, but very low viscosity materials (<0.1 Pa.s) are available that are specifically designed for infiltrating and encapsulating reinforcing fibres in the production of high strength composite materials. One of the advantageous properties of epoxies is their low shrinkage during curing.

Cured epoxy resins generally out-perform most other resin types in terms of mechanical properties, and can be formulated to give compressive strengths of up to 175MPa [13]. As a consequence, however, the resins have an inability to deform plastically and generally exhibit brittle fracture characteristics.

Epoxy resin-based wasteforms are usually highly impermeable to water, and exhibit superior leach resistance. They have a low flammability (flash point >800°C [14]) and are self-extinguishing below their flash points. Most epoxy resins begin to thermally decompose, to produce gaseous products, at around 300°C, with decomposition becoming

rapid at >400°C. Incomplete combustion or pyrolysis of epoxy resins produces phenolics and other toxic organic compounds.

4.3.5 Evolution and degradation

Radiolytic damage has been observed at >10^6 Gy for wet ion exchange resins immobilised in epoxy resin. Irradiation of epoxy resin-based wasteforms results in the generation of modest amounts of gas (G(H_2), G(CO_2) and G(total gas) values of 0.32, 0.08 and 0.36 have been reported [13]).

In general, epoxy resins are highly resistant to environmental degradation, and show excellent resistance to aqueous alkalis and organic solvents, but are attacked by strong acids.

4.4   Polyester resins

4.4.1 Production

Polyester resins are readily available commercially, and are used in a broad range of industries (construction, boat building, automotive, electrical *etc*.). In most applications, the resins are reinforced with glass fibres to produce a material commonly known as Glass Reinforced Plastic (GRP) or fibreglass. Polyester resins have many of the desirable properties of epoxy resins (excellent mechanical properties, durability *etc*.), but are less expensive. The properties and performance of these important materials have been very widely studied.

Polyester resins are produced from the addition polymerisation of a linear polyester (typically produced from the condensation polymerisation of an unsaturated dibasic acid and a glycol) and a cross-linking agent. The cross-linking reaction can be undertaken at room temperature by the use of an initiator and promoter.

There is a wide range of commercially available polyesters made from different acids, glycols and monomers, all having varying properties and performance that can be tailored to specific applications. A type of polyester resin that has found particular use in the immobilisation of radioactive waste is vinyl ester resin. Vinyl esters are synthesised from an unsaturated carboxylic acid (usually methacrylic acid) and an epoxy resin (usually DGEBA, see Section 4.3.1).

4.4.2 Chemical and physical composition

Polyester resins are typically supplied as solutions of the polyester in a monomer, usually styrene. As well as acting as the cross-linking agent, the styrene also makes the material easier to handle by reducing its viscosity. The polyester and styrene typically comprise around 60% and 40%, respectively, of the supplied material. The other main components of the resin are the initiator/promoter (typically 1-3%) and an inhibitor (typically <100ppm), which is used to prevent premature polymerisation.

Special additives can also be incorporated into polyester resin mixes in order to tailor their properties and performance. For example, the addition of thermoplastic polymers (such as t-butyl styrene) can reduce or eliminate shrinkage during curing (one of the inherent disadvantages of polyester resin systems).

4.4.3 Practicality and use

Polyester resins, and vinyl ester resins especially, have been employed in the immobilisation of radioactive waste in several countries, particularly the USA (where they have been approved for the packaging of LLW by the US Nuclear Regulatory Commission) and, to a lesser extent, in the UK. Industrial scale processes have been operated, immobilising wastes with a variety of physical characteristics. Liquid and slurry wastes have been immobilised by the use of high speed, high shear agitation to produce stable water-in-resin emulsions which are then cured to form hard, solid monoliths. Ion exchange resins and zircaloy swarf have been immobilised using infilling processes. The use of emulsification agents allows wastes containing considerable quantities of water to be

immobilised in polyester resins. Special water extendible polyesters have also been developed for the immobilisation of wet wastes. Very high waste loadings of 66%w/w have been achieved for some polyester resin wasteforms.

Polyester resins can be used to successfully immobilise wastes with a wide variety of chemical components such as oil (up to 10%w/w in the waste), detergents (up to 47%w/w) and complexants (up to 34%w/w). Some components in wastes can, however, interfere with the curing of polyester resins, usually as a result of interactions with the initiator or promoter.

Great care is needed in the preparation and use of polyester resins. The resin and any additives must be carefully stirred to disperse all the components evenly before the initiator is added. This stirring must be thorough and careful as any air introduced into the resin mix affects the quality of the final product. It is also important to add the initiator and promoter in carefully measured amounts to control the polymerisation reaction to give the best material properties. Too much initiator will cause too rapid a gelation time, whereas too little initiator will result in under-cure. Polyester resins also have a limited shelf life, as they will set or 'gel' on their own over a period of time. The use of polyester resins has intrinsic hazards associated with the flammability of the uncured resin, and appropriate fire protection measures are required.

A plant operates at the Trawsfynydd power station that immobilises ion exchange resins in vinyl ester resin. The process flow diagram is shown in Figure 6. Vinyl ester is fed into a shielded drum fitted with a sacrificial mixing paddle. Ion exchange resin is then added to the drum from a hopper and the contents of the drum are mixed. After addition of the promoter, the wasteform is allowed to cure.

Figure 6   Process flow diagram for Trawsfynydd vinyl ester resin process
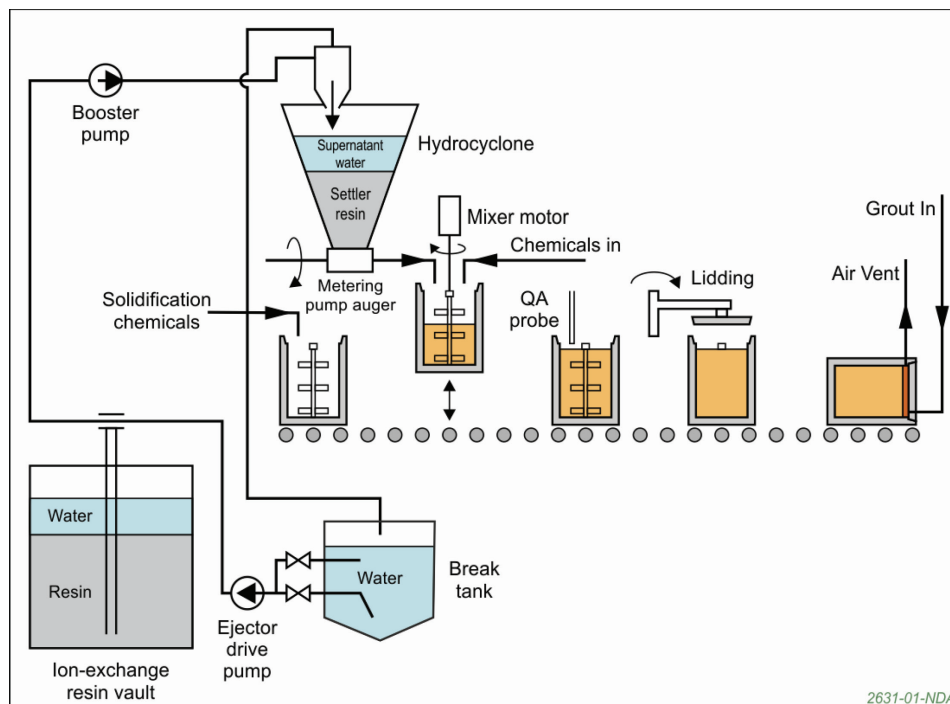
4.4.4 Properties and performance

Uncured polyester resins with viscosities as low as 0.05Pas [13] have been specially formulated to have excellent infilling characteristics for the production of fibre-reinforced composites.

Cured polyester resin-based wasteforms can have high compressive strengths (up to 80MPa reported [16]). As a consequence, however, the resins have an inability to deform

plastically and generally exhibit brittle fracture characteristics. Vinyl esters in particular have good toughness and resilience.

Polyester resin-based wasteforms are non-flammable, with flash points typically being >800°C. They tend to char and lose weight on exposure to burning fuel, but do not themselves sustain combustion [14]. Thermogravimetric analysis of polyester resin-based wasteforms in a nitrogen atmosphere has shown polymer decomposition to commence at ~350°C, with weight loss being most rapid at 450°C [17]. Large-scale fire testing of simulated wasteforms with vinyl ester encapsulants has been carried out for Nirex [26, 27] and has shown similar performance to cementitious systems with low activity loss and good maintenance of wasteform integrity following fires with severities representative of those anticipated during extreme repository accidents.

Polyester resin-based wasteforms show excellent retention of soluble radionuclides such as Sr-90 and Cs-137 in leach tests. Tritium release rates have been shown to be markedly lower from water extendible polyester wasteforms than corresponding cementitious wasteforms [13].

4.4.5 Evolution and degradation

The use of styrene as the cross-linking agent for polyester resins imparts greater radiation tolerance. Wasteforms produced from the immobilisation of sodium sulphate waste in polyester resin have been shown to increase in compressive strength when exposed to doses of up to 10^7Gy [13]. The main radiolysis product was CO_2, with little H_2 being evolved. G(total gas) values as high as 21 have been reported [14].

Polyester resins, and especially vinyl ester resins, are generally very resistant to chemical and thermal degradation.

Polyester resins are resistant to microbial degradation, with tests showing no deterioration in compressive strength or surface hardness [13].

4.5 Urea-Formaldehyde resins

4.5.1 Production

Urea formaldehyde resin is a major commercial adhesive, especially within the forest products industry, where it is used in the bonding of particleboard, medium density fibreboard and plywood.

Urea formaldehyde resins are formed from the condensation polymerisation of urea with formaldehyde. The polymerisation is carried out in two stages. In the first stage, urea is hydroxymethylated by the addition of formaldehyde to the amino groups. This reaction is, in reality, a series of reactions that lead to the formation of mono-, di- and tri-methylolureas. The reaction is typically undertaken at neutral or alkaline pH in aqueous solution. This produces an emulsion with a low free formaldehyde concentration, which is the form in which the uncured resin is usually shipped for use.

The second stage of the synthesis involves the condensation polymerisation of the methylolureas to low molecular weight polymers. The reaction requires the addition of an acid catalyst, often a weak acid such as sodium bisulphate or phosphoric acid, to bring the pH down to ~1.5. In the immobilisation of radioactive waste, the second stage polymerisation reaction is usually undertaken after addition of the waste to the resin emulsion.

4.5.2 Chemical and physical composition

As discussed in Section 4.5.1, uncured urea formaldehyde resin is usually supplied as an aqueous emulsion, which typically takes the form of a viscous, milky solution. Once cured, the resin has a cross-linked, honeycomb type microstructure, which could have implications for wasteform porosity.

4.5.3 Practicality and use

Urea formaldehyde is not commonly used as an immobilisation agent for radioactive wastes, principally because of problems encountered with the generation of corrosive free liquids during curing. Water is produced during the curing of the resin and, while this is largely incorporated into the resin matrix, some freestanding water can be produced. The free water has a low pH (the resin curing reaction is acid catalysed, see Section 3.5.1), and can corrode the wasteform container. Despite these drawbacks, urea formaldehyde resin was the main organic immobilisation agent used in the USA between 1970 and 1980. The adoption of regulations regarding the presence of free liquids in waste packages meant, however, that the use of urea formaldehyde resins was phased out.

Urea formaldehyde resins do benefit from low cost and low cure temperatures, and are compatible with a broad range of wastes, including organic chlorides, phenols, paint sludges and cyanides. Wastes containing considerable quantities of water, such as slurries and ion exchange resins, can be successfully immobilised in urea formaldehyde resins, and waste loadings as high as 70%w/w have been achieved. Since the curing reaction is acid catalysed, however, urea formaldehyde resins are incompatible with wastes that are corroded or otherwise attacked by low pH aqueous solutions.

In common with other thermosetting polymers, great care is required in ensuring that the correct formulation is used when immobilising wastes in urea formaldehyde resins. The curing reaction is pH and temperature sensitive and can be affected by waste components.

Because urea formaldehyde resins polymerise thermally and on exposure to air, their shelf life is limited and depends on storage temperature.

4.5.4 Properties and performance

Uncured urea formaldehyde resins are usually supplied as a viscous aqueous emulsion, although increasing the water content of the emulsion can lower the viscosity to 0.15Pas [28].

The compressive strength of urea formaldehyde resin is typically about 4.8MPa [14], which is significantly lower than the other thermosetting polymers considered in this note (epoxy and polyester resins). Compressive strengths of wasteforms produced from the resin are even lower, typically 0.4 to 2.7MPa.

Leach rates of water soluble radionuclides (strontium-90 and caesium-137) from urea formaldehyde resin-based wasteforms are reported to be higher than wasteforms produced using other organic polymers [14].

A major disadvantage of urea formaldehyde resins is their lack of resistance to moist conditions, especially in combination with heat. These conditions lead to a reversal of the bond-forming reactions and the release of formaldehyde.

Urea formaldehyde resin-based wasteforms burn on exposure to flame, but are self-extinguishing. On burning, the free water at the surface of the wasteform evaporates, leaving a charred and insulating surface. Thermal decomposition of urea formaldehyde resins typically commences at ~250°C.

4.5.5 Evolution and degradation

Doses of >10^5Gy have been reported [14] to result in severe damage to urea formaldehyde resin-based wasteforms (*e.g.* swelling due to radiolytic gas production, increased leach rates). G(total gas) and G(H_2) values of 21 and 6.5, respectively, have been reported for the irradiation of urea formaldehyde resin-based wasteforms [29].

The low pH of urea formaldehyde resin-based wasteforms should ensure that they are not susceptible to microbial degradation.

4.6 Summary

Of the five materials considered above only three (i.e. polyethylene, epoxy resin and polyester resin) are deemed by RWM to be suitable for the conditioning of wastes such as

ILW. Bitumen, although widely used in other parts of the world has significant flammability and chemo-toxicity issues. Similarly, urea-formaldehyde resins have a number of potentially significant drawbacks, including an intolerance to moist conditions and the creation of acidic products when in contact with free water. Accordingly, whilst these two materials may have niche applications for specific waste types, they should not be considered as a first choice when a waste conditioning process involving the use of a polymer encapsulant is being developed. It is recognised that they could be suitable for small-scale use as part of a packaging concept involving a combination of waste conditioning processes.

5   R & D on the use of polymers as conditioning materials

Section 4 provides information on polymers which have potential to be used for the conditioning of LHGW under three headings: practicality and use, properties and performance, and evolution and degradation. The same headings are used in this Section to provide a convenient framework for discussing the findings of R&D work on potential applications of two[6] of the polymers identified above (i.e. epoxy and polyester resins).

5.1   Practicality and use

5.1.1 Heat generation during curing and scale of application

Thermosetting polymers like epoxy and polyester resins can generate a considerable amount of heat as they are curing. This could potentially have a number of undesirable consequences including the vaporisation of any water in the waste, leading to foaming of the resin during curing. Heat generation could also result in cracking of the wasteform as it cools and shrinks, which might undermine its properties and performance, notably the protection of reactive metals from contact with atmospheric moisture.

The scale of the application can affect the amount of heat generated and the thermal characteristics of the curing wasteform, and therefore, the temperature that could be reached during the curing of thermosetting polymers. At a relatively small scale, less heat is generated and it can escape more easily, reducing the potential for undesirable consequences. The temperature profiles recorded during the full-scale encapsulation of an inactive submersible caesium removal unit (SCRU, see Section 6.1.1) in vinyl ester styrene (VES) are reported in [30]. The envelope volume of an SCRU is about 44 litres, and the encapsulation was performed in a PVC cylinder with a volume of 80 litres. The temperature measured by a thermocouple located within the resin reached a sharp peak of 127°C during curing which resulted in the creation of bubbles, caused by the vaporisation of residual water in the SCRU (Figure 7), and significant cracking of the cured wasteform (Figure 8). Despite these effects the encapsulation of the IONSIV beads within the SCRU was good (Figure 9) indicating that an acceptable product could be produced in this particular case.

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[6]   To date these are the only polymers that have been investigated in the UK for the packaging of ILW.

Figure 7   Bubbles created during resin curing

Figure 8   Sectioned product showing cracking in cured resin

Figure 9   Encapsulated IONSIV beads

At larger scales, the temperatures generated during resin curing can be significantly higher, a potential issue recognised when considering the use of organic polymers to encapsulate fuel and fuel-bearing materials retrieved from the legacy ponds at Sellafield, for which the use of a 3 cubic metre box was proposed (Section 6.2.2). Trial pours of an epoxy resin, which had been formulated to have a relatively low heat generation during curing, were made at the 100, 200 and 500 litre scales and resulted in peak measured temperatures of 49, 185 and >260°C respectively, with the products from the two largest trials exhibiting charring of the cured resin [31].

This work indicates that heat generation during curing can be a problem for thermosetting polymer encapsulation processes at the waste package scale (i.e. >100 litres) but less so for smaller volumes. With further R&D work, it might be possible to develop polymer formulations and pouring methods that prevent excessive heat generation at the waste package scale. For example, ultra-low heat generating polymers could be developed[7]; inert 'filler' materials could be added to a polymer to reduce the amount of heat generated and to act as a heat sink during curing; or multiple pours could be used to fill a single waste package.

5.1.2 Gel and set times

The curing of organic polymers is typically characterised in terms of gel and set times. The gel time is often defined as the time taken for the polymer to change from a liquid to a soft but solid gel, and the set time may be defined as the time taken to reach some predetermined measure of hardness. Gel time may be of practical importance in determining how long a batch of polymer can be kept in a useable condition (*i.e.* the working time of the polymer), while both gel and set times may be an important influence on the throughput rates of a waste encapsulation process (it may not be possible to move a waste package out of the filling stage of a process until the polymer has set or at least gelled).

In a waste encapsulation process, there may be a balance to be struck between having a long enough working time to pour a batch of mixed polymer (including allowance for any hold-ups) and having a short enough gel/set time to maintain process throughput. Also, there is usually a trade-off between heat generation and gel/set times, with formulations designed to generate less heat typically taking longer to gel and set. For example, in some 25-kg scale trials with four types of epoxy resin, gel and set times in the region of 3 and 4 hours, respectively, were accompanied by maximum curing temperatures as high as 200°C; more acceptable curing temperatures in the range 40-64°C were obtained at the expense of longer gel times of 15-46 hours and set times of 145-240 hours [32].

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7   Care would need to be taken in any small-scale R&D work with such polymers because of scale-up effects. A polymer that gave acceptable heat generation at large-scale might take a very long time to set in small-scale trials.

5.1.3 Compatibility with waste components

One of the key advantages of organic polymers for the conditioning of ILW is their general compatibility with reactive metals such as Magnox, aluminium and uranium. However, reactions with some waste materials can deleteriously affect the curing of thermosetting polymers by, for example accelerating or retarding the 'gelling' of the polymer. This can have consequences for the ability of the conditioning process to achieve the required wasteform properties and performance. Other interactions between the curing polymer and components of the waste can have undesirable consequences; the example of water vaporisation and the creation of bubbles and/or wasteform foaming is noted above.

A number of epoxy resins were tested for their compatibility with a variety of waste materials as part of the R&D work associated with plans to package fuel and isotope cartridges from the Windscale Piles (Section 6.2.1). Waste simulants included uranium, aluminium, steel and graphite; and the parameters measured included resin gel and set times, curing exotherms, and product compressive strength and shrinkage [32]. The trials found no significantly detrimental effects from any of the waste materials on any of the parameters measured.

In inactive trials performed to support work on the packaging of fuel and fuel-bearing materials from the Sellafield legacy ponds (Section 6.2.2), some effects on gel time and curing exotherm were observed with aluminium, Magnox and corroded Magnox sludge (CMS), but a more serious effect was the foaming that was observed with a combination of either aluminium or Magnox with CMS (Figure 10) [31]. The foaming appears to have been a result of hydrogen generation from reaction between the aluminium (or Magnox) and water in the CMS, perhaps accelerated by the temperature rise caused by curing of the epoxy resin.

Figure 10   Foaming observed during epoxy resin encapsulation of aluminium and CMS

Similar foaming effects have also been observed in experiments performed with only epoxy resin and water, due to vaporisation of the water as a result of heat evolution during resin curing. Figure 11 shows foaming that occurred during the curing of an epoxy resin containing 1.5-4% water [32].

Figure 11   Foaming observed during curing of epoxy resin containing water
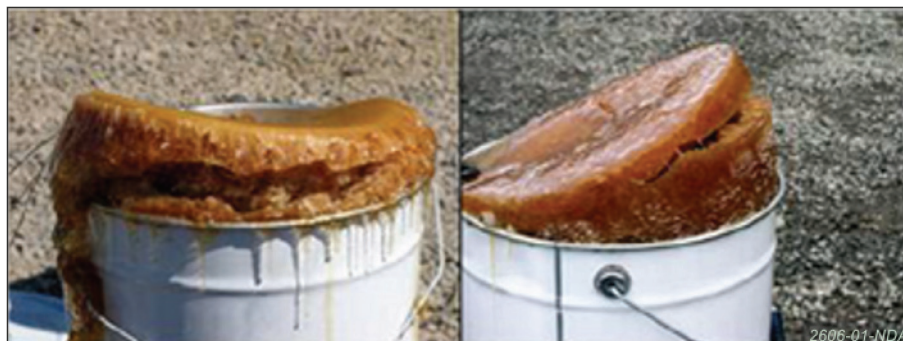
Although water can clearly present problems during certain thermosetting polymer encapsulation processes, in some cases it has been possible to develop processes that are tolerant of residual water. The VES process that has been used for many years to

encapsulate ion exchange resins at Trawsfynydd, for example, uses a polymer formulation and mixing process designed to incorporate water into the final product (Section 4.4.3).

Another example is the process developed to encapsulate SCRUs (Section 6.1.1), in which residual water was displaced from the bed of IONSIV beads by an upward flow of polymer during the encapsulation process.

In general, R&D work has shown that polyester and epoxy resins are compatible with a broad range of dry materials that commonly appear in ILW. The presence of water in waste can, however, cause problems if the polymer and conditioning process has not been designed to accommodate and tolerate the water.

5.1.4 Void filling

Another advantage of thermosetting polymers is that prior to curing, they are single phase liquids that can be formulated to have a very low viscosity. This makes them attractive as materials for encapsulating wastes that are not easy to infiltrate. The non-aqueous nature of organic polymers can also improve their effectiveness when encapsulating hydrophobic materials (e.g. graphite powder) because of their ability to 'wet' such materials.

Inactive trials performed as part of the project to develop encapsulation processes for fuel and fuel-bearing materials from the Sellafield legacy ponds have demonstrated the infilling performance that can be obtained from organic polymers. The trials used simulated uranium metal fuel fragments and associated debris, cemented fuel fragments and punctured steel bottles. All were found to be well infiltrated by the epoxy resins tested, and in many cases the infiltration obtained was better than with cement (Figure 12) [31].

The effectiveness of thermosetting polymers at infiltrating wastes has been demonstrated by the encapsulation of SCRUs with VES. Figure 9, shows how the resin was able to completely infiltrate a bed of IONSIV beads, enclosed within a 50μm steel mesh, inside a steel cartridge body.

VES has been used to encapsulate the contents of cans of radium bearing wastes at RSRL (Section 6.3.1) by the simple expedient of pouring the polymer through a hole cut in the lid of the can [33]. Figure 13 shows a sectioned can of simulated wastes and illustrates a very high degree of infiltration of the waste by the polymer. The supporting development work also demonstrated the advantages of 'tailoring' the polymer formulation to provide low viscosity. This resulted in a change from vinyl ester to epoxy resin with a very low viscosity formulation for the encapsulation of the actual radium-contaminated wastes (Section 6.3.1).

Figure 12   Polymer infiltration of simulated uranium metal fuel fragments and associated corrosion debris

Figure 13   Sectioned can of simulated radium bearing wastes infilled with polyester resin

5.1.5 Flammability

Many polyester resins carry the intrinsic hazard that the uncured resin is flammable. The low flash point of the styrene component of VES resins has been invoked as a reason for preferring epoxy resins for use in the packaging of ILW [32].

5.1.6 Cost

In a comparison of the costs of alternative encapsulation matrices for Sellafield legacy ponds fuel and fuel-bearing materials, the cost of an epoxy resin was quoted as £24,500 per tonne, compared with a cost of only £100-200 per tonne for cement [31]. Some things may, however, at least partially redress or off-set this difference in price: for example, polymers may be somewhat cheaper if procured on a large scale; the use of inorganic fillers could reduce the amount of polymer needed; and it may be possible in some cases to achieve higher waste loadings with polymer than with a cement. For more specialist applications (e.g. the encapsulation of relatively small volumes of radium-bearing wastes) it may also be the case that this cost difference is unimportant, especially if the use of epoxy resin serves a specific purpose in the overall waste package design.

5.2   Properties and performance

### 5.2.1 Cracking of cured wasteform matrix

Wasteform cracking, as a result of thermal stresses as a thermosetting resin cools after curing, is a phenomenon that has been observed during the development of polymer based conditioning processes for ILW (Section 6.1.1). Such cracking could potentially have a number of undesirable consequences for waste packages, for example they could allow atmospheric moisture to access reactive metals, or undermine the ability of a wasteform to restrict the release of radioactive gases such as radon.

Cracking is usually observed in regions of a wasteform that consist essentially entirely of polymer, due to the relatively high curing temperatures and thermal stresses that are

created in such regions. This is illustrated in Figure 8 for a polymer encapsulated SCRU, which also shows that when the polymer and the waste are more interspersed cracking is not observed.

Another potential cause of cracking is heat generation by the waste itself during polymer curing. Wigner energy released from irradiated graphite during its encapsulation in thermosetting resins was a topic of interest for a project that investigated packaging solutions for decommissioning wastes from the Windscale Piles. The potential for Wigner energy release to cause cracking of an epoxy resin encapsulating matrix was investigated in an inactive R&D trial in which a heating element was encapsulated in resin [32]. Cracking around the heating element was indeed observed, but it was found that the cracks could be filled with a second pour of epoxy resin onto the top surface of the cured wasteform. Figure 14 shows a sectioned epoxy-encapsulated heating element where a second resin pour (coloured yellow) was able to penetrate into the cracks in the original matrix.

Figure 14   Sectioned epoxy-encapsulated heating element, showing filled cracks in wasteform matrix
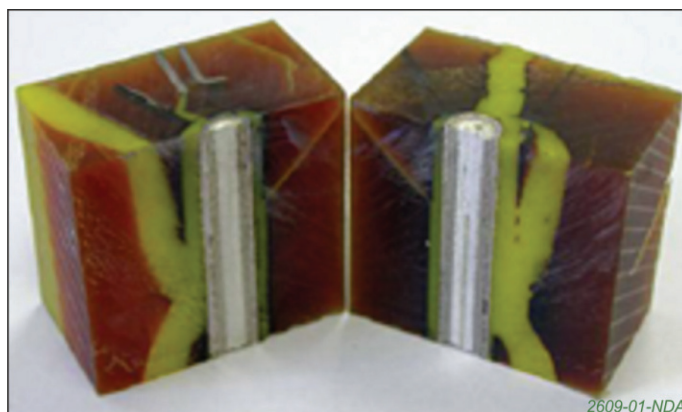

A similar solution to wasteform cracking was used in inactive R&D trials involving the encapsulation of simulated Windscale Piles fuel and isotope cartridges in epoxy resin [32]. In these trials, a layer of cement capping grout was poured onto the top of the cured polymer wasteform. As shown in Figure 15 the yellow-coloured grout was able to penetrate down into the cracks in the original matrix.

5.2.2   Radiolytic gas generation

Radiolytic degradation of organic polymers can produce gases which have the potential for a number of undesirable consequences, notably the maintenance of physical integrity of the wasteform (i.e. cracking) and resulting consequences for the performance of the waste package (e.g. accident performance).

Work has been carried out to investigate the radiolysis of a range of polymers (one polyester resin and three epoxy resins) by gamma radiation and this included measurements of gas generation [34, 35]. For the epoxy resins, hydrogen was the most abundant gas generated and for the polyester resin appreciable quantities of carbon monoxide and dioxide were also generated. Table 1 presents the range of $G(H_2)$ values measured for the four polymers tested and shows that, in all cases, the measured values were relatively modest, and those for the polyester resin were markedly lower than those for the epoxy resins. For comparison, a typical $G(H_2)$ value for cement is ~0.1.

Figure 15   Sectioned polymer wasteform, showing penetration of capping grout into cracks

2610-01-NDA
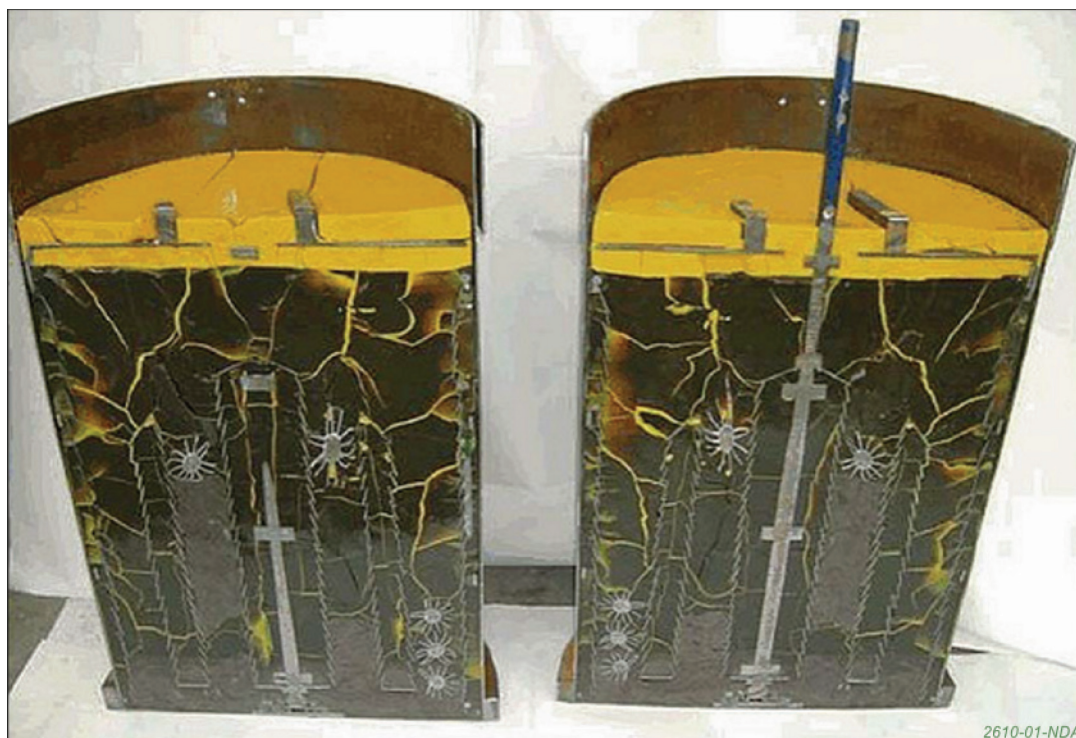
5.2.3 Wasteform gas permeability

Organic polymers can be very effective barriers to the transport of gases, a property which can be very useful in some LHGW conditioning applications. One notable example is for radium bearing wastes where the release of radioactive radon gas from waste packages could result in dose to transport and GDF operators, and members of the public.

Data from R&D trials on radon emanation was cited in support of proposals to encapsulate radium-contaminated wastes in VES by RSRL (see Section 6.3.1) [36]. A radon emanation coefficient ratio (i.e. the emanation rate for the conditioned waste as a ratio of that for the unconditioned waste) was only ~2×10^{-3}, a factor of ~7 lower than that measured for the same type of waste encapsulated using cement.

Organic polymers have also been suggested as a means of reducing gaseous tritium emanation from packages containing decommissioning wastes from the Joint European Torus (JET) fusion device at Culham.

**Table 1   Measured G(H$_2$) values for gamma irradiated polymers**

Polymer	Range of G(H$_2$) values (molecules per 100eV)
Diversified Technologies epoxy resin	0.43 - 0.55
Alchemie epoxy resin	0.19 - 0.37
Huntsman epoxy resin	0.33 - 0.44
Diversified Technologies VES	0.04 - 0.09

5.2.4 Wasteform leach rates

Encapsulation in an organic polymer may, at least in the short-term, be able to reduce the rate of leaching of radioactivity from a waste, because many polymers have a low permeability to water. This may offer some benefit in terms of restricting the mobility of radioactivity in a GDF, although it may be questionable whether any such benefits can be relied upon for any appreciable length of time after final disposal.

Samples of epoxy resins doped with inactive caesium, strontium and cerium (the latter as a surrogate for plutonium) have been leach tested for up to 180 days, and little or no release of the doped species was observed from most of the samples [32]. Leach tests have also been performed on cerium-doped simulants of AWE pyrochemical residues (see Section 6.4) encapsulated in cement and epoxy resin [37]. The results are reproduced here in Figure 16, where the amount of cerium released from epoxy and cement encapsulated simulated waste is expressed as a percentage of that released from unencapsulated simulated waste under the same conditions. The results show that both cement and epoxy encapsulation greatly reduced cerium leaching up to 90 days, but that cement was actually more effective than epoxy over that timescale.

Figure 16   Results of leach tests for encapsulated pyrochemical residues
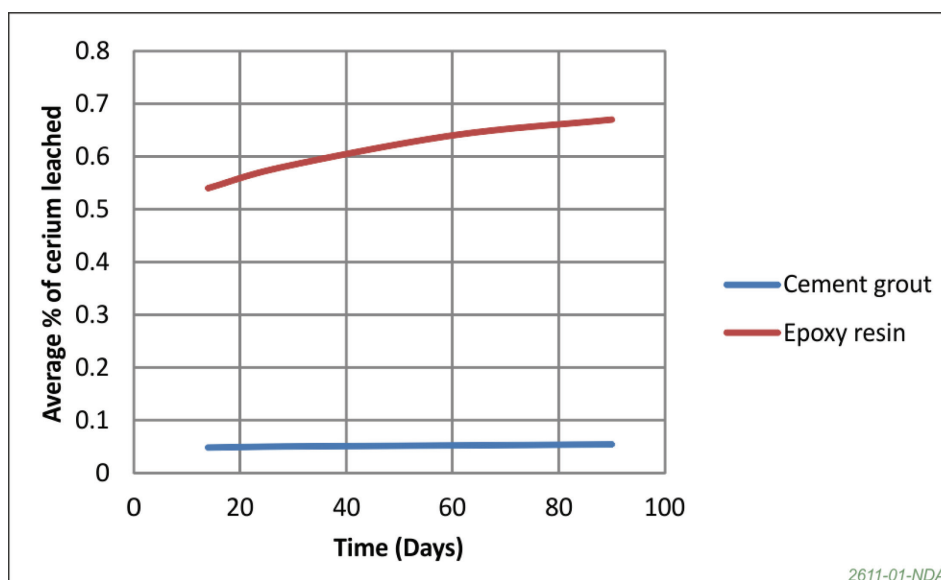
5.2.5 Fire accident performance

Large-scale fire testing of simulated wasteforms with polyester encapsulants has been carried out and has shown that they exhibit similar performance to cementitious wasteforms with low activity loss and good maintenance of wasteform integrity following fires with severities representative of those that could occur during GDF operations [38, 39].

As part of the project to develop processes for the encapsulation of Windscale Piles fuel and isotope cartridges (see Section 6.2.1), a sample of epoxy resin was exposed to a 60 second flame test. Figure 17 shows that the sample suffered little damage, which was restricted to the region immediately affected by the flame. Transfer of heat through the sample was found to be limited, confirming that the polymer is a good thermal insulator.

Figure 17   Epoxy resin sample after flame test
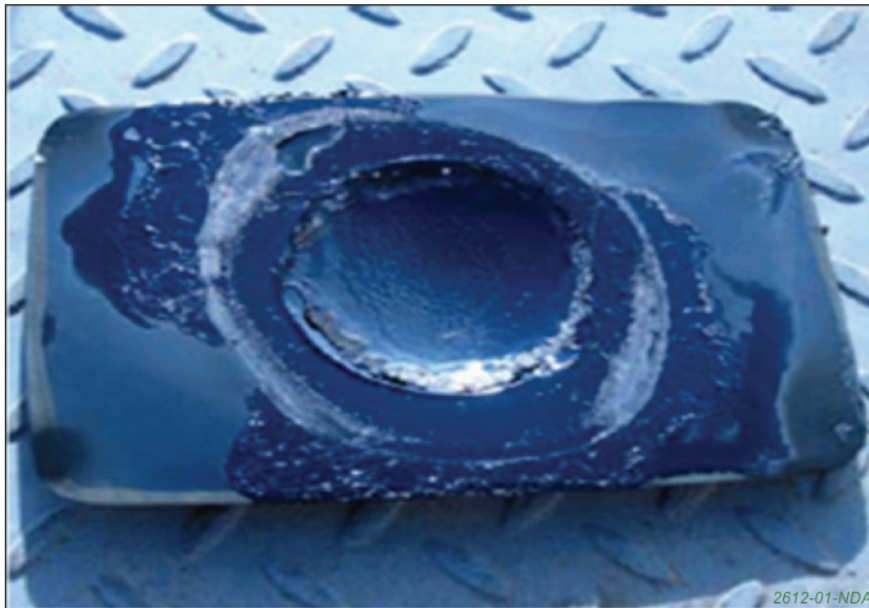
5.3   Evolution and degradation

5.3.1   Radiolytic degradation

The materials used in the conditioning of LHGW can accumulate considerable radiation doses as a result of the radiation emitted by the radionuclides in the wastes as well as from neighbouring waste packages during interim storage (when dose rates will be at their highest) and following emplacement in the GDF. The ability of a wasteform to withstand such irradiation without serious deterioration in its properties and performance is an important criterion in the selection of the conditioning materials. Work has shown that cements are generally very tolerant to radiation dose but that organic materials, such as PVC, are less so [40].

Work to investigate the radiation stability of a number of thermosetting resins has shown that samples of IONSIV ion exchange material encapsulated in VES remain physically stable under gamma irradiation doses of up to 150MGy, with the only visible effects being some discolouration and radiation 'burn' marks [41]. In other tests, samples of one VES resin and two epoxy resins (APS resin supplied by Diversified Technologies Inc. and Huntsman resin) were subjected to gamma irradiation doses of up to 10MGy [34]. The visual appearance of the samples with increasing dose is shown in Figures 18 and 19. There was some discolouration of all of the samples and whilst two of the samples (the VES and the APS epoxy resin) remained physically stable, the other epoxy resin (Huntsman) visibly degraded, becoming softer and distorted to a considerable extent at a dose of 10MGy. Compressive and flexural strength tests were performed on the irradiated samples, and the results are reproduced in Table 2 [34]. This shows that the APS epoxy resin had much lower compressive and flexural strengths than the Huntsman epoxy resin in the unirradiated state, but retained its strength much better after irradiation. The mean compressive strength of the APS epoxy resin was actually increased by irradiation, but its flexural strength was much reduced at 10MGy. Such a loss of flexural strength could be important to how a conditioning material would behave under tensile stresses in the event of impact accidents involving waste packages. The compressive and flexural strengths of the VES were little affected by irradiation up to 10MGy, although it was noted in a more detailed analysis that the results obtained at 10MGy suggested the onset of a change in the properties of the resin [34].

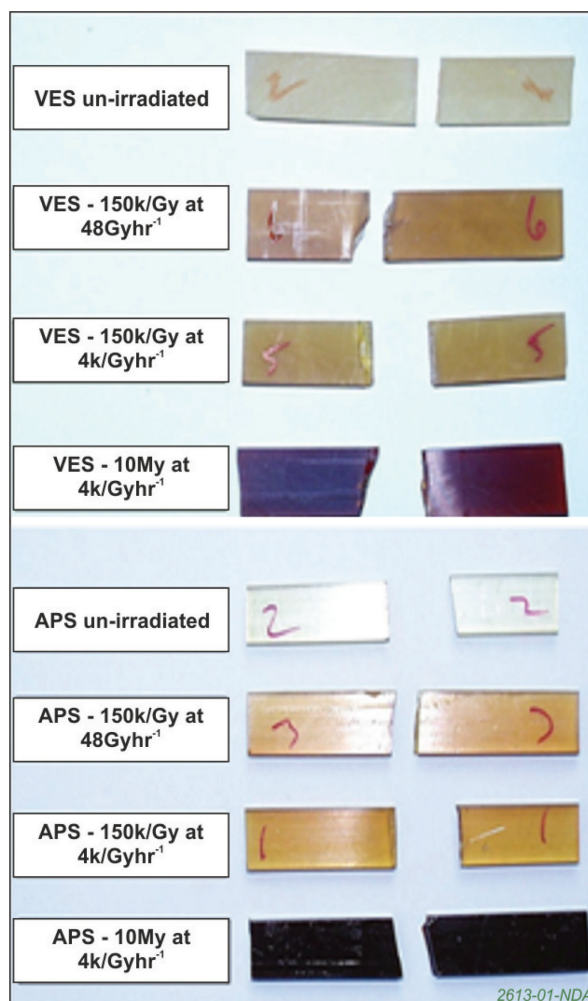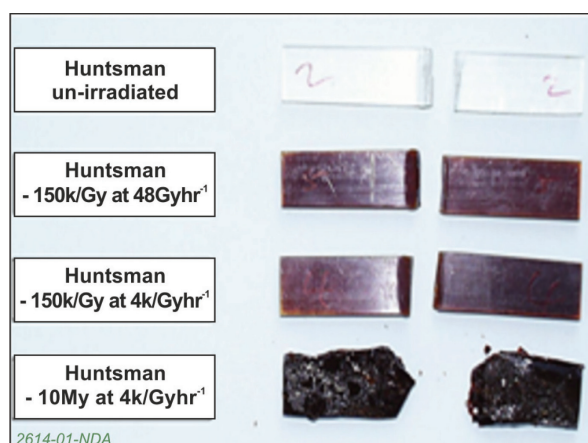**Figure 18   VES samples irradiated to 10 MGy**

Figure 19   Epoxy resin samples irradiated to 10 MGy

It is difficult to draw confident parallels from tests performed at high dose rates to real life situations in which doses would be accumulated much more slowly. Notwithstanding this, it is clear that some organic polymers can tolerate the levels of dose likely to be accumulated by most LHGW wasteforms. However, the R&D work discussed above demonstrates that generalisations cannot be made about the radiation tolerance of polymers and that proposals to use specific resins will need to be supported by evidence of their radiation stability.

Table 2   Compressive and flexural strength test results for irradiated polymer samples

Resin type	Gamma dose (MGy)	Mean compressive strength (MPa)	Mean flexural strength (MPa)
APS (Epoxy)	0	81	35
	0.15	108	36
	10	112	70
Huntsman (Epoxy)	0	210	96
	0.15	215	97
	10	No test possible	No test possible
VES	0	123	108
	0.15	182	115
	10	107	112

5.3.2 Generation of complexants in a GDF

The possibility of organic complexants being generated by polymers and released from waste packages, and thereby possibly significantly affecting the mobility of radionuclides in a GDF near-field, has been raised during discussions regarding the use of polymers for the conditioning of LHGW. Some trials have been performed to investigate the leaching of organic compounds from candidate polymer conditioning materials in aqueous solutions at various temperatures, and after varying degrees of gamma irradiation [34, 35, 42]. Varying amounts of leached organic material were detected in the trials but it has not been determined whether any of those materials would have the potential to significantly affect radionuclide mobility in the GDF environment. As stated above, proposals to use particular polymers for the conditioning of LHGW will have to be supported by the results of suitable trials of their performance under simulated GDF conditions.

6 Disposability assessments involving the use of organic polymers as conditioning materials

This section presents information obtained from a number of disposability assessments of proposals to condition a range of different types of ILW using organic polymers. In presenting information from the selected submissions and assessments, it illustrates how the principles discussed in the preceding section have been applied to the development of proposals for the packaging of real waste.

6.1 Magnox reactor sites

6.1.1 Submersible caesium removal units

SCRUs have been used as a means treating spent fuel cooling pond water treatment at a number of Magnox stations to reduce operator dose due to dissolved radioactive caesium. They consisted of a stainless steel body containing an annular shaped bed of beads of caesium-selective ion exchange material (known as IONSIV) constrained by a 50µm metallic mesh. The SCRUs, which have an overall volume of ~40 litres, operate by drawing pond water into the centre of the annulus, passing it through the inner retaining mesh, through the IONSIV bed and out through the outer retaining mesh.

When the caesium removal capacity of an SCRU is exhausted, it is removed from service and stored pending packaging as ILW. Conditioning the SCRUs for disposal presents a number of challenges. The high external dose rate from the SCRUs led to a preference for an in-situ conditioning method which required some means of infiltrating the bed of IONSIV beads inside the SCRU with a suitable conditioning matrix. This challenge was compounded by the presence of the mesh surrounding the IONSIV bed, through which the conditioning material would have to pass.

Cements had little chance of meeting this challenge, and initial trials with a PFA/OPC grout were unsuccessful, so attention was turned to the use of an organic polymer. The polymer chosen was a VES, a type of polyester resin, similar to the one that had been used for several years to condition ion exchange resins at the Trawsfynydd Magnox reactor site. Inactive full scales trials were carried out on an unused SCRU, the effectiveness of the encapsulation of the IONSIV beads being illustrated in Figure 9.

A proposal by Magnox to use the process for the packaging of active SCRUs was assessed in 2004 and endorsement at the Conceptual stage provided.

6.1.2 Compacted Magnox fuel element debris

Fuel element debris (FED) is generated at several Magnox sites during the preparation of fuel for transport to Sellafield for reprocessing. FED, which comprises Magnox metal in a variety of shapes was generally loose-tipped into storage vaults for future retrieval and packaging. At Trawsfynydd power station some FED was compacted into 500 litre stainless steel drums and stored in that form (Figure 20).

The preferred approach to convert the drums of FED into a disposable product was in-situ encapsulation. It was concluded that the use of a cement would not be a suitable option as the compacted FED could be difficult to infiltrate and also chemical reactions between the cement and Magnox, which would result in the generation of gas, might jeopardise the long-term integrity of the wasteform. As a result the use of a VES polymer, the same as that used proposed for use with the SCRUs (see above) was proposed.

Small scale trials were carried out with simulated FED and the results of this work were used to support a proposal to use the process for the packaging of the FED. Assessment resulted in endorsement of the proposal by way of the issue of a Conceptual stage LoC.

Figure 20   Compacted Trawsfynydd FED

6.2   Sellafield Ltd

6.2.1 Windscale Piles fuel and isotope cartridges

The two Windscale piles, which operated between 1950 and 1957, were graphite moderated, air-cooled reactors built to produce plutonium for the UK defence programme as well as radioisotopes for defence, research and commercial purposes. Following their closure, most of the fuel and isotope cartridges were removed from the piles and placed in ponds awaiting packaging for disposal.

The fuel cartridges (Figure 21) consisted of uranium metal rods, ~300mm long and 25mm in diameter, clad in aluminium and the isotope cartridges comprised aluminium cans with similar dimensions but without the cooling fins, and containing a variety of materials (e.g. aluminium nitride). Most of the fuel and isotope cartridges were essentially intact, although some were damaged to a varying degree as a result of the fire that occurred in Pile 2 in 1957. Because of their relatively low irradiation and 50+ years cooling the fuel and isotope cartridges are considered as ILW for the purposes of their disposal.

The preferred approach to the conditioning of the cartridges involved placing them into 360 litre liners which would be backfilled with either cement or an unspecified organic polymer; the liners would then be grouted into 500 litre drums to produce disposable waste packages. The disposability assessment of these two proposed approaches resulted in the Conceptual stage endorsement of the option using an organic polymer, but not that using cement. The main reason for this decision was that it was believed that the potential for chemical reactions between cement and aluminium cladding and/or uranium metal would result in a deterioration of the properties of the wasteform during interim storage and a loss of the required waste package performance.

Following this decision a significant amount of inactive R&D work was undertaken to investigate the use of a number of organic polymers for the conditioning of both intact and damaged fuel and isotope cartridges. Four polymers were investigated; VES and three different epoxy resins, the results of which are discussed in Section 4.6.

Figure 21   Windscale Piles fuel cartridge

6.2.2 Legacy Ponds fuel and fuel bearing materials

The Legacy Ponds at Sellafield contain a variety of fuel and fuel-bearing materials that have been stored under water for a considerable time. This material includes largely intact Piles fuel cartridges and Magnox fuel elements together with declad, damaged and degraded fuel, pieces of uranium metal and aluminium and Magnox swarf stored in skips.

A variety of treatment and encapsulation techniques for dealing with these wastes have been considered including cements and, because of the presence of large quantities of reactive metals (i.e. Magnox, aluminium and uranium), organic polymers. Building on the work done for Windscale Piles fuel and isotope cartridges (see previous sub-section), a considerable amount of inactive R&D work was done to test two epoxy resins with materials intended to simulate the legacy ponds fuel and fuel-bearing materials. The results of some of this work are discussed in Section 4.6.

A proposal was submitted for the packaging of a wide range of Legacy Ponds fuel and fuel-bearing materials, involving the encapsulation of a range of wastes within skips and liners, for subsequent placing in 3 cubic metre boxes, using a range of encapsulants including cements, magnesium phosphate cement and an unspecified epoxy resin. The proposals were not endorsed for a variety of reasons, including some specific uncertainties about the potential use of epoxy resins in the proposed application, notably the ability to produce epoxy-encapsulated wasteforms at such a large scale and the radiation stability of the epoxy resin at the high doses that would be produced by irradiated fuel.

Subsequently, a review of the potential encapsulating materials for the legacy ponds fuel and fuel-bearing materials was undertaken [31]. This concluded that epoxy resin should not be considered any further for this particular application, because of the risk that it might not prove possible to resolve the outstanding technical uncertainties, notably the effects of excessive heat generation during curing of the resin at such a large scale, and the effects of residual water in the waste on the behaviour of the resin during curing.

6.3 RSRL

6.3.1 Radium-contaminated wastes

The presence of radium-226 in waste presents a particular challenge to the conditioning of that waste for disposal due to the generation of the gaseous radionuclide radon-222. Some of the ILW accumulated at Harwell contained wastes contaminated with considerable amounts of radium-226. In order to manage discharges to the atmosphere of radon-222 during the on-site storage of the wastes, they were put into welded stainless steel cans of various sizes up to about 19 litre capacity. Some of the welded cans contained inner cans of waste of various sizes up to 5 litre capacity. A photograph of one of the welded cans with its lid cut off and lifted to reveal the cans of waste inside is shown in Figure 22.

Figure 22   Storage can containing radium-bearing waste

The 'radium-contaminated wastes' were made up of a very diverse mixture of materials generated during the operation, post-operational clean out and decommissioning of active cells. This included rubber gloves, paper tissues, glassware, pipework, cotton wool and floor sweepings, these materials being typically packed tightly into the storage cans. During the development of plans to package these wastes for disposal a number of concerns were raised about the presence of voidage and loose particulate, and regarding the pressurisation of the sealed cans by radon and radiolytically generated gases. The preferred option for dealing with these concerns was to condition the wastes by in-situ encapsulation within the existing storage cans. Achieving good infiltration of the tightly packed waste within the cans in order to minimise voidage and immobilise radioactive particulate material was a key aim for an in-situ encapsulation process. Also, there were limits on the tolerable rate of release of radon-222 from the cans after they had been encapsulated, which were dictated by requirements relating to on-site storage and future waste package transport and handling. Thus, an encapsulation matrix that could provide hold-up of radon-222[8] was desirable.

Cement grout and an organic polymer were tested in inactive R&D trials that looked into how well the wastes could be infiltrated and immobilised, and how effective the encapsulation matrices were in reducing radon emanation. The polymer chosen was the same VES that had been tested previously for encapsulating SCRUs and FED (see earlier sub-sections).

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[8]   The half-life of radon-222 is only ~3.8 days which means that significant benefits can result from relative short hold up times.

A proposal to package a wide range of wastes, including those contaminated with radium-226 was submitted, assessed and endorsed with a Final stage LoC. The terms of the endorsement included a requirement that, whilst cement grout would be the default encapsulation material, VES would be used for cans with particularly large radium-226 inventories, together with those judged likely to be difficult to infiltrate with grout.

6.3.2 GLEEP fuel elements

The Graphite Low Energy Experimental Pile (GLEEP) was an air-cooled, graphite moderated reactor that was operated at Harwell from 1947 until 1990. Some of the used fuel elements from GLEEP were reprocessed at Sellafield, but others were left in storage at Harwell. All of the stored elements consisted of uranium metal bars clad in aluminium. Various designs of element were used in GLEEP, but all were roughly ~300mm in length and 25mm in diameter, they were stored in 23 litre cans (Figure 23). The low irradiation of GLEEP fuel meant that it was classed as ILW for the purposes of disposal.

Figure 23   GLEEP fuel elements being loaded into a storage can
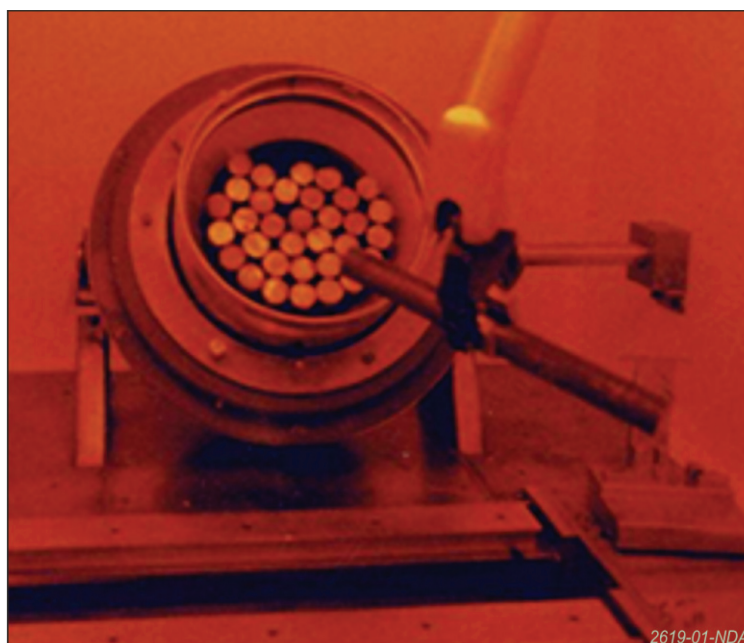
It was originally proposed that GLEEP fuel should be packaged in 500 litre drums using a cement grout. However concerns were raised during the disposability assessment of this proposal over the potential for chemical reactions between the cement and aluminium cladding and/or uranium metal, and the effects that this could have on the long term properties of the wasteform and the performance of the waste packages. Consequently, trials were undertaken on the encapsulation of dummy GLEEP fuel elements within a storage can using epoxy resin, the intention being to place the storage cans within 500 litre drums backfilled with cement grout. The results from this work were used to support a further submission for disposability assessment, which resulted in the endorsement of the proposed packaging approach by way of the issue of a Final stage LoC.

6.4   Atomic Weapons Establishment

6.4.1 Pyrochemical residues

The operation of processes involving the purification of plutonium has resulted in the accumulation of a quantity of plutonium contaminated chloride salts and ceramic crucible fragments that are collectively known as 'pyrochemical residues' (Figure 24).

Figure 24   Simulated pyrochemical residues

The proposed packaging approach involved grinding the contaminated salts and crucible fragments and mixing the resulting powder with epoxy resin in 18 litre cans. The cans would then be cement encapsulated in 500 litre drum prior to disposal. This proposal was the subject of a disposability assessment which resulted in the issue of a Conceptual stage LoC endorsing the approach.

7   Summary

The safety of the geological disposal of radioactive waste is predicated on the containment of the radionuclides present in the wastes by multiple barriers, one of which could be provided by an encapsulating material used to immobilise those radionuclides. Such materials, when combined with the waste, will be required to provide a range of wasteform properties, so that adequate waste package performance can be achieved. Those properties include physical robustness, the ability to survive credible accident scenarios without unacceptable releases of radioactivity and the provision of a physical barrier to the release of radionuclides from the waste package during the GDF post-closure period. The materials used should also contribute to, or at least not unduly undermine, the chemical containment of radionuclides provided by the EBS.

By virtue of their relative cheapness and ready availability, the materials most used for the encapsulation of ILW in the UK have been inorganic cements. Those materials have many desirable properties when used for this purpose, including excellent mechanical, physical and thermal stability, tolerance to a wide range of waste types, and compatibility with systems buffered at high pH, which allows them to make a significant contribution to the chemical containment function of the EBS.

To date, organic polymers have not been widely used in the packaging of ILW in the UK. A number of waste producers have considered their suitability for the packaging of certain challenging wastes for which cement encapsulants may not be suitable. This has notably included wastes containing significant quantities of reactive metals, radium-bearing wastes, and filters whose physical properties make adequate infiltration by a cement encapsulant difficult.

This Guidance has identified three polymeric materials (i.e. polyethylene, epoxy resin and polyester resin) which are deemed by RWM to be suitable for the conditioning of ILW. Two others (i.e. bitumen and urea-formaldehyde resin), have a number of potentially significant drawbacks, which could preclude the endorsement of packaging proposals involving their use (although they may be suitable for more small-scale use with particular waste types).

Waste producers have conducted extensive R&D work regarding the possible use of polymer encapsulants for the packaging of specific wastes, and the outcomes of this work are used to underpin the potential suitability of the three selected polymers. In some cases this work has been used to support submissions for the disposability assessment of proposals to package those wastes, in others it has identified the potential problems that could arise from the use of polymer encapsulants. This work has shown that whilst the use of polymer encapsulants may not be the optimum approach for all wastes types, there are potential applications for certain specific wastes types, as part of an overall approach to the packaging of a waste stream (i.e. for the conditioning of discrete parts of the stream for which cement encapsulation is not suitable) and/or on a small scale for particular problematic wastes.

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Glossary of terms used in this document

alpha activity

Alpha activity takes the form of particles (helium nuclei) ejected from a decaying (radioactive) atom. Alpha particles cause ionisation in biological tissue which may lead to damage. The particles have a very short range in air (typically about 5cm) and alpha particles present in materials that are outside of the body are prevented from doing biological damage by the superficial dead skin cells, but become significant if inhaled or swallowed.

backfill

A material used to fill voids in a GDF. Three types of backfill are recognised:

- local backfill, which is emplaced to fill the free space between and around waste packages;

- peripheral backfill, which is emplaced in disposal modules between waste and local backfill, and the near-field rock or access ways; and

- mass backfill, which is the bulk material used to backfill the excavated volume apart from the disposal areas.

backfilling

The refilling of the excavated portions of a disposal facility after emplacement of the waste.

barrier

A physical or chemical means of preventing or inhibiting the movement of radionuclides.

beta activity

Beta activity takes the form of particles (electrons) emitted during radioactive decay from the nucleus of an atom. Beta particles cause ionisation in biological tissue which may lead to damage. Most beta particles can pass through the skin and penetrate the body, but a few millimetres of light materials, such as aluminium, will generally shield against them.

conditioning

Treatment of a radioactive waste material to create, or assist in the creation of, a wasteform that has passive safety

container

The vessel into which a wasteform is placed to form a waste package suitable for handling, transport, storage and disposal.

containment

The engineered barriers, including the waste form and packaging, shall be so designed, and a host geological formation shall so be selected, as to provide containment of the waste during the period when waste produces heat energy in amounts that could adversely affect the containment, and when radioactive decay has not yet significantly reduced the hazard posed by the waste

disposability

The ability of a waste package to satisfy the defined requirement for disposal.

disposability assessment

The process by which the disposability of proposed waste packages is assessed. The outcome of a disposability assessment may be a Letter of Compliance endorsing the disposability of the proposed waste packages.

disposal

In the context of solid waste, disposal is the emplacement of waste in a suitable facility without intent to retrieve it at a later date; retrieval may be possible but, if intended, the appropriate term is storage.

disposal facility (for solid radioactive waste)

An engineered facility for the disposal of solid radioactive wastes.

disposal system

All the aspects of the waste, the disposal facility and its surroundings that affect the radiological impact.

disposal vault

Underground opening where ILW or LLW waste packages are emplaced.

dose

A measure of the energy deposited by radiation in a target.

dose rate

The effective dose equivalent per unit time. Typical units of effective dose are sievert/hour (Svh^{-1}), millisieverts/hour ($mSvh^{-1}$) and sievert/year (Svy^{-1}).

emplacement (of waste in a disposal facility)

The placement of a waste package in a designated location for disposal, with no intent to reposition or retrieve it subsequently.

gamma activity

An electromagnetic radiation similar in some respects to visible light, but with higher energy. Gamma rays cause ionisations in biological tissue which may lead to damage. Gamma rays are very penetrating and are attenuated only by shields of dense metal or concrete, perhaps some metres thick, depending on their energy. Their emission during radioactive decay is usually accompanied by particle emission (beta or alpha activity).

geological disposal

A long term management option involving the emplacement of radioactive waste in an engineered underground geological disposal facility or repository, where the geology (rock structure) provides a barrier against the escape of radioactivity and there is no intention to retrieve the waste once the facility is closed.

geological disposal facility (GDF)

An engineered underground facility for the disposal of solid radioactive wastes.

hazardous materials

Materials that can endanger human health if improperly handled. As defined by the Control of Substances Hazardous to Health Regulations, 2002.

higher activity radioactive waste

Generally used to include the following categories of radioactive waste: low level waste not suitable for near surface disposal, intermediate level waste and high level waste.

immobilisation

A process by which the potential for the migration or dispersion of the radioactivity present in a material is reduced. This is often achieved by converting the material to a monolithic form that confers passive safety to the material.

intermediate level waste (ILW)

Radioactive wastes exceeding the upper activity boundaries for LLW but which do not need heat to be taken into account in the design of storage or disposal facilities.

International Atomic Energy Agency (IAEA)

The IAEA is the world's centre of cooperation in the nuclear field. It was set up as the world's "Atoms for Peace" organization in 1957 within the United Nations family. The Agency works with its Member States and multiple partners worldwide to promote safe, secure and peaceful nuclear technologies.

Letter of Compliance (LoC)

A document, prepared by RWM, that indicates to a waste packager that a proposed approach to the packaging of waste would result in waste packages that are compliant with the requirements defined by relevant packaging specifications, and the safety assessments for transport to and disposal in a GDF, and are therefore deemed 'disposable'.

low heat generating wastes (LHGW)

A broad category of wastes, generally characterised by relatively low heat output and for which a single geological disposal concept would be employed. LHGW includes ILW, LLW and wastes with similar radiological properties.

low level waste (LLW)

Radioactive waste having a radioactive content not exceeding 4 gigabecquerels per tonne (GBq/t) of alpha or 12 GBq/t of beta/gamma activity.

Managing Radioactive Waste Safely (MRWS)

A phrase covering the whole process of public consultation, work by CoRWM, and subsequent actions by Government, to identify and implement the option, or combination of options, for the long term management of the UK's higher activity radioactive waste.

Nuclear Decommissioning Authority (NDA)

The NDA is the implementing organisation, responsible for planning and delivering the GDF. The NDA was set up on 1 April 2005, under the Energy Act 2004. It is a non-departmental public body with designated responsibility for managing the liabilities at specific sites. These sites are operated under contract by site licensee companies (initially British Nuclear Group Sellafield Limited, Magnox Electric Limited, Springfields Fuels Limited and UK Atomic Energy Authority). The NDA has a statutory requirement under the Energy Act 2004, to publish and consult on its Strategy and Annual Plans, which have to be agreed by the Secretary of State (currently the Secretary of State for Trade and Industry) and Scottish Ministers.

operational period (of a disposal facility)

The period during which a disposal facility is used for its intended purpose, up until closure.

passive safety

Not placing reliance on active safety systems and human intervention to ensure safety.

plutonium (Pu)

A radioactive element occurring in very small quantities in uranium ores but mainly produced artificially, including for use in nuclear fuel, by neutron bombardment of uranium.

post-closure period (of a disposal facility)

The period following sealing and closure of a facility and the removal of active institutional controls.

radioactive decay

The process by which radioactive material loses activity, e.g. alpha activity naturally. The rate at which atoms disintegrate is measured in becquerels.

radioactive material

Material designated in national law or by a regulatory body as being subject to regulatory control because of its radioactivity.

radioactive waste

Any material contaminated by or incorporating radioactivity above certain thresholds defined in legislation, and for which no further use is envisaged, is known as radioactive waste.

Radioactive Waste Management Limited (RWM)

A wholly owned subsidiary of the NDA, established to design and build an effective delivery organisation to implement a safe, sustainable and publicly acceptable geological disposal programme. Ultimately, RWM will evolve under the NDA into the organisation responsible for the delivery of the GDF. Ownership of this organisation can then be opened up to competition, in due course, in line with other NDA sites

radioactivity

Atoms undergoing spontaneous random disintegration, usually accompanied by the emission of radiation.

radionuclide

A radioactive form of an element, for example carbon-14 or caesium-137.

safety function

A specific purpose that must be accomplished for safety.

uranium (U)

A heavy, naturally occurring and weakly radioactive element, commercially extracted from uranium ores. By nuclear fission (the nucleus splitting into two or more nuclei and releasing energy) it is used as a fuel in nuclear reactors to generate heat.

waste acceptance criteria (WAC)

Quantitative and/or qualitative criteria, specified by the operator of a disposal facility and approved by the regulator, for solid radioactive waste to be accepted for disposal.

waste container

Any vessel used to contain a wasteform for disposal.

wasteform

The waste in the physical and chemical form in which it will be disposed of, including any conditioning media and container furniture (i.e. in-drum mixing devices, dewatering tubes etc.) but not including the waste container itself or any added inactive capping material.

waste package

The product of conditioning that includes the wasteform and any container(s) and internal barriers (e.g. absorbing materials and liner), as prepared in accordance with requirements for handling, transport, storage and/or disposal.