

**WASTE PACKAGE SPECIFICATION AND
GUIDANCE DOCUMENTATION**

**WPS/640: Guidance on the Monitoring of
Waste Packages during Storage**

**March 2008
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**WASTE PACKAGE SPECIFICATION AND GUIDANCE DOCUMENTATION
GUIDANCE ON THE MONITORING OF WASTE PACKAGES DURING STORAGE**

This document forms part of a suite of documents prepared and issued by the Radioactive Waste Management Directorate (RWMD) of the Nuclear Decommissioning Authority (NDA).

The Waste Package Specification and Guidance Documentation (WPSGD) is based on, and is compatible with the Generic Waste Package Specification (GWPS). It therefore provides specifications for waste packages that will meet the transport and disposability requirements of the Phased Geological Repository Concept. Guidance is also provided as to how those specifications can be achieved in practise.

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 RWMD 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 RWMD to confirm that they are in possession of the latest version of documentation.

WPSGD DOCUMENT NUMBER WPS/640 - VERSION HISTORY

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

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1 INTRODUCTION

The Radioactive Waste Management Directorate (RWMD) of the Nuclear Decommissioning Authority (NDA) has been established with the remit to implement the geological disposal option for the UK's higher activity radioactive wastes. The NDA is currently working with Government and stakeholders through the *Managing Radioactive Waste Safely* (MRWS) consultation process to plan the development of a Geological Disposal Facility (GDF).

As the ultimate receiver of wastes, RWMD, acting as GDF implementer and future operator, has established waste packaging standards and defined package specifications to enable the industry to condition radioactive wastes in a form that will be compatible with future transport and disposal. In this respect RWMD is taking forward waste packaging standards and specifications which were originally developed by United Kingdom Nirex Ltd, which ceased trading on 1st April 2007 and whose work has been integrated into the NDA.

The primary document which defines the packaging standards and specifications for Intermediate Level Waste (ILW), and certain Low Level Wastes (LLW) not suitable for disposal in other LLW facilities is the Generic Waste Package Specification (GWPS) [1]. The GWPS is supported by the Waste Package Specification and Guidance Documentation (WPSGD) which comprises a suite of documentation primarily aimed at SLCs, its intention being to present the generic packaging standards and specifications at the user level. The WPSGD also includes 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 Waste Package Specification and Guidance Documentation, WPS/100*¹.

Following their manufacture, waste packages are expected to be held in interim surface stores until a GDF is available. Following such storage, waste packages would be removed from stores and transported to the GDF, where they would be emplaced in underground vaults.

The period of time that waste packages will spend in interim surface storage is not fixed but it is assumed that it could extend for up to 150 years. Whatever the actual storage period it is important that waste packages retain their integrity and, following removal from storage, are suitable for transport through the public domain and for ongoing management.

Monitoring the condition of waste packages during storage is an important element of a strategy to ensure that they maintain their integrity and continue to satisfy the performance requirements defined by the GWPS. This document provides guidance to store designers and operators regarding the monitoring of waste packages during interim storage.

2 BACKGROUND

The purpose of this document is to provide guidance on the monitoring of waste package during storage. It provides an identification of the monitoring strategies and techniques, based on best practise and international guidance [2], that can be used to provide evidence to demonstrate package integrity during storage.

¹ Specific references to individual documents within the WPSGD are made in this document in *italic script*, followed by the relevant WPS number.

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The document is focused on the time spent by waste packages in interim surface storage facilities, but it will also have relevance to the underground storage of waste packages in a GDF.

Whilst primarily concerned with the performance of waste packages manufactured with stainless steel containers the principles described are equally valid for waste packages manufactured with waste containers made from other materials.

The key characteristics of an effective monitoring programme for waste packages should be to:

- confirm waste package performance remains consistent with the requirements for subsequent periods of their long-term management;
- provide early warning of changes to the structural and containment elements of the waste package and allow associated safety issues to be managed and actions for any necessary treatments to be put in place;
- provide feedback to waste container and waste package designers and store designers and operators to reduce the potential for repeat occurrence of failures;
- satisfy licensing body requirements and demonstrate legal compliance with store safety case;
- provide public reassurance that waste packages will provide the necessary physical containment.

Guidance on Environmental Conditions During Storage of Waste Packages, WPS/630 provides guidance on the environmental conditions that should be maintained in stores to help ensure that waste packages meet the necessary integrity requirements. This document provides guidance on monitoring during storage to provide reassurance that packages are behaving as expected in the specified environment. Confirmation of waste package integrity will also be required at the time of the removal of waste packages from store; the needs of this monitoring will be the subject of future guidance.

3 DEFINITIONS

In the context of this document the following definitions will be used for the terms integrity, monitoring and inspection.

3.1 Integrity

Integrity is defined as the ability of a waste package to maintain the containment of its contents, as well as the surety of its handling features.

In the context of this document the specific requirement is for waste packages to maintain their integrity in order to facilitate safe and efficient handling during all subsequent stages of their long-term management, which may include continued surface storage at an alternate location, transport and emplacement in a GDF, as well as to ensure their long-term disposability [3].

The following are given as examples of indicators that may provide evidence for the maintenance of package integrity:

- key waste package performance criteria, as defined by the GWPS, continue to be achieved;
- key waste package performance criteria for continued storage, as presented in the store safety case, continue to be achieved;

- the waste package meets the requirements for transport through the public domain;
- the waste package is mechanically sound and may be handled [4] using normal procedures.

These requirements are not exhaustive or independent, but are listed as important factors influencing integrity.

The following are given as examples of indications of package degradation which could lead to loss of package integrity and which, if detected, should be investigated:

- the engineered closures (e.g. the container lid seal and bolting arrangements) cease to function and gas can be released from the waste package through openings other than the filtered vent;
- thinning of the waste container walls;
- dimensional changes of the waste package;
- staining of the waste package by corrosion product.

3.2 Monitoring

In relation to waste package integrity, monitoring can be defined as continuous or periodic observations and measurements to determine changes in the physical condition of a waste package over time.

3.3 Inspection

Inspection can be defined as the examination, or measurement, of the properties of a waste package to obtain data which are used to assess the extent of any degradation processes, potentially including any degree of damage that has occurred. This generally requires benchmarked standards to record the as-built properties of the waste package.

4 WASTE PACKAGE EVOLUTION DURING STORAGE

Most waste packages destined for disposal in a GDF comprise stainless steel containers, filled with radioactive wastes encapsulated using cementitious materials. This design concept provides a mechanically robust entity that can be stored, handled and transported using standard equipment.

The materials of construction and the waste itself will evolve with time; the stainless steel container will tend to corrode (albeit slowly), the cementitious materials will undergo hydration and conversion reactions leading to the formation of different mineral phases and the waste will undergo a variety of physical and chemical changes. The way in which a waste package evolves during surface storage will depend on a number of issues, including the nature of the waste, its radioactivity and the storage conditions. In this section the evolution of the condition of waste packages and the possible degradation mechanisms which should be considered are briefly reviewed, to establish the context for the various monitoring techniques which are outlined in Section 5. The following discussion deals first with the container and then with the wasteform.

4.1 Evolution of waste containers

4.1.1 External corrosion

General corrosion of the stainless steel container will occur but the corrosion rate will normally be very low and is not expected to result in significant wall thinning during the anticipated surface storage period.

Localised corrosion of the external surfaces, handling and stacking features of stainless steel containers could occur if the surfaces became contaminated with aggressive species, such as chloride. Various forms of localised corrosion are possible, including pitting corrosion, crevice corrosion and stress corrosion cracking (SCC, including atmospheric stress corrosion cracking, ASSC).

Microbially influenced corrosion (MIC) can also lead to localised corrosion if specific microbes and suitable nutrients were present.

In high radiation environments, localised corrosion may be enhanced by nitric acid generated by the radiolysis of air [5,6].

In its mildest form, localised corrosion may lead to superficial staining but in severe cases wall penetration could occur, compromising package integrity and leading to the potential for structural damage, with implications for the use of lifting equipment [7].

4.1.2 Internal corrosion

Compared to the outside surfaces exposed to atmospheric conditions, the inside surfaces of containers will be protected by passivation due to the alkaline porewater of the cementitious grout and a very slow general corrosion of the surface will occur. This could be enhanced if long-term shrinkage of the wasteform was to occur, generating an annular void next to the internal surface.

In the event that wastes are ungrouted, there would be a greater potential for initiation of localised corrosion, particularly if the wastes contained chloride, organic wastes or materials which could accelerate corrosion of the stainless steel by galvanic coupling (e.g. graphite); however, the extent of corrosion might be limited by the availability of water.

The nature of the environment will be modified by various processes, including the radiolysis of water and the degradation of organic wastes, releasing potentially aggressive species into the porewater. Although most packages are vented, the access of air to the inner package skin may not be efficient and as oxygen trapped in the waste package is consumed, locally anaerobic conditions may develop.

4.1.3 Filters

Most waste packages are vented through a filter element, to allow the release of gases without loss of particulate activity from the waste. Corrosion of the filter or accumulation of particles could lead to blockage, preventing its efficient operation. This might lead to excessive pressurisation of the waste package which could cause changes which might affect handleability, operational or transport safety.

4.1.4 Polymer degradation

In many designs of waste package, an elastomer seal in the form of an 'o ring' (or similar arrangement) is provided to seal the interface between the container body and the lid. The seal is required to be serviceable primarily in the short-term when the waste package is generating the highest volume of gas, its purpose being to ensure that gas is vented via the filter. The properties of the seal will change with time, as a result of radiation and thermal damage (related to the package contents and surrounding packages), leading to hardening and a possible loss of sealing ability [8]. Following a period of storage, when gas

generation rates have reduced, there may no longer be a major role for this seal and by careful design of the body/lid interface a back-up to the seal can be provided, by way of the mating metal surfaces. Either way, the relationship between seal degradation and package performance will need to be justified.

4.2 Wasteforms

Although there is a large variety of wasteforms, many aspects of their evolution share common mechanisms. For example, the grouts commonly used for waste encapsulation, are generally tolerant to a wide range of conditions and waste materials, if the wasteform composition is appropriately designed. However volume changes resulting from waste or wasteform evolution, either as expansion or contraction, may lead to the most significant changes in properties.

Mechanisms that could cause dimensional changes in wasteforms include:

- desiccation of grout encapsulants, due to radiolysis or chemical reactions;
- phase changes in cement grouts, in particular those due to interaction with waste components;
- reaction between the waste and components of the encapsulant, for example corrosion of waste metals, leading to a corrosion product whose volume differs from that of the original metal, and to consumption of water from the encapsulant.

Dimensional changes in the wasteform could lead to fracturing, resulting in:

- generation of particulates and hence reduced immobilisation of radionuclides;
- increased permeability, for example to radioactive gases.

The timescales for the changes could vary widely, depending on the wasteform design, but could alter wasteform properties during the period of surface storage. However, some of them are dependent on water as a reaction medium, and in such cases they would therefore slow appreciably shortly after setting of the wasteform, and reduce further over time if the available water is consumed by corrosion reactions, microbial activity, radiolysis or other water loss mechanisms.

Other encapsulation media can also show changes, for example changes to the mechanical properties or dimensions, for organic polymer encapsulants, caused by irradiation.

5 GUIDANCE ON MONITORING OF WASTE PACKAGES

A number of techniques are available, or could be extended for remote application, which could be used for monitoring the condition of waste packages within a store.

Note that the principal of 'baselining' should be considered, to establish a starting point against which changes to waste packages can be assessed.

5.1 Monitoring waste containers

5.1.1 Visual examination

Visual inspection of waste packages would detect the presence of general corrosion evidenced by staining, corrosion of any embedded iron which had not been detected in previous inspections, and could detect pitting corrosion and crevice corrosion, depending

on the severity. Stress corrosion cracking may also be detected visually in severe cases. Examples of the results of these corrosion mechanisms are illustrated in [9].

For shielded waste packages² and some unshielded waste packages³ with low external dose rates it would be possible to withdraw a sample package from the store for direct visual examination. However, for most waste packages it would be necessary to carry out the inspection using a remote viewing technique, for example by using colour⁴ CCTV or by retrieval of waste packages into a shielded inspection cell.

Visual examination using an automatic reading device would also check the continued machine readability of the waste package identifier.

5.1.2 Corrosion coupons

The corrosivity of environments in which radioactive waste containers are stored, and the external corrosion rates of containers, could be assessed by exposing coupons of the same material to the storage environment and monitoring their condition. The technique could be used for monitoring:

- general corrosion and pitting corrosion on a uniform surface;
- crevice corrosion, if a crevice former were used;
- stress corrosion cracking, if a pre-stressed sample such as a C-ring or U-bend were used.

Coupon testing has been widely used in a variety of industries to support choice of material, and has become standardised. The standards which are available regarding the use of coupons for corrosion testing and monitoring, with particular emphasis on their use in atmospheric conditions, are summarised in Appendix B. As the presence of radiolysis products, such as nitric acid [5], may have an influence on the corrosion behaviour of stainless steel, it would be preferable to mount the corrosion coupons within the radiation field of the waste containers. There may be practical difficulties in locating and removing the coupons for examination. If the coupons are removed, non-destructively examined and then replaced in the waste store, it should not be necessary to use a large number of coupons. When siting the corrosion coupons, the airflow pattern in the store should be taken into account; for example to allow for areas where condensation, and hence enhanced corrosion, may be more likely to occur.

In order to provide an estimate of the internal corrosion rate of the container walls, corrosion coupons could, in principle, be embedded inside a (dummy) wasteform at the casting stage (i.e. while the encapsulating grout is being cast around the waste). Their corrosion rate would then be monitored remotely, either by using electrochemical techniques [10] (such as linear polarisation [11] or AC impedance measurements [10]), or by measuring the change in electrical resistance of the probes. These techniques would probably necessitate the use of electrical connections into the wasteform.

An alternative to using real packages would be to place dummy packages within the waste store, i.e. a package with identical design features to a real package subjected to representative environmental conditions. The dummy packages could be removed for inspection on a periodic basis. They should be located within the radiation field of the active drums so as to be exposed to radiolysis products from the air [5].

² i.e. 2 metre and 4 metre Boxes.

³ i.e. 500 litre Drums and 3 cubic metre Boxes and Drums.

⁴ The ability to compare colour is vital.

5.1.3 Other monitoring techniques

A number of other techniques could be used for monitoring and inspecting the surface of stainless steel waste containers. They include:

- **dye penetrant testing** for inspecting for presence of surface defects in welds and initiation of stress corrosion cracking. Currently, this technique requires close access by the operator, would only be applicable to shielded waste packages and unshielded waste packages with low radiation levels (e.g. PCM waste). Packages inspected using this technique would require cleaning following inspection to remove all residues from the surface.
- **eddy current testing** is a technique which is routinely used for checking structures for cracks and other defects [12]. In principle the measurement could be carried out remotely.
- **atmospheric corrosion probes** rely on passing a current through a thin foil of the test material and monitoring the changes in the resistance of the foil [13]. A reduction in the thickness of the foil due to corrosion results in an increase in the corrosion resistance. The sensitivity to small areas of localised corrosion would not be as great as for broader general corrosion
- **extraction of the atmosphere** from the store and its introduction to a coupon or dummy package held in a cell outside the store. This could be done with or without an equivalent radiation source present.

5.2 Monitoring seals

For those waste packages where continued sealing is required, the condition of polymers can be monitored by measuring their hardness, using a microhardness device, which could be correlated with a projected lifetime of the polymer and its compression set. A possible approach would be to expose test pieces of polymers similar to those used in the drum seals to the waste store environment (including radiation) and to test them regularly. It would be necessary to mount them in a holder that applied the same degree of load to the polymer as a sealed container, under the same geometrical arrangement. The seal from a dummy container could be tested in the same way.

5.3 Monitoring filters

The condition of the vent and/or filter could be monitored by carrying out a pressure drop test or gas transmission test; this might be more easily performed using a dummy package which included an effective wasteform simulant to generate realistic amounts of gas and particulate.

5.4 Monitoring wasteforms

As the wasteform itself is encased in a container, most techniques used to monitor the wasteform would need to involve indirect measurements. Some techniques are described below.

5.4.1 Dimensional changes

As discussed in Section 4, evolution of the wasteform may lead to its expansion. If the expansion was sufficient to cause deformation of the waste containers it could be detected by measuring the dimensions of the containers, using mechanical, optical or laser measurement techniques (e.g. optical lever techniques, ellipsometry); strain gauges have been described for in-reactor use [14]. The dimensions of dummy drums, containing waste

simulant could be used as an indicator, but the effect of local radiolytic processes would be missed with this approach.

5.4.2 Dummy waste packages

Dummy drums containing waste simulants could also be used, for full-scale verification of laboratory studies, e.g. for destructive examination after a certain period (for example at the end of the storage period, prior to transport) to:

- monitor degradation of the cementitious grout due to carbonation;
- determine any structural changes in the wasteform;
- investigate chemical changes in the composition of the grout;
- inspect for corrosion of the internal surfaces of the container.

In principle environmental sensors to measure internal pH, oxygen concentration, chloride concentration and cement resistivity could be embedded in the simulant wasteform of a dummy package. A dummy package could also be instrumented, for example with strain gauges or instrumented bolts, to detect deformation due to environmental degradation.

Dummy packages might also represent the as-built state of waste packages so that, if advances in monitoring revealed defects, it could be judged whether these had evolved or were unchanged since production of the package.

5.4.3 NDT techniques

There are a number of NDT techniques that may be capable of development to be applicable to the monitoring and inspection of active and simulant wasteforms during storage, including X-ray radiography, neutron radiography, ultra-sonics, thermography and acoustic emission [15, 16, 17]. The techniques could provide information about the development of cracks or voids within the wasteform, or the extent of corrosion of metallic wastes.

5.4.4 Direct measurements

Removal of the lids of containers would allow internal visual inspection, hardness tests on surfaces and removal of samples of the wasteform for chemical and physical analysis.

5.5 Monitoring of environmental conditions

In addition to the techniques recommended above for monitoring the condition of the packages in the stores, it is important that the environmental conditions within the stores should also be monitored and controlled to ensure that suitable storage conditions are maintained. This is particularly important in the case of monitoring of chloride on waste package surfaces and guidance on monitoring levels of chloride on surfaces is given in Appendix A.

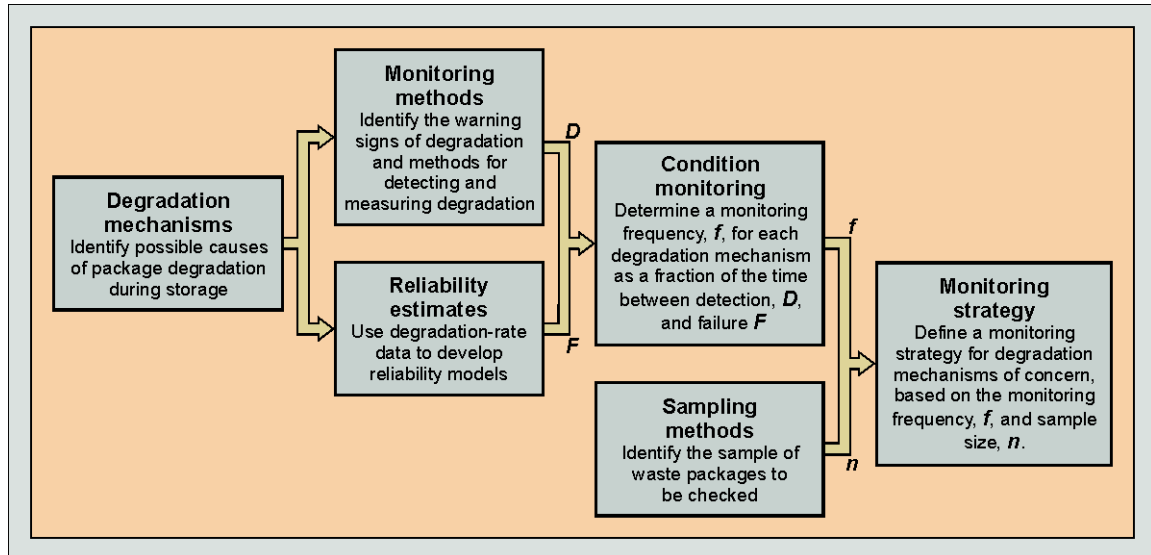
6 DEVELOPMENT OF A MONITORING STRATEGY

Previous sections have described the issues associated with waste package evolution and techniques available for monitoring waste package integrity. The next step is to consider how this should be worked-up into a practical monitoring strategy.

Pre-requisites for the monitoring strategy will be definition of a 'baseline', based on the Waste Product Specification, specification of the storage environmental conditions and an assessment of the performance of waste packages under these conditions. The objective is to validate performance and detect change. Thought should also be given to defining the

degree of change that would require further investigation and action. The different stages in the development of a condition monitoring strategy are illustrated in Figure 1

Figure 1 Key Components of Condition Monitoring Strategies.



A condition monitoring strategy may be summarised as:

- Identification of potential degradation mechanisms (Section 4) which lead to changes in properties.
- Identification of monitoring techniques to detect such changes. A number of techniques are available, or could be extended for remote application, which could be used for monitoring the condition of stainless steel packages within a waste store (Sections 5.1 to 5.4). Not all changes may be directly detectable; some may have to be inferred (for example, by using dummy packages or small-scale samples).
- Estimation of package reliability based on degradation rate data (Section 6.1).
- Determination of monitoring frequency as a fraction of the time between the point of detection of degradation, D , and the expected time of waste package failure, F (Section 6.1).
- Identification of a means of selecting a representative sample of packages to be monitored (Section 6.2).

The derivation of a monitoring strategy requires consideration of several other factors relating to the feasibility of its implementation, such as:

- The radiological doses associated with different monitoring operations;
- The potential for damaging waste packages during monitoring operations, including physical retrieval for inspection;
- The costs of monitoring;
- The practicalities of operating and maintaining monitoring equipment.

The transfer of methodologies from other industries should be considered (e.g. Risk Based Inspection [18], Corrosion Prevention and Control Programmes, etc.).

6.1 Frequency of monitoring

The frequency of measurements, f , should be chosen on the basis of the expected rate of degradation and the perceived risk to the integrity of the containers. Several mathematical models are available to characterise degradation-rate data, the most commonly adopted being the exponential distribution, the Weibull distribution, and the lognormal distribution [19,20]. Combinations of these life distributions can be used to generate waste package reliability curves.

The exponential model assumes a constant failure rate and is not generally applicable to age-related failure mechanisms. The Weibull distribution provides a wider range of failure rate curves than the exponential distribution, and is often used to model data relating to failure caused by degradation phenomena. The lognormal distribution has been applied to degradation mechanisms such as corrosion and crack propagation, and thus, may represent the most appropriate model for waste package degradation.

Failure rate data for waste packages in long-term storage are inevitably not available. Accelerated testing to failure may be interpreted to convert test failure times to actual failure times under operating conditions. Also, techniques are available to extrapolate degradation data to obtain failure times [20].

If sufficient data exist to generate a reliability function, e.g. based on one of the mathematical models above, then curves can be constructed to allow times until failure, F , for different failure modes to be determined. Using such curves, a monitoring frequency, f , for each degradation mechanism can be determined as a fraction of the time between detection, D , (when degradation can first be measured) and time to failure F .

The monitoring frequency should allow time for preventative action or additional protection to be put in place.

6.2 Waste package sampling

In order to build confidence in the distribution and levels of characteristics of all packages in a store, a sample survey of a subset of packages must be undertaken. A small sample may be sufficient to provide reassurance that packages are behaving as expected in the specified environment. If unexpected changes are detected or suspected a larger sample would be required, based on statistical principles. There are two types of sample, non-probability samples and probability samples [21].

Non-probability methods include convenience sampling, judgmental sampling, critical sampling, and quota sampling. The drawback of non-probabilistic sampling is that the sample may not be representative of the population, and only limited insight can be gained into the reliability of population estimates.

Probability samples are those in which every element of the population has a known, non-zero chance of being selected. Sample size can be determined by consideration of the reliability needed for the resulting population estimates. The larger the sample the greater will be the reliability of the estimate. It may also be necessary to ensure that the sample size is sufficient to distinguish a general trend showing small increases in a parameter (such as package dimensions) from inherent variability associated with manufacturing tolerance.

The main methods by which a population may be sub-divided while maintaining probability sampling are stratification and cluster sampling.

6.2.1 Stratified sampling

It may be convenient to partition the sampling frame into groups or strata, such that random sampling can be performed separately in the strata. Stratified sampling offers potentially significant gains in reliability. Separate parameter estimates can be made for population

parameters for each sub-domain as well as for the overall population. For example, waste packages could be categorised for sampling according to age. Different package age groups could be defined and random samples could be taken from within each age group to ensure packages from all age groups were monitored. Waste packages could also be categorised for sampling according to waste stream.

6.2.2 Cluster sampling

Cluster sampling is a modification of random sampling that offers an efficient means of sampling many packages, such that equipment operations and package disturbances are minimised. Discrete clusters of waste packages in a store may be identified, where each cluster comprises a similar number and arrangement of waste packages. A random sample of clusters is then selected from the population of clusters. All, or a random sample, of the waste packages in the cluster samples may be selected for monitoring. Possible clusters are stillages and waste package stacks. The required number of clusters for a specified confidence interval may be determined based on consideration of standard errors.

Cluster sampling may provide the most efficient means of randomly sampling many packages in a store, but one potential shortcoming is the possibility of systematic variation between clusters, which would result in high standard errors. Such a problem might occur if environmental conditions varied significantly across a store.

6.3 Use of dummy packages in sampling

The use of dummy packages and coupons, described in Section 5, may offer advantages in terms of retrieval and practicality of inspection. In combination with information from experimental studies (e.g. small-scale inactive and/or active test pieces) a small number of dummy packages or coupons may be sufficient to provide reassurance that package integrity is being maintained in the specified environment. To maximise their usefulness, the number of packages or coupons should be optimised using a statistical analysis. Without the support of information from experimental studies many test packages and corrosion coupons might need to be dispersed randomly throughout a store to provide a moderately reliable indication of the condition of the population of waste containers in a store. placement of many test packages and coupons could reduce the capacity of a store.

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APPENDIX A GUIDELINES ON METHODS FOR MONITORING CHLORIDE DEPOSITION ON WASTE CONTAINER SURFACES

A.1 Introduction

One of the critical parameters affecting the corrosion of metals during storage is the surface concentration of chloride ions. The purpose of this appendix is to provide some guidance about methods that could be used for monitoring the concentration of chloride ions on the surface of waste containers during storage. There are currently no specific standard methods for such measurements in waste stores, but there are a number of relevant standards relating to assessing surface cleanliness before coatings are applied to metal substrates. These are discussed in this appendix. Possible sources of chloride ions are outlined and methods for collecting and analysing chloride on surfaces are described. This appendix does not deal with the measurement of airborne chloride.

A.2 Sources of chloride

In general, airborne chloride may arise from distant sources, associated with the sea, industry and/or agriculture, or from chloride generated locally. Maritime aerosols, containing particularly sodium and calcium chlorides, are concentrated within a few tens of kilometres of the coast, but some of the smaller, lighter particles are distributed fairly uniformly across inland areas by wind transport. In urban and industrial areas, chloride is derived from the combustion of coal [A1], and hydrogen chloride vapour [A2] may also be present. Organic forms of chloride could result from the local use of chlorinated solvents or other industrial activity. Solvents from painting and cleaning activities will adsorb onto airborne particles, which could then be transported to the surfaces of containers. Within a waste store, dust containing chloride may be generated by local human activity, for example by the use of internal combustion engines.

A.3 Techniques for sampling surface chloride

Three main methods have been used for removing samples for analysis of surface chloride concentrations. These are:

- Swabbing;
- Direct flushing of the surface;
- Tape lift.

A.3.1 Swabbing

In this method [A3], a defined area is wiped with one or more pieces of filter paper or cotton wool which have been dampened with deionised water. The swabs are placed in sample bottles, which are filled with demineralised water to extract soluble chloride, and the solution is then analysed, either by titration, for example with mercury nitrate, or by ion chromatography. From the analysis a surface chloride concentration can be calculated. It is usually expressed in units of $\mu\text{g cm}^{-2}$. Care must be taken to avoid contamination by handling (e.g. by wearing clean disposable gloves for each measurement). A blank, dampened sample swab, which has not been wiped over the surface, should be taken and analysed at the same time as the sample swabs. It would be advisable to use pre-washed swabs if very low concentrations of surface chloride are expected, since commercially available filter papers contain a small concentration of residual chloride. The sensitivity of the swabbing technique will depend on the detection limit of the analytical equipment used but surface concentrations as low as $0.1\text{-}0.2 \mu\text{g cm}^{-2}$ are readily achievable. The disadvantage of this method is that laboratory based analytical equipment is required.

A.3.2 Direct flushing of the surface

In this technique a liquid is placed in contact with the surface, then collected and analysed. The holder for the liquid may be an adhesive patch with a central compartment (the 'Bresle' patch [A4]) or a rubber sleeve with an adhesive ring at one end. If an adhesive patch is used the liquid is injected into and out of the hollow compartment using a syringe, then removed for analysis. Commercial field kits (e.g. [A5]) are available for measuring the surface concentration of chloride by flushing the surface with a proprietary solution and then analysing the chloride concentration in the solution. The procedure for using these kits is as follows. A rubber sleeve, sealed at one end, is filled with a proprietary organic-based solution and sealed against the test surface using an adhesive ring. The liquid is then massaged against the surface to be tested, to dissolve any chloride on the surface, and the sleeve removed from the surface. The solution is tested by dipping a glass indicator stick into the solution and the chloride concentration, in parts per million or μgcm^{-2} , is determined from the colour change. The detection limit is $\sim 5\mu\text{gcm}^{-2}$. In a similar field kit [A6], the solution is applied in the same way but analysed on-site by liquid drop titration [A7] or by using 'titrator' strips. The detection limit is $\sim 2\mu\text{gcm}^{-2}$.

A.3.3 Tape lift

The total amount of dust accumulated on surfaces can be measured by a tape lift method [A8,9]. In the aerospace and electronics industries, surfaces are regularly sampled by applying a standard grade of tape and analysing the adherent particles, for example by electron microprobe analysis or wet extraction. This technique could be used to measure chloride contamination.

A.4 Techniques for analysis of chloride samples

A.4.1 Chemical analysis

Care should be taken to avoid contamination when handling chloride-monitoring samples, in view of the fact that approximately 1 μg of chloride is present in a fingerprint. The samples should be handled with disposable polythene gloves and stored in clean glass or HDPE bottles. Methods for the pre-treatment of sample containers are outlined in ASTM D 5012 –89 [A10]. The preferred analysis technique for chloride is ion chromatography, combined with atomic emission spectroscopy or mass spectrometry. To ensure complete dissolution of chloride it may be necessary to acidify the sample solution with a high purity mineral acid (e.g. nitric acid). The errors associated with this technique are $\pm 10\%$ and the limit of detection is typically 1ngcm^{-3} .

A.4.2 Conductivity methods

Conductivity measurements [A11] can be used to measure the chloride concentration on a dampened filter paper in contact with the test surface or to analyse the chloride concentration in a solution that has been used to flush a surface.

Allan et al [A12] used a device based on conductivity to monitor chloride deposition on stainless steel during nuclear reactor construction. The total conductivity of a damp filter paper was used to estimate the surface salt concentration and a percentage was apportioned to sodium chloride. Proprietary meters [A13] are available for measuring the concentration of chloride on the surface by conductivity measurements. A dampened filter paper, which is mounted in the open face of the instrument, is placed on the surface of interest and the conductivity of the filter paper is measured. For a known volume of solution added to the filter paper, the conductivity can be related to the concentration of surface contamination. The sensitivity is $0.1\text{-}20\mu\text{g cm}^{-2}$. A drawback with such measurements is that the conductivity may be due to various ionic species other than chloride. If required, the filter papers can be removed for further analysis in the laboratory, for example by extraction with water and subsequent analysis by titration or ion chromatography.

Conductivity measurements can also be used to analyse liquids that have been used to flush surfaces. For example, solution removed from a Bresle patch [A14] can be transferred to a conductivity meter and the reading converted to a surface contamination level. To use this method an assumption has to be made about the chemical form of the chloride (e.g. sodium chloride).

A.5 Techniques for evaluating solid deposition rates

The collection coupon technique outlined in ASTM standard 1739-98 [A15] is a useful basis for evaluating the rate of precipitation of solids onto surfaces. In the standard, the size of the collecting surface is dictated by the need to contain atmospheric precipitation of water. Inside a store this constraint would not apply. The standard also calls for a windshield to be incorporated into the collection vessel. Again, within a building, this would not be essential, although there may be some areas that have stagnant air and others with high air flow rates. Thus, the siting of the sampling point should take account of the airflow patterns within the building. The sample period should be approximately thirty days to allow significant accumulation. The coupons should be weighed and then placed in water for subsequent chemical analysis of the washings. Some studies [A16] indicate that the amount of chloride detected depends on the nature of the metal surface. Therefore, coupons of the target material and finish should be used wherever possible.

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APPENDIX B SUMMARY OF STANDARDS USING CORROSION COUPONS

Standards for corrosion testing are produced by a number of organisations, the most important of which are ASTM and BSI. The relevant standards are listed in the following sections and a few are briefly reviewed.

B.1 ASTM Standards

ASTM G 50-76 [B1] defines conditions for exposure of metals and alloys in atmospheric conditions. It sets forth the general procedures that should be followed in any atmospheric test. It is presented as an aid in conducting atmospheric corrosion tests so that some of the pitfalls of such testing may be avoided. As such, it is concerned mainly with panel exposures to obtain data for comparison purposes. This is the standard which has been applied to the atmospheric corrosion coupons used in the 4 metre Box monitoring programme. The test samples are mounted at an angle of 30° to the horizontal on an insulated test rack.

G4-95 [B2] covers procedures for conducting corrosion coupon tests in plant equipment under operating conditions to evaluate the corrosive attack upon engineering materials. It does not cover electrochemical methods for determining corrosion rates. While intended primarily for immersion tests, the general guidelines provided can be applicable for exposure of test coupons in plant atmospheres, provided that placement and orientation of the coupons is non-restrictive to air circulation.

For carrying out stress corrosion tests, specimens can be made in the form of U-bends, C-rings or bent beams. U-bend specimens are prepared by bending the sheet around a U-shaped former, and clamping the two legs of the U together with a bolt (ASTM G30-94, [B3]). C-ring specimens can be prepared from pipe (ASTM G 38-73, [B4]) and bent-beam can be cut from sheet or plate material (ASTM G 39-99, [B5]). In principle, all these specimen designs could be used to investigate the risk of stress corrosion cracking in a storage environment.

G101-97 [B6], presents methods for estimating the atmospheric corrosion resistance of low-alloy weathering steels, such as those described in Specifications A242/ A242M, A588/A588M, and A709 Grade 50W, from chemical composition data and from actual short-term atmospheric exposure data.

G116-99 [B7] covers the evaluation of atmospheric galvanic corrosion of any anodic material that can be made into a wire when in contact with a cathodic material that can be made into a threaded rod. When certain materials are used for the anode and cathode, this practice has been used to rate the corrosivity of atmospheres. The wire-on-bolt test was first described in 1955 and has since been used extensively under the name CLIMAT Test (Classify Industrial and Marine Atmospheres) to determine corrosivity of atmospheres.

B.2 BSI Standards

Some BSI standards of interest are:

Methods for Corrosion Testing of Metallic Coatings. Guidance on Stationary Outdoor Exposure Corrosion Tests, BS 5466-7:1982 (ISO 4542-1981).

BS EN ISO 7384:1995, *Corrosion Tests in Artificial Atmospheres. General Requirements* Specifies general requirements for the specimens, apparatus and procedure of corrosion tests in artificial atmospheres.

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BS EN ISO 7441:1995 *Corrosion of Metals and Alloys. Determination of Bimetallic Corrosion in Outdoor Exposure Corrosion Tests*. Specifies methods for the determination of bimetallic corrosion of metals and alloys, and metals and alloys with metallic and non-metallic non-organic coatings, in outdoor exposure corrosion tests.

BS EN ISO 7539:1995 *Corrosion of Metals and Alloys. Stress Corrosion Testing. Parts 1 to 7* General guidance on the selection, use and interpretation of the significance of various test procedures that have been developed for the assessment of the resistance of metals and alloys to stress corrosion..

BS EN ISO 8565:1995 *Metals and alloys. Atmospheric Corrosion Testing. General Requirements for Field Tests* Establishes general requirements for stationary corrosion tests of metals and metallic coatings under atmospheric conditions carried out in the open air or under shelters.

BS ISO 11463:1995 *Corrosion of Metals and Alloys. Evaluation of Pitting Corrosion*

B.3 Other Standards

ISO produce a number of relevant standards:

ISO 9223:1992 *Corrosion of metals and alloys -- Corrosivity of atmospheres -- Classification*

ISO 9224:1992 *Corrosion of metals and alloys -- Corrosivity of atmospheres -- Guiding values for the corrosivity*

ISO 9225:1992 *Corrosion of metals and alloys -- Corrosivity of atmospheres -- Measurement of pollution*

ISO 9226:1992 *Corrosion of metals and alloys -- Corrosivity of atmospheres -- Determination of corrosion rate of standard specimens for the evaluation of corrosivity*

B.4 References

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- B2 *Standard Guide for Conducting Corrosion Coupon Tests in Field Applications*, ASTM G 4-95, (1995).
- B3 *Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens*, ASTM G 30-97, (1997).
- B4 *Standard Practice for Making and Using C-Ring Stress-Corrosion Test Specimens*, ASTM G 38-73, (1995).
- B5 *Standard Practice for Preparation and Use of Bent-Beam Stress-Corrosion Test Specimens*, ASTM G 39-99, (1999).
- B6 *Standard Guide for Estimating the Atmospheric Corrosion Resistance of Low-Alloy Steels*, ASTM G 101-97, (1997).
- B7 *Standard Practice for Conducting Wire-on-Bolt Test for Atmospheric Galvanic Corrosion*, ASTM G 116-99, (1999).

