

**WASTE PACKAGE SPECIFICATION AND
GUIDANCE DOCUMENTATION**

**WPS/904: Guidance on the Characteristics
and Demonstration of Robust Formulation
Envelopes for Cementitious Wasteforms**

**February 2007
Number: 530482**

**WASTE PACKAGE SPECIFICATION AND
GUIDANCE DOCUMENTATION**

**WPS/904: Guidance on the Characteristics
and Demonstration of Robust Formulation
Envelopes for Cementitious Wasteforms**

**February 2007
Number: 530482**

WPS/904

February 2007

Conditions of Publication

This technical note is made available under Nirex's Transparency Policy. In line with this policy, Nirex is seeking to make information on its activities readily available, and to enable interested parties to have access to and influence on its future programmes. This document may be freely used for non-commercial purposes. However, all commercial uses, including copying and re-publication, require Nirex's permission. All copyright, database rights and other intellectual property rights reside with Nirex. Applications for permission to use this technical note commercially should be made to the Nirex Business Development Manager.

Although great care has been taken to ensure the accuracy and completeness of the information contained in this publication, Nirex can not assume any responsibility for consequences that may arise from its use by other parties.

©United Kingdom Nirex Limited 2007. All rights reserved

Bibliography

If you would like to see other publications available from Nirex, a complete listing can be viewed at our website www.nirex.co.uk, or please write to Corporate Communications at the address below, or email info@nirex.co.uk.

Feedback

Readers are invited to provide feedback to Nirex on the contents, clarity and presentation of this report and on the means of improving the range of Nirex reports published. Feedback should be addressed to:

Corporate Communications Administrator

United Kingdom Nirex Limited
Curie Avenue
Harwell
Didcot
Oxfordshire
OX11 0RH
UK
Or by e-mail to: info@nirex.co.uk

WASTE PACKAGE SPECIFICATION AND GUIDANCE DOCUMENTATION

**GUIDANCE ON THE CHARACTERISTICS AND DEMONSTRATION OF ROBUST
FORMULATION ENVELOPES FOR CEMENTITIOUS WASTEFORMS**

This document forms part of a suite of documents prepared and issued by Nirex to assist waste packagers condition and package Intermediate Level and certain Low Level radioactive wastes.

The Waste Package Specification and Guidance Documentation (WPSGD) is based on, and is compatible with the Generic Waste Package Specification (GWPS) and therefore provides specification and guidance on waste packages that meet the transport and disposability requirements derived for the Nirex phased geological disposal concept.

The WPSGD is intended to provide a 'user-level' interpretation of the GWPS to assist Waste Packagers in the early development of plans and strategies for the management of radioactive wastes. Waste Packagers are advised to contact Nirex at an early stage to seek detailed assessment of specific packaging proposals.

The WPSGD will be subject to periodic revision and Waste Packagers are advised to contact Nirex to confirm that they are in possession of the latest version of documentation.

This document has been compiled on the basis of information obtained by Nirex. The document was verified in accordance with arrangements established by Nirex that meet the requirements of ISO 9001. The document has been fully verified and approved for publication by Nirex.

CONTENTS

1	INTRODUCTION	1
2	BACKGROUND	3
2.1	Aims of this Document	3
2.2	The Nirex PGRC and LoC Assessment Process	3
2.3	The Generic Waste Package Specification	4
3	CHARACTERISTICS OF A ROBUST FORMULATION ENVELOPE	4
3.1	Definition of a Robust Formulation Envelope	4
3.2	Sources of Variability	6
3.3	Demonstration of Achievability	10
3.4	Demonstration of Product Properties across the Formulation Envelope	11
3.5	Summary	16
4	DEMONSTRATION OF ROBUSTNESS	17
4.1	The Role of Inactive and Active Wasteform Trials	17
4.2	LoC Submissions	19
4.3	On Plant Measurements	19
5	REFERENCES	20

1 INTRODUCTION

Nirex was established in 1982 with an objective of assisting producers of intermediate level (ILW) and long-lived low level radioactive waste (LLW) to package those wastes in a form compatible with disposal in an underground repository.

Nirex has fulfilled this objective by developing a long-term management concept, the Phased Geological Repository Concept (PGRC) [1], and by developing standards and specifications for the packaging of waste based on this concept. This is important because radioactive wastes in unconditioned form can pose a significant hazard to people and the environment and Nirex packaging standards have been designed to improve the safety and long-term behaviour of the wastes.

The mission of Nirex was strengthened in 2004 and agreed with Government as follows:

'In support of Government policy, develop and advise on safe, environmentally sound and publicly acceptable options for the long-term management of radioactive materials in the UK.'

Four objectives have been set to determine the scope and manner of implementation of this mission and one of these requires that Nirex set standards and specifications for the packaging of waste, and advise waste packagers on how to treat and package radioactive waste in accordance with those standards and specifications, through the Letter of Compliance (LoC) process¹.

In order to facilitate the safe and efficient packaging, transport and disposal of waste, Nirex has defined packaging standards and specifications based on the requirements of the PGRC, involving transport of waste to a phased geological repository, monitored and retrievable underground storage with the option to seal and close the repository in the long-term.

The PGRC is underpinned by a suite of documents, including the Generic Waste Package Specification (GWPS) [2]. The GWPS defines and describes the packaging standards and specifications that have been derived from the PGRC and is used in the UK as the basis for the packaging of ILW and certain LLW.

The GWPS is the primary document defining Nirex packaging standards and specifications and is supported by the Waste Package Specification and Guidance Documentation (WPSGD). The WPSGD comprises a suite of documentation primarily aimed at waste packagers, its intention being to present the generic packaging standards and specifications at the user level, together with explanatory material and guidance that users will find helpful when it comes to application of the specification 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 Nirex Waste Package Specification and Guidance Documentation, WPS/100*².

¹ Formerly known as the Letter of Comfort process.

² Specific references to individual sections of the WPSGD are made in this document in *italic script*, followed by the relevant WPS number.

WPS/904

February 2007

The diverse physical, chemical and radiological nature of ILW and LLW in the UK means that particular challenges arise in the packaging of certain wastes. To assist waste packagers with the preparation of proposals for the packaging of such wastes, Nirex has produced, and continues to add to, a suite of documents known as Guidance Notes. A full list of the Guidance Notes produced by Nirex, together with an abstract of each, can be found in *Introduction to Nirex Waste Packaging Guidance Notes, WPS/900*.

An underlying principle behind the production of the GWPS is for radioactive wastes to be packaged in a passively safe form. This is commonly, although not universally, achieved through the immobilisation of the waste in a cementitious wasteform, either through the infiltration of solid waste items or the incorporation of sludge or liquid waste into the cement matrix [3]. In all such cases, it is necessary to develop a tailored cement formulation to ensure that the particular physical and chemical properties of the waste can be accommodated and the resulting properties of the wasteform are satisfactory.

It is recognised that all wastes will be subject to some degree of variability in physical and chemical properties. Furthermore, the waste packaging process will also be subject to variations. Consequently, the actual composition of a wasteform will lie within an envelope of potential waste and cement composition. In order to guarantee the quality of the expected products from a waste packaging process, it is therefore necessary to identify the characteristics of a formulation envelope that is robust to these expected variations. Such a formulation envelope will define the extent of potential composition and process variations that are deemed to yield a waste package that is compliant with all of the requirements of the PGRC.

A robust formulation envelope will therefore:

- deliver products that are, and continue to be, consistent with the requirements of the GWPS;
- take into account the potential sources and magnitude of variations that may affect the properties and characteristics of wasteforms and waste packages; and
- be achievable, given the materials and plant to be used.

The document should be read in conjunction with the GWPS and with the sections of the WPSGD relevant to the waste package type being considered. The latter comprise:

- Series 300: Waste Package Specifications for Standard Waste Packages
- Series 500: Wasteform Specifications for Standard Waste Packages
- Series 700: Explanatory Material and Design Guidelines for Waste Package Specifications
- Series 800: Explanatory Material and Design Guidelines for Wasteform Specifications.

It should be noted that although this document is primarily aimed at waste packages with cemented wasteforms, the principles of envelope demonstration will be the same for other encapsulants (i.e. polymers).

2 BACKGROUND

2.1 Aims of this Document

The particular aims of this document are to:

- define what is meant by a 'robust envelope' in the context of the packaging of ILW and LLW by identifying the required characteristics;
- identify the sources of (inherent) variability that make the definition of a formulation envelope a necessity and will delimit the minimum boundaries of a formulation envelope;
- give advice on the demonstration of formulation envelope robustness, based on the performance requirements for wasteforms and waste packages.

The remainder of this section provides summaries of the Nirex PGRC, the LoC assessment process³ and the Nirex approach to setting standards and specifications for the packaging of ILW and LLW which form the basis for the LoC process.

2.2 The Nirex PGRC and LoC Assessment Process

The PGRC [1] has been developed by Nirex as a viable option for the long-term management of ILW and certain categories of LLW in the UK and, as such, forms the basis for Nirex waste packaging standards and specifications which form the GWPS [2]. The PGRC envisages that, following a period of interim surface storage at the site of arising, packaged wastes would be transported to a repository facility. Such a facility would be constructed in stable geology deep underground to provide long-term isolation of the radioactivity in the wastes in order to protect human health and the accessible environment. The PGRC allows for the facility to be operated in a phased approach with the ultimate aim of sealing and closure. Each phase would be reversible and time would be available to build confidence at each stage before moving to the next.

The safety philosophy adopted in the PGRC is one of containment of radionuclides by multiple barriers of which that provided by the waste package is a key component. The waste package can actually be considered as two independent but complimentary barriers, the waste container and the wasteform, each of which plays an important role in containment. In consequence of this the GWPS sets performance requirements for both of these components, against which the overall performance of the waste package is judged as part of the LoC assessment process.

The LoC process, has been developed as a means of assessing the disposability of packaged wastes against the requirements of the GWPS. In undertaking LoC assessments Nirex determines whether wastes when packaged will have characteristics compliant with plans for transport to, and operations at the repository facility, and ultimately whether the wastes could be accommodated within the repository long-term post-closure safety case. As described in regulatory guidance [4] this assessment of disposability is required to provide a component of overall safety case for the operators packaging plant and the waste packages that will ultimately be produced.

³ A full description of the LoC process can be found in *WPS/650*.

WPS/904

February 2007

Upon completion of an assessment of a packaging proposal, Nirex will provide an Assessment Report relating to the further progression of the proposed packaging route, which may be accompanied by the issue of a LoC endorsing the packaging proposal. The Assessment Report may recommend prior treatment of the waste to deal with specific concerns. These, and other particular uncertainties and risks arising from the chosen packaging method(s) will be highlighted in the Assessment Report, as Action Points. Subsequent to the issue of an Assessment Report, Nirex will continue to monitor progress with the resolution of such Action Points.

2.3 The Generic Waste Package Specification

Since its inception, a major area of Nirex's work has been in the provision of advice to the packagers of ILW and LLW in the UK. This has involved the definition of packaging standards and specifications, known as waste package specifications. The process of the production of waste package specifications culminated in 2005 with the production of the GWPS [2]. Derived from the PGRC and its associated generic documentation, which comprise the system specifications and safety assessments that define the PGRC, the GWPS provides the basis for the assessment of proposals for the packaging of ILW/LLW in the UK.

The packaging standards and specifications presented in the GWPS are generic in two respects in that they are::

- derived from a full consideration of all future phases of waste management, as defined by the PGRC; and
- independent of the location of the site of the repository, which could be implemented at a range of different sites within the UK, representing a range of geological environments.

The format of the GWPS is to define:

- general requirements that are applicable to all waste packages;
- the range of Nirex standard waste containers;
- specific requirements for the standard waste package design that are created using the standard waste containers;
- requirements for the conditioned wasteforms that are placed into containers;
- requirements for quality management and for the creation and maintenance of records about each individual waste package.

The GWPS specifies what is to be achieved, but avoids placing undue limitations on the methods by which the requirements may be met.

3 CHARACTERISTICS OF A ROBUST FORMULATION ENVELOPE

3.1 Definition of a Robust Formulation Envelope

During the manufacture of waste packages from a particular waste stream, variations will exist in a number of characteristics of the raw waste and the conditioning materials as well as in the plant process conditions. A formulation envelope defines the range to which such variation can extend for a particular waste and packaging process whilst still

yielding waste packages that would be compliant with all of the requirements of long-term management as defined by the PGRC.

A robust formulation envelope would therefore be one that would take into account the magnitude of all potential sources of variation that may affect the properties of the packaged waste and consistently delivers waste package products that are consistent with the requirements of the GWPS, as well as being achievable, given the materials and plant to be used.

Thus, from a knowledge of the raw waste and the conditioning process, supported by sufficient wastefrom development work and the experience gained during both inactive and active commissioning, a packaging plant operating within such a robust formulation envelope can be demonstrated to be capable of consistently producing ‘acceptable’ waste package products. Management of quality and compliance checking on plant will provide further validation of compatibility, and provide evidence that the waste packages produced remain compatible with the requirements for ongoing waste management.

The means by which a formulation envelope can be defined is shown diagrammatically in Figure 1 for two typical wastefrom parameters; waste water content and solids loading.

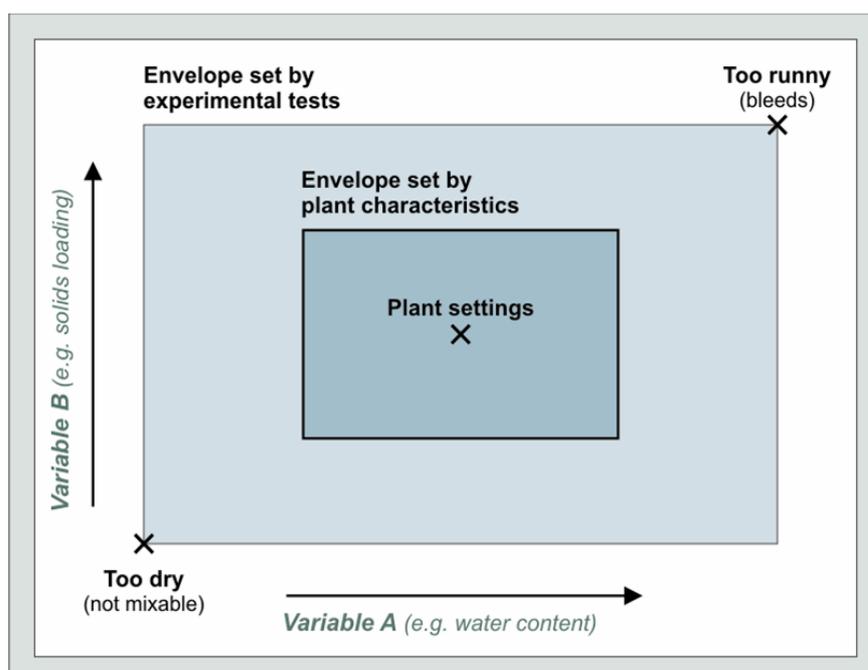


Figure 1 Definition of the formulation envelope

February 2007

Wasteform trials will have identified the optimum combination of these two quantities to allow plant settings or 'target' values to be defined. Variability in the conditioning plant itself will define an wasteform envelope within which all products of the plant would be expected to lie. Such an inner envelope would be expected to be surrounded by an envelope which would define the most bounding limits within which all products would be satisfactory but outside of which some product characteristics would not be compliant. The extent of this outer 'robust envelope' will have been defined by experimental trials which ideally would encompass conditions both inside and outside the bounds of the envelope to help ensure that the boundaries of the envelope are as well defined as possible.

A formulation envelope is typically presented in terms of the limits within which a waste package, or more specifically the wasteform it contains could be demonstrated as being compliant with the requirements of the GWPS. This would include, for example:

- Composition of the raw waste;
- Radionuclide inventory of the raw waste;
- Waste loading;
- Physical or chemical pre-treatments to be applied to the waste;
- The temperature of the waste and encapsulant feeds;
- Encapsulant blend ratio and water/cement ratio (w/c)⁴;
- Wasteform volume;
- Mixing parameters; speed and duration.

Associated with this will be the range of performance or characteristics generated by the process and which results in products that are acceptable as well as being consistent with the requirements of the plant, including throughput.

3.2 Sources of Variability

For the robustness of a formulation envelope to be suitably demonstrated, it is necessary to have an understanding of the variability associated with the waste, conditioning materials and proposed process. Some of the variability may be a function of the inherent variability of the waste, plant and conditioning materials such that it may not be fully controlled or eliminated. This section considers the potential sources of variability that may influence wasteform properties and that should, therefore, be accommodated by the formulation envelope.

3.2.1 Waste Variability

Wastes are subject to variability both between and within waste streams and in terms of their radionuclide inventory and physical and chemical characteristics. Unlike many of the process variables identified in Section 3.2.2, waste variability may be difficult to control and minimise in some cases. Further, for some waste streams, the true limits of variability may be difficult to establish until retrieval has been accomplished.

⁴ 'w/c' is used throughout this document to refer to the ratio of the mass of water to the mass of powders in the cementitious grout, including OPC, BFS, PFA and HAC, etc

Potential sources of waste variability include:

- Chemical composition of flocs, liquors and sludges, including ratios between different components, pH, etc. Variations may be a function of, for example, waste heterogeneity as a result of settling during storage or because waste arises in variable batches. Variations in chemical composition could affect both the product physical and mechanical properties and the process (mixability, set, bleed and exotherm);
- Physical quantities of different solid wastes (metallic and non-metallic) within a single waste stream; e.g. the quantity of aluminium in a mixed waste stream may vary and be difficult to control. These variations may affect the physical and mechanical properties of the wasteform, its radionuclide inventory and its evolution;
- Radionuclide inventory of waste, including fissile, short-lived soluble radiotoxic, gaseous and heat generating radionuclides;
- Blend ratios of slurries/flocs of different composition; in addition to the variability within a single waste stream, some waste streams may be blended for packaging;
- Solids content of slurries/flocs; variations in the solids content of wastes may vary because of settling or agglomeration during storage;
- Volume of water; e.g. associated with solid wastes;
- Condition of materials at time of packaging; e.g. the degree of corrosion that a metallic waste has undergone during storage may significantly affect the rate of gas generation both at early age and during interim storage.

Determination of the potential extremes of waste envelope requires that the variability of the waste be understood and, therefore, that the waste has been adequately characterised. This will permit the application of appropriate plant design, controls and checking.

3.2.2 Process Variability

Process variations are an inherent characteristic of a packaging facility, and must therefore be accommodated within the formulation envelope. Although it may be possible to reduce plant tolerances in many cases, there will be costs associated with any such reduction, such that a formulation envelope that is robust to broader plant tolerances may represent a significant saving in terms of plant design and construction. A robust formulation envelope will be demonstrably achievable given the variability due to plant tolerances associated with a facility, including:

(a) Waste and pre-treatment processes:

- Delivery of waste materials; variance from the target quantity will be associated with the metering of wastes. This will affect the total quantity of waste and the relative quantities of waste and wasteform components;
- Chemical pre-treatment; e.g. the addition of lime to acid slurries to achieve a target pH prior to encapsulation. Relevant variables are the quantity of reagent added and the duration of pre-treatment;
- Physical pre-treatment of solid wastes; e.g. supercompaction of waste to produce pucks. For example, compaction force may have a bearing on the propensity for puck reassertion, such that there may be a maximum allowable compaction force, or on the quantity of residual voidage, such that there may be a minimum

February 2007

compaction force. The removal of water from solids and the use of shredding/cutting are further examples of a potential variations to which a formulation envelope should be robust;

- Pre-treatment of sludge/slurry wastes; e.g. dewatering will affect w/c in the mix and the concentration of solids and dissolved ions per unit volume of waste such that the tolerance of the envelope to different degrees of dewatering should be known;
- Waste temperature; can be controlled to an extent. Waste temperature may affect the rate at which cement hydration proceeds and the peak exotherm temperature experienced by the wasteform. This may have implications for the process in terms of mixability, fluidity, setting and bleed and on the physical and mechanical properties of the wasteform. The formulation envelope should therefore be tolerant to the expected range of waste temperature;
- Distribution of solid wastes prior to grouting; e.g. cans may require to be specifically orientated in order to achieve adequate infiltration, such that the drum loading process should be able to consistently achieve that orientation. If it cannot, then the tolerances associated with drum loading exceed the limits of the formulation envelope, such that the drum loading process or the ability of the grout formulation and process to infill cans in other orientations should be modified;

(b) Encapsulation

- Delivery of encapsulant materials; for grouted products for which a pre-mixed grout is prepared, variance from the target quantity associated with the metering of cement powders will affect the blend ratio (including w/c) of the encapsulant, and variance from the target quantity of grout added to a container of waste will affect the total wasteform volume and waste loading.
- Order in which wasteform components are added, e.g. that:
 - > powders are loaded into the hopper;
 - > waste, powders and additives are metered to the drum, e.g. superplasticisers added with the mix water generate a different response if added to the wasteform after powder addition.

It is considered that this variable is largely controllable given adequate plant controls and that, therefore, robustness of the formulation envelope to these variations will not need to be demonstrated. In many cases, it is considered that formulation envelopes will not accommodate changes in the order in which waste and encapsulant are added;

- Waste agitation; the in-drum mixing of slurry wastes, for example, may rely on solid particles being in suspension prior to the addition of the conditioning agent. The method of agitation should offer a known and reproducible level of suspension that is consistent with the production of an acceptable wasteform;
- Grout/ powder temperature; comments as for waste temperature;
- Grout addition rate (solid infills) or powder addition rate (in-drum mixed);
- For in-drum mixed products, variance from target quantities of the encapsulant and encapsulant components will affect the blend ratio (assuming that powders are not pre-mixed), w/c, waste loading and total wasteform volume. In all cases, the maximum volume of raw materials that could be added to the disposal

February 2007

container when all tolerances are taken into account should not exceed the maximum effective volume;

- Mixing parameters (i.e. paddle speed and mixing time); this may have implications for the adequate incorporation of cement powders and wastes, and therefore may affect wasteform homogeneity/uniformity. Mixing parameters may also have an effect on grout fluidity. Variations are expected to be small, barring fault conditions;
- Duration, acceleration and frequency of vibration (vibro-grouted solid infills); variations in the acceleration, frequency and duration of vibration applied to wastes in the disposal drum may affect the packing density of the waste when applied prior to grout addition and the degree of infilling when applied to a container during grout infilling;

(c) Post encapsulation

- Curing conditions; the conditions (primarily temperature and humidity) under which wasteforms and their capping grout are cured can influence the properties of wasteforms in terms of their early age dimensional stability and through water losses from the wasteform surface;
- Drum movement times; dependent on early-age strength development. Drum movement prior to the achievement of adequate wasteform strength could disrupt the integrity of the matrix, particularly in response to small impacts that may be expected to occur during the course of normal handling;
- Accuracy of analytical methods used to determine the chemical composition and radionuclide inventory of wastes; analytical tolerances may impact the ability of the process to ensure that the waste is within the formulation envelope.

This section is not intended to be exhaustive, but rather to illustrate common sources of variability that may have an effect on product properties. Other sources of variability may be relevant in some cases, depending on the process adopted.

3.2.3 Variability of Conditioning Materials

Variations in the cement powders and other materials used in encapsulation (e.g. superplasticisers, sodium hydroxide, lime) may affect the physical and mechanical properties of the wasteform, and parameters relevant to the packaging process such as hydration exotherm, setting time and bleed. It may be difficult to predict the changes that will occur, if any, to the performance of the wasteform as a result of variations. Variations are expected to be limited, but not eliminated, if the cement powders used conform to the relevant standards and specifications.

- Chemical properties of the cement powders used to encapsulate wastes will vary, for example, in terms of SO_3 concentration and the quantities of minor constituents present;
- Physical properties of the cement powders used to encapsulate wastes may vary in terms of specific surface area and particle size distribution. For example, early-age strength development is dependent on the fine fraction and for a given surface area, a narrowing of particle size distribution increases the degree of reaction at 28 days;
- Condition at time of use; provided that the powders are delivered to specification, this will be largely a function of storage conditions.

3.3 Demonstration of Achievability

It should be demonstrable that the plant can deliver the waste and process conditions within the limits of the formulation envelope. It should also be clear that confirmatory tests will ensure that any deviation from the defined envelope, or from the expected behaviour of products within the defined envelope, is apparent.

Demonstration of the achievement of the robustness of a formulation envelope will include the following elements:

- Identification of the limits of waste variability (Section 3.2.1);
- Identification of the plant tolerances (Section 3.2.2);
- Identification of the raw material tolerances (Section 3.2.3);
- Evidence that the formulation envelope is consistent or compatible with the plant delivery range and raw material tolerance envelopes;
- Evidence that all products that fall within the formulation envelope are consistent with the requirements of the GWPS (Section 3.4);
- Justification of the formulation envelope, e.g. the range and results of small- and large-scale inactive and active trials as applicable;
- Identification of confirmatory tests that will be applied during active operations (Section 4).

In addition, it should be demonstrable that the formulation is compatible with the operational requirements of the plant. Although the following are not specific requirements of the GWPS, operability is likely to be judged against criteria including:

- Bleed; the presence of bleed in the waste package is inconsistent with the requirements for the immobilisation of free liquids and may have implications for plant throughput. Extremes of formulation should not, therefore, result in the formation of bleed water, unless the plant and process have been designed to remove it, and the effects of water removal on the wasteform are understood. The formation of bleed may be sensitive to, for example:
 - > blend ratio and w/c;
 - > the quantity of solids in a sludge/slurry waste, the quantity of liquids associated with solid wastes and the degree of saturation of waste feeds;
 - > the scale at which the samples are mixed, where more bleed would be expected at small scale as a result of the lower hydration exotherm;
 - > the presence, loading and distribution of solid waste items that may cause grouts to separate, e.g. filter membranes.
- Setting time; long setting times may reduce throughput and affect the ability of the plant to process the wastes in an appropriate time. Setting time may be sensitive to, for example:
 - > type of cement, blend ratio and w/c;
 - > the concentration, in the waste and wasteform, of retarders or combinations of waste constituents that can cause retardation of cement hydration;
 - > the temperature of the waste and inactive feeds;

February 2007

- > scale, whereby set will tend to be accelerated at full-scale as a function of the increased hydration exotherm.
- Exotherm; the evolution of excessive heat during wasteform hydration may have implications for radionuclide release (volatile and soluble radionuclides), as well as implications for the properties of the cured product. Hydration exotherm may be sensitive to, for example:
 - > type and specification of cement, blend ratio, w/c and the physical quantity of encapsulant (the latter being a function of waste loading);
 - > the presence and concentration of encapsulant and waste constituents, or combinations of constituents, that accelerate hydration;
 - > the distribution of solid items in the wasteform (including mixing paddle), which can act to conduct heat away from the centre of the wasteform.
- Mixability of in-drum mixed products or similar; the plant should be capable of producing a homogeneous product across the formulation envelope. Mixability may be sensitive to, for example:
 - > the particle size distribution and shape of solids in a slurry or bulk particulate waste stream, which may affect mix viscosity, or result in the presence of unimmobilised agglomerations of particulate material within the wasteform;
 - > type of cement, blend ratio and w/c;
 - > the temperature of the waste and inactive feeds;
 - > paddle design;
 - > mix speed;
 - > powder addition rate.
- Grout fluidity; for solid wastes packaged by the addition of a cementitious infilling grout, the fluidity of the grout at the time it is added to the waste will be significant. Grout fluidity may be sensitive to, for example:
 - > type and specification of cement, blend ratio and w/c;
 - > the process environment, powder and water feed temperatures;
 - > the duration of mixing and hold-up prior to addition of the grout to the waste container;
 - > rate of shear.

3.4 Demonstration of Product Properties across the Formulation Envelope

This section identifies the range of wasteform properties that determine performance under conditions relevant to storage, transport, handling and disposal. For each property, the specifications and potential worst-case extremes are considered. The identification of worst-case extremes can reduce the number of samples that are required to be tested in order to demonstrate the robustness of a formulation, and is therefore of benefit. Statistical means of experimental design may also help to reduce the number of experimental determinations required. Guidance is provided to indicate the variations that may be significant factors affecting a property, and may therefore be considered when defining worst-cases. However, this guidance is illustrative, and not intended to be exhaustive; the development of worst-cases should be carried out using knowledge or experiment on a case-by-case basis.

WPS/904

February 2007

Throughout this section, reference is made to grouting, the infilling of solid wastes within the disposal container by the addition of a fluid grout; in-drum mixing, the mixing of liquid or slurry wastes with an encapsulant within the disposal drum using a mixing paddle which typically remains within the wasteform after mixing ('lost' paddle); and supercompaction, a process by which wastes are reduced in volume by mechanical compaction, and the resultant pucks surrounded by a grout annulus within a disposal container.

The ability of wasteforms to meet some of the requirements of the GWPS is considered to be a complex function of other wasteform properties and characteristics, particularly impact and fire performance. In some other cases, acceptability may be based on reasoned argument rather than practical demonstration.

3.4.1 Free Liquids

The GWPS states that:

'All reasonable measures shall be taken to exclude free liquids from the wasteform'.

Free liquids may arise as a function of bleed or as unimmobilised liquids associated with poorly infiltrated solid wastes. Wastes may also contain non-aqueous phase liquids (NAPLs).

The demonstration of the immobilisation of aqueous and non-aqueous free liquids in the waste may need to take into account the robustness of the formulation envelope to variations including:

- For solid wastes, those parameters affecting grout fluidity;
- The water content of the waste;
- The cement specification and type, blend ratio and w/c;
- The presence and concentration of NAPLs in the waste and wasteform;
- Those parameters affecting mixability.

Demonstration of the minimisation of free liquids generated as bleed is considered in Section 3.3.

3.4.2 Mechanical Strength

The GWPS states that:

'The wasteform shall provide sufficient mechanical strength to allow the waste package to be transported and handled without compromising the ability of the waste package to meet any aspect of the GWPS'.

In addition, there may be minimum strength requirements associated with plant operation, e.g. drum movement.

Demonstration of adequate wasteform strength can be achieved by measuring the compressive strength of suitable samples during formulation development and by monitoring set during the waste package production process.

The demonstration of acceptable strength may need to take into account the robustness of the formulation envelope to variations including:

- Type and specification of cement, blend ratio and w/c;
- Product age;
- Waste loading;
- The presence and concentration of hydration retarders and accelerators in the waste, which may affect both time to initial set and ultimate wasteform strength.

3.4.3 Voidage

The GWPS states that:

'All reasonable measures shall be taken to ensure that the volume of voidage within the wasteform and the waste package (such as ullage space and other holes or spaces) is minimised'.

For grouted solid wastes, the demonstration of acceptable voidage may need to take into account the robustness of the formulation envelope to variations including:

- The packing density;
- The orientation of waste items such as cans;
- The pre-treatment of wastes to allow them to be infiltrated, e.g. holing/puncturing;
- Those which may affect grout fluidity, e.g.:
 - > cement type, specification;
 - > w/c and blend ratio;
 - > particle size distribution of the cement powders;
 - > mix time and speed;
 - > paddle design;
 - > temperature of waste, encapsulant and process environment;
 - > the use, type, timing of addition and quantity of additives such as superplasticisers.
- Processes used to enhance infiltration, such as vibration.

For in-drum-mixed wastes, the demonstration of acceptable voidage may need to take into account the robustness of the formulation envelope to variations including:

- Those which may affect the mixability, e.g.:
 - > salt and solids content;
 - > sludge particle size and particle size distribution;
 - > temperature of waste, encapsulant and process environment;
 - > paddle design;
 - > mix speed;
 - > quantity, type, blend and w/c of encapsulant.

WPS/904

February 2007

- The presence and concentration of waste components that may increase air entrainment.

For supercompacted wastes, the demonstration of acceptable voidage may need to take into account the robustness of the formulation envelope to variations including:

- The compaction force;
- The properties and distribution of waste items being compacted;
- Those which may affect grout fluidity (see Section 3.4.1).

3.4.4 Homogeneity

The GWPS states that:

'Local concentrations of materials within the wasteform that may compromise any aspect of the GWPS should be avoided'.

Examples of relevant local concentrations are agglomerated particulate material, heat generating or fissile radionuclides, or materials that are subject to deleterious modes of degradation.

The demonstration of acceptable homogeneity/uniformity may need to take into account the robustness of the formulation envelope to variations including:

- The distribution of solid items within the container prior to grouting;
- Waste density (floatation of wastes);
- Those parameters affecting mixability and infiltration (see Section 3.4.1).

3.4.5 Wasteform Evolution

The GWPS states that:

'Changes in the characteristics of the wasteform as it evolves shall not result in degradation that will compromise the ability of the waste package to meet any aspect of the GWPS'.

Waste packages are assessed in terms of their long-term performance under the timescales and conditions pertaining to interim storage, transport, handling and disposal. Consideration is given to the ability of the package to continue to meet the requirements of the GWPS.

Any assessment of the potential modes, outcome and significance of waste and wasteform degradation may need to take into account the effects of variations including:

- Cement type, blend ratio and w/c;
- Waste loading;
- The relative quantities of different materials in the waste, including those subject to and accelerating corrosion, microbial degradation and waste matrix interactions;
- The distribution of waste items within the wasteform;
- Those parameters affecting voidage (Section 3.4.1);
- The presence of waste components that may accelerate corrosion, e.g. chlorides;

February 2007

- Factors affecting the temperature of the wasteform, e.g. hydration exotherm, heat output and curing and storage temperatures;
- The quantity of water in the wasteform that is available for reaction, including microbial degradation;
- The inventory of materials whose presence and/or degradation products may increase the solubility of radionuclides;
- Factors affecting the mass transport properties of the wasteform, i.e. the ability of the wasteform to release any gases generated

3.4.6 Dimensional Stability

The GWPS states that:

'Dimensional changes of the wasteform should not compromise the requirement to immobilise radionuclides or any other aspect of this specification'.

Experience has shown that wasteforms can typically accommodate expansion or shrinkage up to 2000 $\mu\epsilon$, although in some cases, wasteforms may accommodate greater dimensional changes without deleterious effects [5].

The demonstration of acceptable dimensional stability may need to take into account the robustness of the formulation envelope to variations including:

- The shape and distribution of solid waste items;
- Factors affecting the occurrence and magnitude of waste matrix interactions, e.g.:
 - > the chemical characteristics of the waste;
 - > the type and specification cement, blend ratio and w/c;
 - > waste loading;
 - > physical properties of the matrix, e.g. permeability;
 - > the availability of water;
- Type and specification of cement, blend ratio and w/c;
- The waste loading of reactive metals such as magnesium, aluminium and uranium, and the factors determining their corrosion rate and products (see Section 3.4.5);
- Hydration exotherm (see Section 3.3);
- Compaction force and properties of the waste within a compacted puck, which will affect the potential for and degree of reassertion.

WPS/904

February 2007

3.4.7 Nuclear Properties

Dose Rate

The GWPS states that:

'The dose rate at 1 metre from the surface of a transport package shall not exceed 0.1mSvhr⁻¹ and the dose rate on its external surface shall not exceed 2mSvhr⁻¹.

In the case of unshielded waste packages, the dose rate values should not exceed the values given above when the waste package is shielded by a 280mm thick steel shield (density 7700kgm⁻³) in direct contact the package.

The requirements given above shall be directly applied to shielded waste packages and are in addition to the dose rate restriction resulting from controls on activity content⁵'

Criticality Safety

The GWPS states that:

'The presence of fissile materials, neutron moderators and reflectors in the waste package shall be controlled to ensure that they do not present a criticality safety hazard during any of the active phases of the PGRC. It shall also be ensured that, following closure of the repository, the possibility of local accumulation of fissile material such as to produce a neutron chain reaction is not a significant concern to long-term repository performance'.

The demonstration of acceptable nuclear properties should take into account the robustness of the formulation envelope to variations including:

- Radionuclide inventory of wastes;
- Waste loading;
- Analytical tolerances;
- Waste distribution;
- Those factors determining the degree of self-shielding afforded by the wasteform and container, e.g. density, homogeneity/uniformity.

3.5 Summary

A robust formulation envelope will demonstrably take account of the inherent variability in the waste and conditioning materials, and any limitations of the plant and will also reflect the preferences of the waste packager (e.g. highest waste loading preferable). Product evaluation testing should demonstrate that wasteforms across the formulation envelope will meet the requirements of the GWPS.

⁵ As Type IP-2 transport packages the contents of shielded waste packages are limited to Low Specific Activity (LSA) material and Surface Contaminated Objects (SCO) as defined by the IAEA Transport Regulations.

It is expected that varying levels of detail regarding the formulation and process envelopes will be submitted to Nirex by waste packagers at different stages in the LoC process. At the Conceptual stage, a submission should include a detailed description of the waste to be packaged, including estimates of the average and maximum waste package inventories, and an outline of the packaging concept and of necessary research and development that will be carried out. At the Interim (project pre-commitment) stage, the results of development work on the properties of the wasteform and waste package, including encapsulation trials, should be complete and reported, and outstanding design and development work identified. At the Final (pre-operational) stage, evidence will be required, e.g. commissioning reports or results, to demonstrate that the as-built packaging plant is capable of making the product, and that the product fully meets the requirements of the GWPS. This should include identification of any confirmatory and compliance testing that will be adopted during waste packaging operations.

4 DEMONSTRATION OF ROBUSTNESS

As shown in Section 3.2, there are a number of sources of potential variability and this could potentially lead to a large number of combinations when wasteform trials are being planned. However, it is acknowledged that waste packagers are likely to wish to limit the number of full-scale trials and test pieces required, indeed it is unlikely to be practicable to produce and evaluate samples that represent all possible variations. Reasoned argument should therefore be used to show that some of the variations will not have a deleterious effect on the properties of the wasteform. It may be argued that others are adequately demonstrated at small or intermediate scale, particularly at earlier stages in the LoC process or by wasteform development trials etc. from other packaging projects using the same conditioning process with similar waste types.

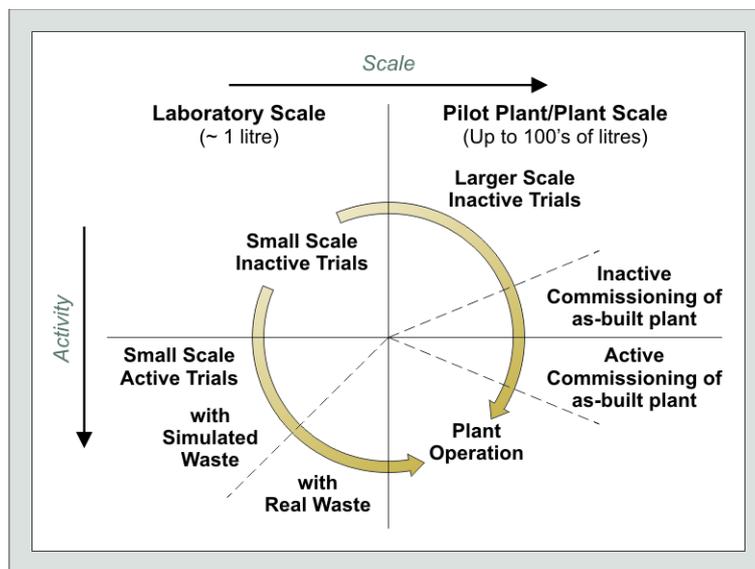
It may be of benefit for 'worst-case extremes' to be identified and justified for certain waste and/or conditioning material parameters, as a means of limiting the number of samples for which a particular wasteform property will need to be demonstrated. An example of a worst case extreme is an in-drum grouted solid waste with a grout at lowest w/c, which would have lowest fluidity. For complex wastes and processes, it may be more difficult to define worst-case extremes for particular properties because of the number of interactions between wasteform components. The complexity of the packaging process is therefore likely to be reflected in the number of worst-case extremes adopted and tested. In all cases, it would be beneficial to define and validate worst-cases at small scale. The same reasoning applies to active trials as to full-scale trials.

4.1 The Role of Inactive and Active Wasteform Trials

Wasteform trials are frequently used to give confidence that a particular wasteform formulation will ultimately result in acceptable wasteform and waste package characteristics in the final waste package product.

As shown in Figure 2, such trials can be grouped into four categories, each of which has a distinct role to play in providing information to support the different stages of LoC submissions.

Figure 2 Categories and Progression of Wasteform Trials



It should be noted that not all of the stages shown in Figure 2 would normally be required and that information obtained in the earlier stages (i.e. small scale/inactive) may be sufficient to give confidence in the final product, especially if supported by evidence from the packaging of similar wastes using similar packaging processes. This may justify the omission of some or all of the subsequent stages.

Formulation envelope definition and demonstration by such trials could progress by one or both of the two routes shown in Figure 2:

- a) From small-scale inactive trials to larger-scale (i.e. up to full waste package size) to trials during inactive commissioning of the packaging plant;
- b) From small-scale inactive trials to small-scale active trials, with simulated or actual waste to confirmatory trials during active commissioning of the packaging plant.

Scale may have an important effect on some wasteform properties. Examples of wasteform properties that may show significant change as a function of scale-up are: hydration exotherm and related parameters such as setting time and early-age strength development, bleed, mixability and dimensional stability. If development work utilises plant other than that which will be used for actual waste packaging, then the possible effects on the process and products should be considered.

Inactive trials will utilise simulants that should be designed to match the physical and chemical properties of the waste as closely as possible. In demonstrating the robustness of a formulation envelope, the nature of the simulants should be reported. The appropriateness of simulants as inactive analogues of wastes can be confirmed through active trials. The design of simulants should capture the characteristics of the waste at all extremes of waste envelope, which include:

- For solid wastes:

- the chemical composition of the solid materials;
- the shapes and dimensions of the materials;
- the condition of the materials after storage.
- For sludge and slurry wastes
 - the chemical composition of the waste;
 - the particle size distribution, shape and loading of solids;
 - the effects of ageing of the unpackaged waste during its storage.

Characterisation must adequately capture the heterogeneity of the waste as it will be presented for encapsulation.

4.2 LoC Submissions

An LoC submission should identify and justify the formulation envelope in terms of:

- Clear definition of the target ranges for all relevant parameters (as reflected in the Waste Product Specification (WPrS), i.e. the limits of the formulation, process and waste envelopes;
- Reporting of trials/work used to define the formulation envelope and other target values. This should include the scale and simulants used in the development work;
- Control measures and quality checks that will be used on plant to provide confidence that products are consistent with the formulation envelope as envisaged and therefore with the requirements of the GWPS;
- Accuracies associated with the derivation of waste package radionuclide inventories and inactive composition.

The level of detail provided and the degree of justification possible will increase as the Loc submission progresses. At the Conceptual stage, for example, an indication of the likely target formulation may be presented based on previous work for similar wastes. At the Final stage, full justification would be expected, or an indication of final tests to be carried out on plant during inactive commissioning.

4.3 On Plant Measurements

On plant, the following should be considered, as they offer increased confidence in the robustness of the formulation envelope and will therefore minimise the uncertainty associated with the acceptability of packages for disposal:

Confirmatory tests, e.g.:

- set, e.g. measured by penetrometer;
- bleed;
- exotherm, e.g. measurement of temperature by thermometer at the container surface to give an indication of the core wasteform temperature, which may be measured directly during development;
- fill level;
- mixability monitored by mixer torque or other means;

WPS/904

February 2007

- grout fluidity and temperature measured immediately prior to grout delivery to the container;
- waste testing prior to delivery to container to ensure that it is within the defined waste envelope;
- Compliance tests, e.g. small scale samples for product evaluation testing and archiving, dose rate, mass;
- Quality indicators, e.g. mixer torque, acceleration and frequency of vibration.

5 REFERENCES

- 1 Nirex, *The Nirex Phased Disposal Concept*, Nirex Report N/074, 2003.
- 2 Nirex, *Generic Waste Package Specification*, Nirex Report N/104, 2005.
- 3 R M Guppy, S P Vines, S J Wisbey, *The Benefits of Cementitious Encapsulation Matrices for the Conditioning of Intermediate Level Waste*, ICEM 2003.
- 4 HSE, EA, SEPA, *Conditioning of Intermediate Level Radioactive Waste on Nuclear Licensed Sites. Guidance to Industry*, March 2005.
- 5 G A Fairhall, *Effect of process operational variables on the product properties of encapsulated intermediate level wastes*, Radioactive Waste Management 2, Volume 1, BNES 1989.

United Kingdom Nirex Limited
Curie Avenue
Harwell, Didcot
Oxfordshire
OX11 0RH

t +44 (0)1235 825500
f +44 (0)1235 831239
e info@nirex.co.uk
w www.nirex.co.uk