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State of the Art in packaging, storage, and monitoring of cemented wastes
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Abstract

Solid and liquid radioactive waste is progressively being generated by the nuclear industry and institutional producers like healthcare and research. Such waste must be appropriately conditioned in order to be acceptable for storage and eventual disposal. Among possible conditioning processes, encapsulation of waste by means of an industrial cementitious grout is currently implemented by many EU member states. Medium to long-term storage, indicated in the National Programmes of many European countries as the strategy to deal with the delays of available disposal solutions, requires monitoring of waste packages for possible degradation phenomena and managing any arising issues prior to transport to the final repositories. Therefore, innovation in the area of degradation prevention and early detection by means of advanced monitoring systems based on innovative techniques provides significant opportunities for all member states in terms of improved storage operations, reduced cost, increased safety and better understanding of the characteristics of waste prior to final disposal.

Within this framework, the first important objective of the PREDIS-WP7 project on “Innovations in cemented waste handling and pre-disposal storage” is understanding and tracking the State of The Art (SoTA) of current methods and procedures used for cemented waste management with specific focus on monitoring during long-term storage. The approach to gathering the information needed for the SoTA included use of a questionnaire circulated to a large number of organizations registered as End Users of the project.

The results of the survey which involved eleven respondents provided an initial picture of the main aspects related to the storage of cemented waste packages such as the types of waste streams stored, main waste package typologies, storage management strategies, degradation phenomena expected or observed, and monitoring systems currently employed.

The SoTA may be updated in later years of the project to incorporate progress in technology and newly gathered data hopefully by physical information exchange at meetings with or site visits to End Users when the COVID-19 Pandemics will be finally overcome.

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Notification

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HISTORY OF CHANGES

Date	Version	Author	Comments
2021-04-14	1.1	Sogin	Updated of paragraph 8.2 "*Fiber optic sensing system*". Update of Table n.9 "*Cemented Waste package typologies and main characteristics".*

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1 Acronyms

AAR	Alkali Aggregate Reactions
ASR	Alkali-Silica Reactions
BFC	Blast Furnace Slag
DEF	Delayed Ettringite Formation
EDTA	Ethyleneiaminetetraacetic Acid
FA	Fly Ash
HLW	High Level Waste
ILW	Intermediate Level Waste
LLW	Low Level Waste
LMW	Low Molecular Weight
NDE	Non Destructive Evaluation
NDT	Non Destructive Testing
OPC	Ordinary Portland Cement
PVC	Polyvinylchloride
RFID	Radio Frequency Identification
RTR	Real Time Radiography
SCM	Supplementary Cementitious Materials
SoTA	State of The Art
VLLW	Very Low Level Waste
WAC	Waste Acceptance Criteria
WMO	Waste Management Organisation

2 Introduction

Solid and liquid radioactive waste is progressively being generated by the nuclear industry and other applications like healthcare and research. Such waste must be treated and conditioned appropriately in order to be acceptable for storage and eventual disposal.

Among possible conditioning processes, encapsulation of waste by means of industrial cementitious grout has been and is currently implemented by many member states as a common conditioning medium thanks to the favourable properties of the resulting wasteform for immobilizing and containing radionuclides. Hence, significant volumes of ‘cemented waste packages’ have already been produced and will continue to be generated in the future, requiring medium/long-term storage pending the availability of disposal repositories.

Such extended storage is prone to increase the probability of degradation phenomena (e.g. corrosion, swelling, chemical reactions, etc.) requiring interventions like re-treatment/re-conditioning/re-packaging prior to transport to the disposal repository.

These abnormal events may be limited enough so that they only require simple recovery actions but, in some cases, the common degradation phenomena may impact many packages with similar characteristics, thus requiring large scale interventions with high associated costs.

Therefore, innovation in the area of degradation prevention and early detection by means of advanced monitoring systems would entail significant positive effects for all member states in terms of improved storage operations, including cost, safety, and better understanding of the characteristics of waste prior to final disposal.

Within this framework, the first important objective of the PREDIS-WP7 project is understanding and tracking the State of The Art (SoTA) of current methods and procedures used for cemented waste management with specific focus on monitoring during long-term storage. In particular, as described in detail in the present report, the SoTA involves reviewing and recording information on the cemented packaging systems, storage systems, storage management procedures, waste acceptance criteria (WAC) and monitoring techniques currently in use.

The scope of the SoTA is not only setting boundary conditions (materials, test parameters, etc.) for technical innovation tasks (experimental, modelling) but it also constitutes the starting point for performing the Gap Analysis and enabling a comparison between the current state of knowledge and the state that will be reached at the end of the PREDIS project following implementation of innovative techniques and solutions.

The original approach for gathering from End Users the information needed for the SoTA included both visits to the main waste management organisation (WMO) storage facilities and the distribution of a questionnaire to these organizations. Unfortunately, the COVID-19 pandemic made the visits impossible and forced the organizers to refer only to the questionnaire results. The questionnaire was distributed to the registered End Users at the end of 2020 and the results gathered from eleven organizations are summarised in §7 of the present report.

As one might imagine, the unscheduled cancelation of the visits to the storage facilities has undeniably caused the exclusion of the original major source of information for the SoTA. However, the results of the questionnaire do represent a valid instrument for collecting current methods and procedures for cemented waste management. Owing to the lack of information that can only be collected through direct contact with WMOs and actual survey of the stored waste packages, we plan to update this report in later years of the project when further information can be gathered.

3 Context of the SoTA

As previously stated, the PREDIS-WP7 project on Innovations in cemented waste handling and pre-disposal storage has some important objectives including compilation of this SoTA in current methods and procedures used for *cemented waste management* with specific focus on *monitoring during preparation, handling and long-term storage*.

The SoTA report and the results of the survey will be a useful resource for the other activities and challenges of the PREDIS-WP7 project such as:

- Identify, evaluate and demonstrate store and package quality assurance (mainly NDE) and monitoring technologies
- Demonstrate the capability of geochemical and chemo-mechanical models to describe the chemical and mineralogical evolution of cemented waste packages and to demonstrate their suitability for disposal
- Develop, adapt and demonstrate digital twin technology, methods for data handling and an overall digital decision framework
- Identify opportunities for increased store automation, reducing human exposure to radiation
- Identify options for post treatment of packages and potential approaches to improve package design, construction, and maintenance

Methods and procedures for waste package quality assurance, integrity and safe storage will be evaluated and assessed as a part of this process. Non-destructive evaluation (NDE) and monitoring technologies will be emphasised. As the work progresses, relevant data will be recorded both directly from waste packages and within storage facilities to get a full picture of all conditions and parameters necessary to predict the long-term behaviour and to allow the development of a decision framework. This framework will be based on existing knowledge, measurement data and predictions from digital twins. Digital twins are simulations of radioactive waste packages built from digitised inventory data, characterisation data, chemical and radiological modelling data and monitoring data. Additionally, these simulations will incorporate the results of machine-learning algorithms trained on digital datasets to produce descriptions of the geochemical evolution and the geo- and thermomechanical integrity of radioactive waste packages during pre-disposal management steps.

4 Waste conditioning process by cementation

Waste packages have been produced in the past and many will be produced in the future using the cementation conditioning process as part of the waste route prior to disposal.

As known, *Predisposal Management* encompasses all steps of the radioactive waste life cycle that collectively cover the activities from waste generation up to disposal, in terms of pre-treatment, treatment, conditioning, storage and transport. Pre-treatment includes any operations prior to waste treatment, to allow selection of technologies that will be further used in processing of waste such as collection, characterisation, segregation, decontamination, and chemical adjustment. Treatment of radioactive waste includes those operations intended to improve safety or cost by changing the characteristics of the radioactive waste. The basic objectives of treatment are volume reduction, decontamination (removal of radionuclides from the waste), and alteration of the physical and chemical composition [9].

The conditioning process, which is the main subject of our attention, is carried out on radioactive waste in order to produce a package suitable for handling, transport, temporary storage, and disposal with the aim of minimizing the risks associated with the transfer of radionuclides and toxic substances from waste to the environment. These operations may include converting the radioactive waste into a solid and stable form and its introduction into a container with adequate characteristics. This processing of radioactive waste provides passive safety for interim storage and prepares the waste packages for eventual disposal.

The concept of passive safety is the basic general requirement needed for a waste package during all phases of long-term management. In addition to the waste container, the wasteform must have characteristics to immobilize the radionuclides and other hazardous materials, providing a significant degree of physical and chemical containment of the materials associated with radionuclide, so as to make an adequate contribution to the overall performance of the waste package.

The parameters that can affect the quality and characteristics of the matrix must be identified and established, as well as monitored during the life of the waste package.

The physical, chemical, and radiological properties of the wasteform should not have any degrading effects on the performance of the waste package. The evolution of the wasteform over time should be such that it guarantees the characteristics of the waste package necessary for short/long term storage, transport and subsequent disposal. In any case, even if there are changes in the characteristics of the waste package, they shall be observed, detected, and monitored so as not to compromise the general performance and relevant safety requirements of the waste packages themselves (see § 7).

PREDIS WP7 only considers cement as a conditioning matrix used for immobilization of various types of wastes. Cement has many good mechanical, physical and chemical properties, so many waste producers have conducted extensive cement formulation development programs and continue with new research to define the best cement and additive mix compatible with different characteristics of radioactive waste streams.

The qualification of the conditioning process takes place by carrying out specific tests on specimens of the conditioning matrix and of the container material and on prototypes of the product, made by simulating the waste to be conditioned and the conditioning process. If the qualification tests are performed on laboratory samples, the characteristics of these samples must be related to those of full-scale products. If the qualification tests are carried out starting from products simulating the real radioactive waste, it is necessary to establish appropriate correlation criteria between the product simulant and the actual radioactive waste. During the qualifying tests, the parameters and the relative range of variability have to be controlled in the production phase of waste packaging, in order to verify compliance with relevant requirements. In some cases, mathematical models and calculation codes can be used and validated.

The cement, in addition to being an economical and easily available material, due to its fluidity characteristics in the initial phase of the conditioning process can be used to immobilize various types of waste, both in fluid (liquid as well as fine particulate) and in solid state.

In PREDIS WP7, two main conditioning processes with cement are considered:

- "*Homogeneous conditioning*": refers to waste which is intimately mixed with a medium such as a cementitious grout to obtain a monolithic wasteform. The main types of waste suitable for homogenous conditioning are:
    - Nonorganic liquids (presence of reactive, corrosive, fissile, alpha contaminated materials, etc.)
    - Organic liquids (presence of chelating, oils, complexing, fermentable, oils, paraffins, fissile, alpha contaminated materials, TBP, etc.)
    - Liquids from nuclear medicine/research
    - Sludges
    - Fluid waste (powders, fine particulates, resins, etc.)

This process can be performed by mixing waste with the cement and then pouring them into the container or with the so-called "in drum mixing" which requires a mixer to be inserted into a waste container or special containers equipped with an internal device such as a paddle for simultaneously pouring and mixing the waste and cement matrix to form a wasteform, as homogeneous as possible. (see Figure 1, Figure 2, Figure 3, Figure 4).

Figure 1 - Sectioning of a full-scale drum from inactive trials using simulant Dounreay Fast Reactor raffinate [16] [17]

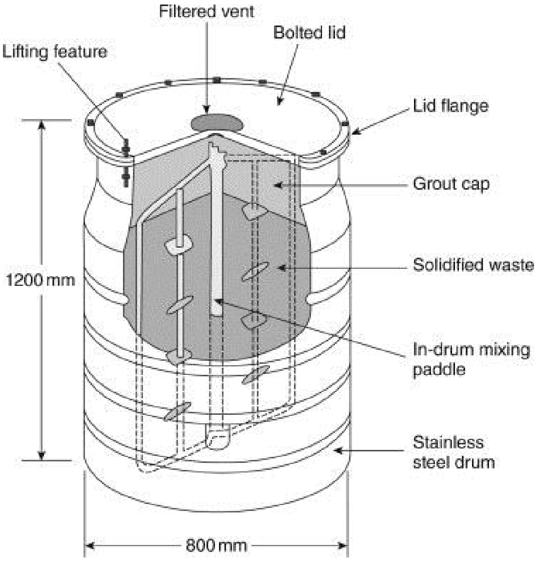

Figure 2 - 500 litre drum with in-drum mixing furniture [20]

Figure 3 - Cemented drum [24]

Figure 4 - In drum mixer [24]

“*Heterogeneous conditioning*” refers to solid waste which is enclosed and immobilized within a medium such as a cementitious grout. The main typologies of those wastes are:

- Cementitious rubble
- Metal scraps/equipment/metal pieces in general from dismantling/maintenance/operation activity/research
- Compacted waste in pucks/pellets (metal, plastic, etc.)
- Large Metal components
- Plastic material (PVC, PET, etc.)
- Rubber
- Sealed sources
- Waste in small containers

The waste is placed in a waste container and a fluid cement is poured inside; if necessary, the process can include the use of vibrating platforms or pressure grouting to improve infiltration of the cement into the cavities of the solid waste to be conditioned and prevent the formation of voids.

Figure 5 shows same pictures of heterogeneous cemented solid waste packages.

As far as possible, the solidification process for fluid and solid waste, as listed and described above, should produce a wasteform with the following main characteristics and properties ([5], [6], [14])

- Physical immobilisation of radionuclides and other hazardous materials
- Physical and chemical compatibility of the waste with any matrix materials and with the container
- Low void fraction
- Exclude free liquid and liquid that may degrade
- Low permeability and leachability
- Chemical, thermal, structural, mechanical and radiation stability during all stages of long-term management
- Resistance to chemical substances and microorganisms

Compacted ILW solid wastes *Magnox fuel cladding swarfs* *Ceramic fuel zircalloy cladding hulls*

Figure 5: Examples of composite wasteforms using encapsulation in cements [23]

The wasteform and the container can both contribute to the overall performance of the waste package, in terms of normal evolution and prevention of degradation phenomena (see § 5 and § 6). So, it is very important in terms of durability of the waste package, to select the correct cement matrix, as well as the package type (material, design, functional requirements, etc.) for the conditioning of a specific type of waste. The cement formulation would be assessed as part of an assessment of degradation evolution of a proposed cemented waste package. Example of degradation processes are the potential chemical reaction between the wasteform and the inner surface of the waste container and the expansive phenomena due to corrosion of the waste components, which could induce stress on the waste container itself. Moreover, it is also important to analyze the evolution of the wasteform due to chemical, biological and radiation reactions that can modify its performance over time, with significant deleterious effects on the overall performance of the cemented waste package.

5 Thermo-hydro-mechanical-chemical processes

5.1 Waste package inventory

A typical cemented waste package consists of the wasteform[1] and the container. The container may be made of metallic material (such as stainless steel with a thickness of at least 1 mm) and may be provided with a coating to reduce corrosion during interim storage.

The wasteform is a heterogeneous mixture of different types of waste such as organic waste (cellulose, rubber, ion exchange resins, filter materials, Polyvinylchloride (PVC), bituminized waste, etc.), metallic waste (steel, etc.) and liquid waste intimately mixed or encapsulated in a matrix constituted by hydrated cement and aggregates. The waste may be pre-treated (e.g. pressed in pellets, absorption, etc.) prior to solidification or solidified without pre-treatment. A schematic diagram of typical cemented radioactive waste packages produced at the Paul Scherrer Institute in Switzerland containing waste from medicine, industry and research is presented in *Figure 6*.

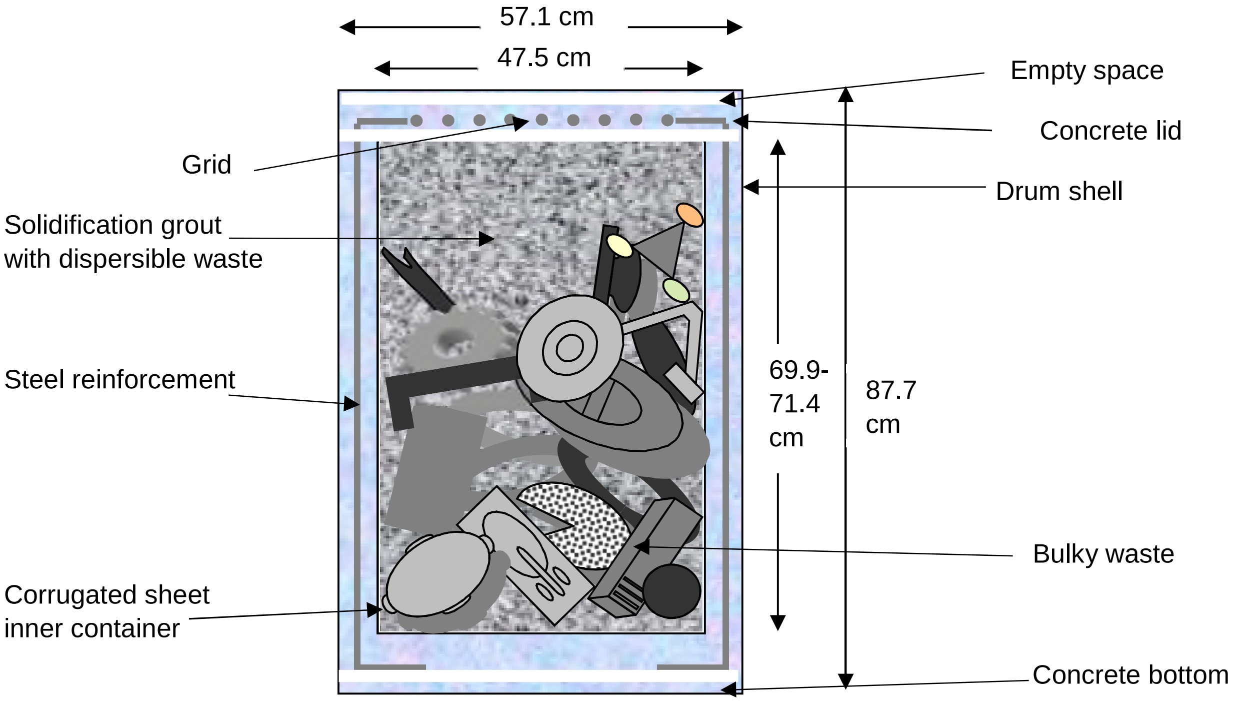

Figure 6 - Schematic diagram of a cemented waste package: Cement solidified dispersive and bulky waste in a 200 L steel drum. (Wällisch, A. 2020. Paul Scherrer Institut, Villigen, Switzerland. Pers. Comm.)

5.1.1 Cementitious materials

Ordinary Portland Cement (OPC) is the most commonly used type of cement for the conditioning of low and intermediate level radioactive waste, from here on termed LLW and ILW ([36], [54], [63], [114]). This is because of its low cost of manufacturing and its favourable chemical and physical properties. When in contact with water, Portland cement produces a high pH environment protecting metallic materials in the waste against corrosion and reducing the solubility of many radionuclides, and upon hydration it forms products with excellent radionuclide immobilisation properties. Cemented waste packages are further characterized by a low

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[1] Wasteform: waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging. Wasteform is a component of the waste package ([1]).

permeability preventing the radioactive waste from leaching, and good compressive strength facilitating transport and handling.

OPC is produced by burning mixtures of limestone and clay-type materials at a temperature 1450°C in a cement kiln to form clinker which is ground to a fine powder in a cement mill and mixed with gypsum ([36], [54]). Clinker consists of mainly four solid phases, and some minor constituents, listed in *Table 1*. The proportions of these phases can vary to influence the properties of the cement paste.

Name	**Cement nomenclature**	**Chemical formula**	**Wt %**
Alite	C_3S	$3CaO \cdot SiO_2$	30 – 60 Wt%
Belite	C_2S	$2CaO \cdot SiO_2$	15 – 40 Wt%
Tricalcium aluminate	C_3A	$2CaO \cdot Al_2O_3$	3 - 8 Wt%
Tricalcium Alumino Ferrite	C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	2 – 8 Wt%
Free lime		CaO	Minor amounts
Gypsum		$CaSO_4$	Minor amounts

Table 1 - Main components of unhydrated OPC ([54])

The cementitious material used for solidification of the waste is obtained by mixing OPC and mineral aggregates with water at water to solid (w/s) ratios varying between 0.4 and 0.6 ([54]). Above a w/s ratio of 0.35, not all water will be consumed during hardening. The excess water will remain in the cement pores and can participate in degradation reactions of organic materials present in the waste or in metal corrosion reactions. The mixing with water will start a series of hydration reactions leading to the hardening of the cement (see section 5.2.1).

Mineral aggregates are inert granulate materials added as fillers to decrease the heat produced during hydration, and to reduce the effects of shrinkage of the cement paste during the hardening process. In the past, often quartz sand was used. The aggregates are assumed to be inert in cementitious environments. However, in many cases, in the long term, deterioration reactions such as alkali-silica reactions (ASR) (may take place resulting in the formation of secondary minerals with larger volumes and physical cracking. (see section 5.2.3). Recently, limestone up to 5 Wt% has been preferred as aggregate to keep pH values above 12.5 and to avoid ASR.

In many cases, the OPC is mixed with supplementary cementitious materials (SCM) such as fly ash (FA) and blast furnace slag or small amounts of silica fume to optimise the properties of the binder to the specific application, to decrease the CO_2 footprint of the cementitious material used and to reduce cost ([54], [63]). In addition, sometimes, special “radionuclide getters” such as zeolites (clinoptilolite), bentonite or vermiculite, are added as well to improve the retention of critical radionuclides such as Cs and Sr.

Recently, new types of binders have been proposed for solidification showing a better chemical compatibility with waste ([44], [88]). These include calcium aluminate cements, calcium sulphoaluminate cements containing calcium aluminate and ye’elemite, respectively, as important clinker constituents, phosphate cements, and alkali-activated binders. These new types of binders will not be further discussed in the present review because their use in waste solidification is still limited.

5.1.2 Metals

Cemented radioactive waste packages commonly contain significant amounts of metals: Candidate materials for containers containing L/ILW waste include stainless steel, carbon steel, and cast iron ([89]).

Operational waste can also contain large amounts of metals including steel, cast iron, copper, brass (alloy of Cu and Zn), aluminium, and zinc ([115]). In general, the quantities of Cu, Al and Zn in the waste are much lower than those of iron and can be ignored when modelling the evolution of cemented waste packages during interim storage.

5.1.3 Organics

The organics present in cement-stabilized radioactive waste originates from two sources: 1) the cementitious binder itself and 2) the waste.

The cementitious binder used for the solidification of the waste commonly contains various organic compounds (up to 1 Wt%) added to allow working with lower calcium/silica ratio without impairing the fluidity of the cement paste ([54]). These so-called superplasticisers are high molecular weight organic compounds such as sulfolignine, melamine/naphtaline-sulfonate, polycarboxylates, polyacrylates and polyphosponates. Many commercial superplasticiser formulations contain a mixture of the organic compounds listed above ([54]).

Various other organic materials are commonly present in low and intermediate level waste. Important types of organic materials include plastics, bitumen, ion exchange resins, cellulose and low molecular weight (LMW) organics such as citric acid, ethylenediaminetetraacetic acid (EDTA), oxalic acid, hexamethylenetetramine, and tartaric acid.

Plastics are a large class of synthetic organic materials with a chemical structure consisting of a polymer backbone and side-chains[2]. Common plastics include polyamides, polycarbonates, polyester, polyethylene, polypropylene, polystyrene, polyurethanes, PVC, etc.

Bitumen is often used as a solidification matrix for L/ILW. It is obtained from vacuum distillation of petroleum and consists mainly of long chains of aromatic hydrocarbons containing[3] S, O and N. It is insoluble in water.

Ion exchange resins are used in nuclear facilities for the decontamination of reactor coolant water and spent fuel storage pools. They are made up of a three-dimensional styrene-divinylbenzene polymer backbone occupied with functional groups. Most commonly, a mixture of strongly acidic cation exchange resins containing sulfonate functional groups ($R\text{-}SO_3H$) and strongly basic anion exchange resins containing quaternary ammonium functional groups (e.g., $R\text{-}CH_2\text{-}N(CH_3)_3OH$) is used ([99]).

Cellulose is a polysaccharide made up of linear chains of D-glucose units. It is present in radioactive waste in paper, cardboard, wood, cloths and cotton ([115]).

LMW organic compounds include cement admixtures (e.g., gluconate), detergents, complexing agents (e.g., citric acid, ethylenediaminetetraacetic acid (EDTA), gluconic acid, oxalic acid, hexamethylenetetramine, and tartaric acid.

5.2 Chemical processes in cemented wastes

The temporal evolution of the waste packages during interim storage is the result of a series of chemical and physical processes that may take place after filling the container with the mixture of waste and cementitious materials. During the conditioning of L/ILW, the waste material is placed into a container (e.g. steel drums) followed by the addition of cement clinker, aggregates and water. The reaction between the clinker materials and the water (hydration) results in the formation of a hydrated cement paste. During interim storage, the cement-solidified radioactive waste encapsulated in the waste drums can undergo chemical reactions that may cause the degradation of the waste packages and eventually a loss of waste package integrity. These degradation processes include abiotic and/or biotic degradation of the organic waste components eventually resulting in the formation of CO_2 and CH_4, carbonation of the cementitious materials, alkali-aggregate

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[2] https://en.wikipedia.org/wiki/Plastic
[3] https://de.wikipedia.org/wiki/Bitumen

reactions, corrosion of metallic waste components and steel surfaces of the drums ([59], [68], [114]). The extent to which such reactions take place depends on the presence of water in the waste packages. Each of these processes will be briefly described in the following sections.

5.2.1 Cement hydration

In the presence of water, the clinker materials and the SCMs will rapidly react following a complex process to form a series of hydrates accompanied by the production of heat and the consumption of H2O ([54], [80], [79]). The mixing water becomes strongly alkaline ($12.5 \leq pH \leq \sim 13.3$) due to the dissolution of soluble alkalis (NaOH and KOH), gypsum and anhydrite. The products from clinker hydration consist mainly of portlandite (Ca(OH)2), amorphous C-S-H phases with varying Ca:Si ratios depending on the type of cement (~1.8 in OPC going down to ~1.0 in blended cements), AFm phases such as monosulfo-aluminate hydrate (AFm-SO4) and moncarbo-aluminate hydrate (AFm-CO3), and ettringite (AFt). A typical composition of a hydrated cement paste (sulfate-resisting cement CEM I 52.5 N HTS) is given in Table 2 ([79]). The water added to the mix is progressively bound into the cement hydrates. At higher w/s ratios some of the water is not consumed by the hydration reactions and remains in isolated pores in the cement paste. A detailed description of the chemical processes taking place during cement hydration is given by ([79], [80]).

Hydrated phase	**Content (Wt %)**
Calcium silicate hydrates (C-S-H)	~44
Portlandite	~19
Monocarbonate (AFm-CO_3)	~7
Ettringite (AFt)	~9
Hydrotalcite	~2
$CaCO_3$	~2
Non-hydrated clinker minerals	~16

Table 2 – Modelled phase composition of a sulfate resisting cement paste containing 4 % calcite (CEM I 52.5 N HTS) after hydration for 6 months with a starting w/s ratio of 0.4 ([79])

5.2.2 Degradation of organic materials (biotic-abiotic)

The decomposition of organic materials in the waste may take place both through abiotic (mainly hydrolysis) and biotic processes. The decomposition processes taking place and the decomposition rates depend on the type of organic material present in the waste and on the chemical conditions (pH, redox conditions, presence of water, etc.).

The chemical conditions in cemented waste packages immediately after conditioning are characterized by a high pH environment ($12.5 \leq pH \leq 13.3$) and oxic conditions. With time, redox conditions may become anoxic due to the consumption of the O_2 by metal corrosion and other O_2-consuming processes. Both abiotic and biotic degradation reactions require the presence of water. Hence, the progress of organic degradation reactions strongly depends on the availability of water in the waste packages. Assuming that the radioactive waste is dry at the time of conditioning, two sources of water remain: 1) water added for the hydration of the cement clinker, which did not react. 2) Humidity from the air in the storage room. Under optimal storage conditions it can be assumed that the humidity in the waste packages is higher than in the storage rooms. The second source of water can therefore be discounted.

Biotic degradation processes involving microbial activity are significantly hindered when the pH of the pore water in the waste packages is > 11 ([115] and references therein). However, some microorganisms have developed mechanisms to survive in extreme environments even under the alkaline conditions present in cement ([81]). Furthermore, the heterogeneity of the contents of the waste packages will result in strong spatial variation in the chemical conditions and local pH values may be much lower. Hence, microbial activity cannot be excluded.

The decomposition rate depends further on the type of organic compounds. Wieland et al. (2020) ([114]) divide the organic material in cemented L/ILW waste packages into two categories: slowly decomposable and rapidly decomposable organic materials. The first category contains high molecular weight (HMW) organic materials such as bitumen, polystyrene (ion exchange resins), plastics, and rubber, whereas cellulose (cotton, paper, cardboard, wood, etc.), low molecular weight (LMW) organics, and cement additives are categorized as rapidly degradable organic waste. The decomposition of the first category of organic materials is assumed to be negligible as the period of interim storage is assumed to be relatively short (< 100 years).

An important part of the category of fast decomposable waste is cellulose. The degradation of cellulose under highly alkaline conditions (pH > 11), is controlled by abiotic hydrolysis processes producing mainly α-isosaccharinic acid (α-ISA) and β-isosaccharinic acid (β-ISA) together with minor quantities of other organic acids such as formic, lactic, glycolic, pyruvic, glyceric, threonic and 2-hydroxybutanoic acids ([55], [56]). The degradation kinetics of cellulose are still under discussion but the most recent data show that this process can be divided into a fast decomposition phase, taking 2 – 3 years and a slow decomposition phase. The fast decomposition reaction consists of a stepwise conversion of terminal glucose units to ISA. The extent of the decomposition in this phase depends on the type of cellulose. Van Loon et al. (1999) ([112]) report that in the case of Aldrich cellulose ~30% of the material decomposed within 2 years, whereas only ~1% of cotton cellulose decomposed within this time. The slow degradation process takes up to 5000 years and produces similar decomposition products to the fast process ([55], [92]). Further abiotic decomposition to CO_2 and/or CH_4 is strongly kinetically hindered. Glaus and Van Loon (2008) ([55]) found evidence that in the presence of O_2, α-ISA is abiotically degraded to LMW organic compounds. Under anaerobic conditions abiotic decomposition only occurs to a minor extent.

Under less alkaline conditions (pH <~11) cellulose is primarily decomposed by microbial activity ([115]). Microorganisms decompose organic material via oxidation to consume the energy released during this reaction. Under oxic conditions, O_2 is the main electron acceptor in this oxidation process. When all the O_2 is consumed, other e^- acceptors (e.g., sulfate) take over this task. The biotic cellulose degradation processes can be described by the following overall chemical reactions: The first step is the hydrolysis of the polymers by cellulolytic microorganisms to form glucose monomers. (eq. 1):

$$[C_6H_{10}O_5]_x + xH_2O \rightarrow xC_6H_{12}O_6 \qquad (1)$$

In the presence of O2, these sugars are then further oxidized with as final end products CO_2 and H_2O (eq .2):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad (2)$$

Under anaerobic conditions, the oxidation of the monomeric sugars is accompanied by the reduction of other e^- acceptors such as sulfate (eq. 3):

$$C_6H_{12}O_6 + 3SO_4^{2-} \rightarrow 6CO_2 + 3H_2S + 6OH^- \qquad (3)$$

Under strongly reducing conditions, finally, the sugar monomers may be decomposed to CO_2 and CH_4 by a fermentation process called methanogenesis (4):

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \qquad (4)$$

The microbial decomposition of LMW organic ligands such as citric acid, EDTA, gluconic acid, hexamethylenetetramine, oxalic acid, and tartaric acid, is fast and is expected to be completed within 100 years after conditioning of the waste ([68]). An approximate average decomposition reaction can be based upon the degradation of acetic acid giving the following overall reaction under oxidizing conditions:

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O \quad , \tag{5}$$

and under reducing conditions:

$$C_2H_4O_2 \rightarrow CO_2 + CH_4 \quad . \tag{6}$$

The thermodynamically stable end products of both abiotic and biotic processes thus are CO_2 and H_2O under aerobic conditions and CO_2 and CH_4 under reducing conditions.

5.2.3 Carbonation

Cement in radioactive waste drums may come into contact with two sources of carbonate: 1) limestone present as aggregates in the cement binder, 2) CO_2 generated during the decomposition of organic waste materials. This CO_2 may dissolve in remaining pore water in the waste packages to form CO_3^{2-} anions which may react with the cement phases, in particular, C-S-H phases: Portlandite and $AFmSO_4$.

1) Thermodynamically, AFm-CO_3 is more stable than AFm-SO_4. Hence, in the presence of water, SO_4^{2-} anions in AFm-SO_4 will be substituted by CO_3^{2-} anions originating from the dissolution of $CaCO_3$ in the limestone. The SO_4^{2-} anions released from the AFm phases will produce more AFt phases ([76]). The lower density of AFt compared to other cement hydrates results in a slightly larger bulk cement volume due to the lower density of ettringite and thus in a lower pore volume. Lothenbach et al. (2008) ([76]) calculated that after 28 days of hydration, the presence of 4Wt% limestone in OPC leads to an increase in the bulk volume of hydrated cement material with ~3% resulting in a difference in porosity of ~0.5 vol. %. Differences observed in experiments were however significantly smaller which was explained by the fact that Al uptake in C-S-H phases was not taken into account in the calculations.

2) Dissolved carbonate generated during the decomposition of organic waste converts portlandite and C-S-H phases in the cement paste into $CaCO_3$(s). These carbonation processes can be described for portlandite, C-S-H phases with a C:S ratio of 1.667 and with a C:S ratio of 0.833 by the following overall reactions ([114]):

$$Ca(OH)_2(s) + CO_2(aq) \Leftrightarrow CaCO_3(s) + H_2O \tag{7}$$

$$(CaO)_{1.667} \cdot SiO_2 \cdot (H_2O)_{2.1}(s) + 1.667CO_2(aq) \Leftrightarrow 1.667CaCO_3(s) + SiO_2(s) + 2.1H_2O \tag{8}$$

$$(CaO)_{0.833} \cdot SiO_2 \cdot (H_2O)_{1.33}(s) + 0.833CO_2(aq) \Leftrightarrow 0.833CaCO_3(s) + SiO_2(s) + 1.33H_2O \tag{9}$$

These reactions show that the carbonation of hydrated cement phases releases water but water is also required to catalyse the carbonation reaction ([114])

5.2.4 Alkali Aggregate Reactions (AAR)

Often silica-rich materials are added to the concrete as quartz aggregates or as silica fume3 ([54]). The early age reaction between siliceous aggregate and cement paste are often beneficial to the densification of the cementitious matrix. However, the late age reaction of silica in aggregate often results in a degradation. This reaction takes place between silica and the Na/K content in concrete pore solution, thus denoted as ‘Alkali-Silica-Reaction (ASR) ([38], [60], [98]). The resulting ASR product mainly consisting of silica and alkali hydroxide plus some calcium. In the presence of moisture, this product expands and exerts internal pressure, which generates cracks first in the aggregates and later on into the concrete. ASR damage is among the most commonly diagnosed durability problems for aged infrastructures ([51]).

Unlike the general surface reaction of silica at early age, the ASR often takes places at existing micro-cracks in aggregate ([70]). Despite years of study, the mechanism of ASR is still not completely understood. Nonetheless, a few parameters are proven to largely influence the dissolution of silica. First, a high pH value of concrete pore solution is necessary to efficiently dissolve silica. This is usually the case for OPC concrete, but not for concrete with pozzolanic admixture such as fly ash and silica fume ([78]). Second, the presence of alkalis, such as Na and K, largely accelerates the dissolution of silica by forming SiO-Na+/K+ complexes on the silica surfaces ([48]). By contrast, the presence of Al in pore solution seems to inhibit the dissolution of silica ([40][45]). The dissolution of silica is under coupled action of all these parameters.

The geochemical nature of the aggregate also dominates its potential for undergoing ASR. Standard tests have been established to evaluate such a potential ([107]). For example, aggregate (191-ARP, 2003) or mortar (106-AAR, 2000) prisms are immersed in alkaline solutions for a certain period to measure the amount of dissolution or the elongation, respectively. According to the standard tests, two groups of siliceous minerals demonstrate the ability to react and expand when in contact with the alkalis in concrete: 1) metastable under atmospheric conditions types of silica (opal, chalcedony, tridymite, cristobalite) including some disordered forms of quartz, 2) alumina–silicate glasses mainly in the matrix of intermediate to acid volcanic rocks ([74], [94]). Their reactivity usually increases when the degree of structural order is low and/or the crystallite size is small. Meanwhile, standard tests may fail to predict the reactivity of certain aggregates over long-term exposure to real conditions. Aggregates that pass the standard test may exhibit ASR after a few years of service ([74]).

Thermodynamic modelling of ASR was not possible due to lack of knowledge of the ASR product. However, recent modelling has been undertaken after a relevant database was established for the ASR products ([103]). ASR products with systematically varying Ca-to-Si ratios and (Na+K)-to-Si ratios were prepared in the laboratory and their solution chemistry was measured. The lab-synthesized product was proven to be highly comparable to the ASR product from different affected concrete infrastructures. It should be noted that both the synthesized product and the product from affected concrete are considered the ‘second-stage’ ASR product. The ‘first-stage’ ASR product forming in pre-existing cracks are usually much less crystalline than the ‘second-stage’ product ([47]), yet its structure and role in generating the expansion stress is poorly understood ([71]). More experimental evidence is evidence is needed to solve this puzzle.

5.2.5 External-internal sulfate attack

Sulfate attack can have external or internal causes. In the latter, the sulfate attack is caused by a soluble source being incorporated into the concrete at the time of mixing, such gypsum in the aggregate. The more common type is the external sulfate attack, which is caused by the penetration of sulfates in solution, into the concrete from outside. It typically occurs where water containing dissolved sulfate penetrates the concrete.

Sources of sulfate, which can cause sulfate attack, include seawater, oxidation of sulfide minerals in clay adjacent to the concrete (this can produce sulfuric acid which reacts with the concrete) and bacterial action in sewers (anaerobic bacteria produce sulfur dioxide which dissolves in water and then oxidizes to form sulfuric acid).

Sulfate attack requires intimate contact between sulfate anions and the cement paste of the concrete. Therefore, in a sulfate attack ions must be transported from the surface into the concrete bulk. Sulfate ingress is driven by a concentration gradient (diffusion) and impeded by the permeability of the sample. Consequently, it has been shown that the use of a lower w/s ratio will result in better resistance to external sulfate attack ([84]).

Yu et al. (2013) ([117]) measured the sulfate profile of Portland cement mortars immersed in a sodium sulfate solution and were able to identify three distinct zones. (a) an outer surface lacking in sulfate, owing to the absence of calcium to bind the element, (b) an increasing sulfate concentration to a maximum depth of 0.5–1 mm (c) a gradual decrease in sulfate concentration to background levels over a depth of several millimetres.

The external and internal sulfate attack is usually associated with the formation of ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$. In that theory, it is assumed that ettringite takes up more space than the AFm phases from which it forms when water and sulfate ions come from the exterior. Therefore, this has led to the development of “sulfate resisting” cements characterized by low content of the C_3A phase. However, the mechanisms underlying sulfate related degradation are still poorly understood, despite considerable research effort. Several theories for possible expansion mechanisms exist in the literature. Brown and Taylor (1999) ([43]) identified swelling, topochemical reactions, increase in volume of solids and crystal growth pressure.

5.2.6 Corrosion of metals in concrete environment

Radioactive waste packages are at all time in contact with air during interim storage. However, microbial activity, metal corrosion and other O_2-consuming processes can cause O_2 depletion and create an anoxic environment when no O_2 supply from the environment is possible in tightly closed waste packages. Depending on the type of waste and containers, all O_2 may be consumed in less than 10 years ([113]). Hence, both oxic and anoxic corrosion can take place. All metals present in the radioactive waste packages except Cu can undergo oxic corrosion.

The largest part of the metal inventory of the waste packages is usually steel and cast iron ([114]). Under the alkaline conditions prevailing in cemented waste packages, Fe corrosion in contact with an O_2-saturated solution can be described by two half-cell reactions (eq. 10 and 11). Fe^{2+} readily undergoes hydrolysis to form ferrous hydroxide ($Fe(OH)_2(s)$). This gives the overall reaction presented in eq. 12 ([34], [35]):

$$2Fe(s) \rightarrow 2Fe^{2+} + 4e^{-} \tag{10}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{11}$$

$$2Fe(s) + O_2 + 2H_2O \rightarrow 2Fe(OH)_2(s) \tag{12}$$

When all O_2 is consumed in the waste packages, steel will corrode anaerobically. The second half cell reaction then becomes:

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \quad , \tag{13}$$

and the overall reaction becomes:

$$Fe(s) + 2H_2O \rightarrow Fe(OH)_2(s) + H_2(g) \tag{14}$$

This ferrous hydroxide forms a stable, passive, and insoluble film on the steel surface (passivation) serving as a physical barrier between the steel barrier and the concrete pore water, thus, significantly slowing down the corrosion process. In the presence of O_2, Fe^{2+} is thermodynamically unstable and is oxidized further to Fe^{3+}. Hence, a part of the Fe^{2+} present in the passive film will oxidize. Thus, passive films commonly exhibit a bilayer structure consisting of an inner hydroxide layer, 1 – 3 nm thick, rich in Fe^{2+} and an outer hydroxide layer strongly enriched in Fe^{3+} ([35], [95]). The thickness of the inner hydroxide layer remains more or less constant while the thickness of the outer, Fe^{3+} rich layer increases with progressing corrosion time. It is assumed that the inner Fe^{2+}-rich layer mainly protects the Fe from corrosion.

Two main factors that can compromise the stability of the passive film leading to its dissolution and the initiation of corrosion processes: the presence of complexing ligands in the pore solution (e.g., chloride (Cl^-) or sulfate (SO_4^{2-}) and concrete carbonation ([34], [35]).

As described above, CO_2 originating from organics degradation can dissolve in the pore water in the waste package and react with the cement hydrates (e.g., portlandite, C-S-H phases) to form $CaCO_3$. These carbonation reactions are accompanied by a reduction in pH to values as low as 6 leading to a destabilization of the passive film on the metal surface, thus, initiating the corrosion process.

The exact role of chlorides in the depassivation of iron surfaces is still under discussion: One explanation is based upon the formation of stable, soluble Fe^{2+} -chloride complexes, increasing the Fe^{2+} solubility and destabilizing the passive $Fe(OH)_2(s)$ layer on the surface of the metal thus making it more susceptible to corrosion.

$$Fe(OH)_2(s) + 2Cl^{-} \rightarrow FeCl_2 + 2OH^{-} \tag{15}$$

In the absence of a passive layer under aerobic conditions, $Fe(OH)_2(s)$ will oxidize further to form corrosion products: initially amorphous hydrous ferric hydroxide ($Fe(OH)_3(s)$ which then gradually dehydrates to more crystalline forms such as goethite (α-FeOOH) and lepidocrite (γ-FeOOH) ([73]).

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3(s) \rightarrow FeOOH + H_2O \quad (16)$$

Under anaerobic conditions it is assumed that $Fe(OH)_2(s)$ further oxidises to magnetite (Fe_3O_4) via the Schikorr reaction (Smart et al., 2017):

$$3Fe(OH)_2(s) \rightarrow Fe_3O_4 + H_2(g) + 2H_2O \quad (17)$$

The formation of goethite or magnetite during steel corrosion results in significant volume expansion leading to cracking of the grout in the waste packages. Indeed, α-FeOOH and Fe_3O_4 have Pilling-Bedworth ratios of 2.9 and 2.1, respectively meaning that the molar volumes of α-FeOOH and Fe_3O_4 are 2.9 times and 2.1 times larger than that of Fe(0) in steel ([52]).

Corrosion rates in cementitious environments are generally found to be in the range of 0.1 – 1.0·µm $year^{-1}$ ([54][104]). However, decreasing pH due to e.g. ASR reactions may significantly increase corrosion rates. Protective metal oxide films formed during alkaline passivation only appear at pH values above ~11.

5.3 Environmental impacts

Environmental conditions in an interim storage facility define the boundary conditions (temperature, pressure, humidity, etc.) of the stored individual waste packages as a function of time. As shown in 5.4 these storage parameters are important for the chemical evolution of the cementitious waste packages because water availability is a limiting or driving factor for most of the geochemical reactions in the cementitious waste packages, and temperature and pressure influencing intrinsic geochemical reactions. There might be a differentiation between waste packages, which are isolated from their environment, i.e. closed packages without any exchange of water between waste package environment and the inner part of the waste package, and open waste packages allowing water vapour and gas exchange with its environment. Both types are discussed in 5.4.

5.4 Geochemical modelling

The geochemical modelling of cement or cementitious waste packages is the numerical description of the individual geochemical processes as described in the chapters above. It includes equilibrium geochemical processes as well as kinetic processes taking place within cementitious material at different time scales. It also includes the modelling of the geochemical evolution of cementitious material and interactions of cementitious materials with the environment (interaction with air, water, radionuclides …), which is in this specific case the modelling of the geochemical evolution of the waste packages in an interim storage facility. The results of such modelling provide the pore water composition, the mineral composition, the porosity distribution and the distribution of radionuclides in solution and sorbed onto specific minerals and their temporal evolution.

A lot of geochemical codes, e.g. GEMS-Selector ([69]), PHREEQC ([90]), ORCHESTRA ([83]) and databases, e.g. SUPCRT92 ([58], [64]), Thermoddem TDB ([41]), ThermoChimie ([42], [53]), PSI/Nagra TDB ([108]) are available; some were especially developed to describe cementitious systems, e.g. CEMDATA TDB ([75]). Among these codes, there is a distinction between equilibrium codes, describing just the equilibrium state of a specified element composition at a given temperature and pressure, and coupled reactive transport codes also taking into account advection/diffusion processes taking place within the pores and pore water of a cementitious system, e.g. OpenGeoSys ([65]), MCOTAC ([93]), OpenGeoSys-GEM ([68]), TOUGH2 ([97]), ORCHESTRA ([83]) among others. Taking into account transport processes may yield geochemical fronts evolution within initially homogeneous cementitious materials, when in contact with air or water at the surface, for example. A further coupling of geochemical processes and mechanical processes, e.g. strain evolution within cementitious samples due to mineral transformations, is described chapter 5.5.

With respect to the scale of geochemical modelling a huge development occurred during the last twenty years due to the new microscopic techniques and computational tools yielding atomic bonding lengths, mineral structure identification or atomistic and molecular modelling on the sub micrometre scale, which leads to a better understanding of processes at the macroscopic scale.

A multi-scale representation of morphological heterogeneities of concrete from a modeller's view point are shown in figure 1 of Patel et al (2018) ([91]) with increasing detail of geochemical (and mechanical) transport. Their multi-scale classification from macro (>10^{-1} m, continuum phase), meso (10^{-1}-10^{-4} m, aggregates, cement paste, interfacial transition zone), micro (10^{-4}-10^{-6} m, capillary pores, C-S-H matrix, clinker, portlandite and other hydration products), sub micro (10^{-6}-10^{-9} m, high density and low density C-S-H phases consisting of elementary building block in matrix of gel pores) to nano (< 10^{-9} m, C-S-H globules with interlayer pore spaces) scale has to be extended to an even larger scale of an interim storage facility, i.e. the sum of all the waste packages in an interim storage facility, whereas their continuum phase represents about the content of a homogeneous cementitious waste package. One should also keep in mind that modelling at different scales implies the use of different tools for individual scales and process descriptions. Depending on available experimental data, computational performance, detail of process understanding and foreseen prediction time, different approaches might be applied describing cementitious waste packages, i.e. mixing tank model describing the cement package as a homogeneous system that evolves according to cement/waste/environment interactions with averaged properties for the whole waste package. A more detailed description would be a spatially discretised waste package with node or volume specific properties (heterogeneity with respect to chemical and mineral composition, porosity, water content, boundary conditions, radionuclide inventory, etc.) taking into account advective and diffusive transport processes in the gas and liquid phase coupled with geochemical equilibrium and kinetic reactions, which would allow predictions of specific chemical fronts within a waste package. The latter is computationally much more expensive and would need a detailed description of the initial state of a waste package (mineral, waste, porosity, humidity distributions). Both are described below.

5.4.1 Mixing tank approach

The mixing tank approach describes the waste package evolution as an average behaviour of a specific waste package with respect to cement, aggregate and waste composition. This composition might be different for different waste packages but is homogenised for a single waste package. The spatial resolution is on the metre scale. There is no information available on the interior of a waste package on the centimetre or sub-centimetre scale. However, processes such as degradation of organic compounds, steel corrosion, degradation of silica aggregates, carbonation of the cement paste etc., are assumed to occur simultaneously and are modelled simultaneously by assuming complete mixing within the waste package (see for example Wieland et al. (2018)). The mixing tank approach provides information on the progress of reactions within individual waste packages, fulfilling mass conservation for geochemical calculation for a single waste package and indicates the relative importance of the various coupled processes occurring in a single waste package. As shown by Wieland et al. (2018) ([115]), water availability within a waste drum is a critical parameter for many processes taking place in a waste package. Wieland et al. (2018) ([115]) demonstrated this by using the GEM-Selektor (GEMS) v3.3 code ([69]) together with the Nagra/PSI thermodynamic database ([108]), the CEMDATA 14.01 database ([77]) and MIRAM 14 database ([87]) for two different scenarios. (1) an intact waste package (no water or gas can enter the waste from outside the waste package or get out of the waste package), and (2) a non-intact waste package where there is exchange with the environment assumed and water availability is not limited, e.g. due to humidity in the air outside the waste package.

They identified also that the water to cement ratio used for conditioning the waste package plays a role, since this initially added water is bound by cement phases and a remaining portion would be available for water-consuming reactions. Their geochemical modelling reveals also that the inventory of a waste type determines when the water is exhausted and the water-consuming reactions will stop, and that zeolites play a crucial role as they bind water in the structure. Their calculations show that the timescale for which the different waste types are chemically reactive are very short in case of the bituminized waste types (less than a decade up to few decades), while time scales are longer in case of the cemented waste types (a few decades to a few thousand years). Their application of the mixing tank model yield already important indication for waste package evolution, i.e. the reactivity of all waste types is strongly determined by the access of water within a waste package and decreasing for "dryer" conditions. Water, which may enter the waste package from outside, may reduce the gas production in the waste package, whereas carbonation of the C-S-H phases and subsequent conversion into calcite as well as alkali uptake strongly influences the pH development.

Although the given example represents a simple mixing tank model, quite complex geochemical processes and their interplay have been taken into account, which allows for comparison of different waste package compositions and their temporal evolution with respect to gas production, pH development, mineral transformation and porosity evolution etc. These are important indicators for waste package integrity during extended interim storage. Nevertheless, this “simple” mixing tank approach needs quite detailed information on the initial composition of the waste package and the environmental (e.g. air humidity) and geometrical (intact or non-intact waste package) boundary conditions; and calculation times do not have to be underestimated because of the geochemical complexity of the mixing tank model that could be defined already for the homogeneous waste package.

5.4.2 Reactive transport modelling

Reactive transport modelling is about mixing tank models distributed in one-, two- or three-dimensional space, where at each volume, cell or node in space a mixing tank model is defined with different cement, mineral, waste, porosity compositions. In addition, advection and diffusion processes due to hydraulic and concentration gradients are responsible for coupled geochemical and transport processes. Whereas the mixing tank model describes a homogeneous waste package, the reactive transport model of a waste package may have an unlimited spatial resolution with respect to processes taking place at different scales within a waste package. An unlimited computational power would be necessary to achieve a very detailed spatial and temporal description of a waste package. Nevertheless, such reactive transport calculations would be necessary to test the results of the mixing tank approach described above and to identify localised processes which may have more severe influence on the waste package integrity, for example, than taking into account averaged processes homogenised within a whole waste package.

Kosakowski et al. (2020) ([67]) used the newly developed reactive multi-species multi-phase code OGS-MP-LT ([59]) based on the OpenGeoSys framework ([65]) with an effective parameterization for concrete degradation and kinetic rate laws for organic degradation and corrosion. Coupling of transport and chemical processes was realised via source/sink terms for water and gases. With this tool, the authors investigated the water and gas transport in a typical waste package during interim storage in 2D cylinder spatial geometry.

For such a setup, node, cell or volume specific initial and boundary conditions and assumptions on the environment (conditions outside the waste package) must be defined to model the waste package evolution. Modelling results provide water saturation distribution in the waste package, localised fluxes of gas and water, gas generation, pH, porosity, or chemical reactivity distribution within the waste package etc. as well as cumulated gas production rates, for example, within the whole waste package (for details see [67]).

When comparing their results with those obtained by Wieland et al. (2018) ([115]) for a mixing tank approach, significant differences were observed for the temporal evolution of gas generation rates and water consumption. Because material heterogeneity was considered for the reactive transport modelling, initial geochemical conditions deviate significantly from the averaged system of the mixing tank model. These differences have direct consequences on gas generation and water consumption, which are much higher in the spatially heterogeneous model. As the water availability in both approaches is the limiting factor for the chemical processes, and the distinguishing factor between waste and backfill materials in the heterogeneous reactive transport approach, the pH in the waste is low and related metal corrosion and associated consumption of water are high. Water in the waste is consumed quickly, while water transport in the liquid phase and by humidity transport in the gas phase is limited by the low permeability of the enclosing backfill material. Gas generation is limited by the transport of water in and across the backfill material. The comparison of both approaches shows that the mixing-tank model is not necessarily "conservative" in the sense that it systematically over- or underestimates the influence of specific processes. Therefore, to assess the limitations of mixing tank models, reactive transport model applications are necessary to confirm or not mixing tank model applications, even though calculation times might be tremendously longer.

Recently, new upscaling approaches and machine learning algorithms have been proposed to overcome the issue of long calculation times, especially caused by geochemical calculations with e.g. GEMS, which have to be performed at each node for each time step. Prasianakis et al. (2020) ([96]) proposed, for example, to use machine learning techniques and neural networks to systematically improve the accuracy of reactive transport models at acceptable computational costs. They used a neural network on geochemical speciation data produced from dedicated geochemical solvers (e.g. GEMS). Their reactive transport simulation benchmarks show that the neural network approach performs better than the full speciation reactive transport simulations or look up table-based approaches, both in terms of computational efficiency and memory requirements. Based on these results, an improved applicability of reactive transport calculations is expected for the modelling of the geochemical evolution and integrity of cementitious waste packages.

Other options to increase computational efficiency for reactive transport models is to make use of a new generation of lightweight chemical solver that was specifically designed to be used in combination with transport frameworks ([83], [106]). Experience from recent benchmark exercises demonstrate that this resulted in significantly reduced calculation times ([61], [82]).

To facilitate incorporation in existing transport codes a C^{++} version of this solver is being developed (translated for the original Java version) as one of the products of the EURAD DONUT project.

5.5 Geomechanical modelling

Chemo-mechanical modelling is warranted for specific degradation processes to estimate the chemical impact on the evolution of stiffness, strength and crack initiation and propagation, which may additionally impact fluid and chemical transport processes. Of the relevant processes identified in Section 5.2, AAR, external and internal sulfate attack and gas pressure originating from corrosion of metals will result in volumetric expansion of cemented wasteform, which in turn affects the mechanical behaviour of the material. In contrast, carbonation results in shrinkage, very similar to classic drying shrinkage problem, but associated with strength increase. The extent of carbonation shrinkage is dependent on the external CO_2 concentration, internal relative humidity, and porosity, and may therefore predominantly manifest as a surface process.

This paragraph discusses chemo-mechanical models for the aforementioned chemical degradation processes except gas-induced cracking. Typically, the effect of volumetric deformation induced by chemicals can be accommodated in a stress-strain constitutive law via strain based ([33], [86], [101], [111]) or pressure-based formulation ([49], [102], [105]). The strain-based approach simply relates, for example, the eigenstrain due to delayed formation of ettringite (DEF) to the amount of delayed ettringite produced as shown in Equation (18) ([101]), whereas, in the case of a pressure-based formulation (poromechanics), pressure induced due to the delayed formation of ettringite is accounted for in the effective stress equation as shown in Equation (19) ([102]).

$$\varepsilon = \varepsilon_0 + \varepsilon_{sh} + \varepsilon_\chi ; \quad \varepsilon_\chi = \varepsilon_\infty \xi(t) , \tag{18}$$

where the first two terms on the right-hand side refer to elastic strain and shrinkage strain and the last term refers to DEF strain, which in turn is related to the ultimate DEF strain (ε_∞) and reaction extent $\xi(t)$. This is just one example. In fact, the total strain equation can have many more terms such as viscoelastic and cracking strains and the definition of DEF strain can take other forms too ([85], [105]).

$$\sigma_i = (1 - D_i)\tilde{\sigma}_i ; \quad \tilde{\sigma}_i = \tilde{\sigma}_i' - b_g P_g , \, , \tag{19}$$

where σ_i is the main stress in the main direction i, $\tilde{\sigma}_i$ is the total stress (includes DEF pressure) in the undamaged part of the concrete, $\tilde{\sigma}_i'$ is the effective stress in the undamaged part of the concrete depending only on the elastic strain in the matrix, D_i is the damage induced in the main direction by DEF swelling and external loading in the solid skeleton of the concrete, b_g is the Biot coefficient and P_g the pressure due to DEF.

The above example for DEF is equally applicable for ASR or external sulfate attack or carbonation shrinkage except that the underlying relationships between the type of newly crystallized product and pressure or strain needs to be changed. See, for example, an extensive literature review published by Esposito and Hendricks

(2017) on ASR ([50]), studies on external sulfate attack ([37], [62], [100], [110]), and studies on drying shrinkage ([39], [101], [110]) that can be used for carbonation shrinkage analysis. It is important to note that, in the author's knowledge, transport of ASR gel has not been addressed in existing chemo-mechanical models, which limits the use of these models to study phenomena such as those encountered in the Belgian scenario where ASR gel from existing waste drums were found to have leaked from the upper lid.

Whilst the above offered a simple generic framework, recent trends in modelling problems of volumetric deformation focus on multiscale approaches wherein the strain or the pressure terms are obtained from micromechanical modelling ([49], [85]) or numerical homogenization ([116]). Micromechanical approaches are preferred given simple analytical equations, whereas numerical homogenization approaches can be expensive and difficult especially when more than one process is involved (e.g. temperature, moisture, chemistry, etc.). Mesoscale models are also gaining increasing attention wherein damage propagation in the cement paste matrix or mortar matrix and aggregates are examined due to chemical impact. See, for example, the work concerning ASR by Comby-Peyrot et al. (2009) ([46]) and external sulfate attack by Idiart et al. (2011) ([62]).

There appear to be no studies related to the impact of gas-induced cracking of concrete. Existing studies only look at fluid flow properties for a given distribution of cracks. Nevertheless, this process in cemented wasteforms may be handled within the same constitutive framework, but with unsaturated poromechanics, wherein gas pressure has to be taken into consideration in addition to the pore water pressure (e.g., Lewis et al., 1998). Note that this is not a mature field even in hydraulic fracturing in natural host rocks. In particular, within the radioactive waste management field, there are still no well-cited models although developments have recently been initiated by major organizations[4].

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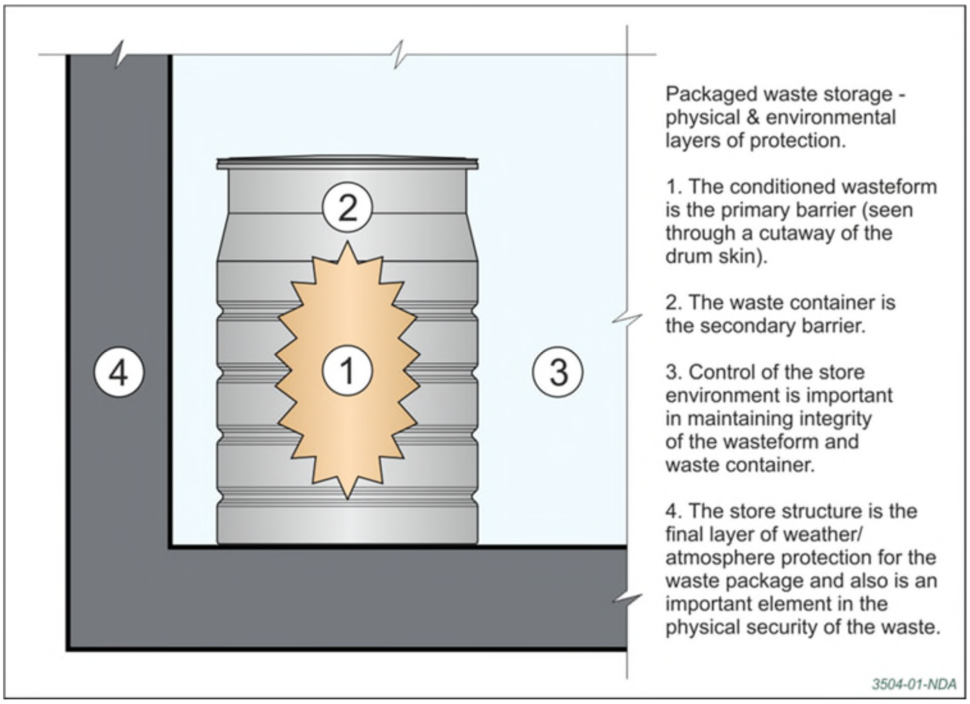
[4] https://decovalex.org/index.html

6 Cemented waste packages storage strategies

The function of the storage facility is to provide safe housing of the waste packages such that the operators and the public are adequately protected from radiological hazards which could arise during normal and accident scenarios. Containment of the waste is required to be maintained over the storage period. Therefore, it is important to ensure that deterioration of the waste package which is providing primary containment of the waste does not occur. Package deterioration, degradation and ageing phenomena also need to be prevented to avoid problems when the waste is ultimately retrieved from the store and dispatched to the disposal facility.



Packaged waste storage - physical & environmental layers of protection.

1. The conditioned wasteform is the primary barrier (seen through a cutaway of the drum skin).

2. The waste container is the secondary barrier.

3. Control of the store environment is important in maintaining integrity of the wasteform and waste container.

4. The store structure is the final layer of weather/ atmosphere protection for the waste package and also is an important element in the physical security of the waste.

3504-01-NDA

Figure 7 - Representation of the Storage System [12]

Long term interim storage is becoming an important issue in countries where construction of LILW disposal facilities is postponed. As a consequence, storage is an essential enabling component of decommissioning to provide confidence that packages will be disposable at the end of the storage period.

As described above, the baseline treatment option for radioactive wastes is often cement encapsulation, even if many countries are exploring the strategic opportunities where alternative treatment technologies could offer advantages in terms of cost savings, risk reduction, waste product quality, and volume reduction [8].

The ability to control and inspect waste package status is an important storage system requirement for maintaining safety over the period in which waste package deterioration might be expected and for maintaining the “as-received” integrity of the waste package until it is retrieved for disposal.

The waste packages retrieved from the interim storage facility for disposal must comply with the specified waste disposal acceptance criteria. These are derived from a detailed safety assessment for both the store and the two phases of the repository (operational and post-operational) [1].

In order to ensure the adequate waste packages conditions, a number of inspections may be required during short-term or long-term storage. This is especially true when interim storage has evolved into prolonged storage where repositories have not become available in the time frame originally anticipated. Attributes that should be monitored include the adequacy of identification and the physical condition of the container. Such inspections may be performed remotely using optical aids (cameras, telescopes, etc.) in order to minimize personnel exposure. The adequacy of such remote inspection techniques should be demonstrated, particularly if they are relied on as the sole means of detecting container degradation. Inspection techniques should also include visual inspection where possible.

The storage facility must protect the waste from environmental conditions, including humidity, heat and cold, or any other environmental condition which would degrade the wasteform or container. Local climatic conditions may result in the need for cooling or dehumidifying the store atmosphere to avoid possible deterioration of the waste packages.

The design of the facility usually permits package stacking, sorting and visual inspection. Provision for maintaining a database keeping chain-of-custody for each waste package in storage must be included in the design. Key information about the waste package should include the total radionuclide content, the waste matrix used for immobilization, the treatment and/or conditioning method (as applicable), and the unique package designator.

Storage requirements mandate external dose rate and contamination limits for waste packages to be accepted by the facility in order to protect personnel. Storage facilities should be designed to allow control of any contamination from gaseous or liquid releases. Adequate ventilation should be available to deal with any gas generation during the entire storage operation period [18].

Therefore, in the design of storage facilities for conditioned radioactive waste, consideration must be given to:

- Waste package handling.
- Clear identification of stored waste packages and record keeping.
- Provision for inspection and monitoring of stored waste.
- Provision to prevent possible degradation of waste packages during storage.
- Provision for adequate environmental conditions (heating, cooling, humidity control) to ensure proper conservation of waste packages during their storage in the facility.
- Provision for cooling heat generating waste, if any.
- Provision for fire protection where combustible waste is present.
- Provision for gas dissipation if gas generation is anticipated.
- Provision for criticality control where a considerable amount of fissile material is present in the waste.
- Retrieval of the waste for further treatment, immobilization or disposal (or in the event of an accident which requires relocation of the waste),
- Maintenance.

6.1 Storage Configurations

Waste storage, which has been used or is currently in use falls into three general categories: subsurface storage, area storage and engineered storage.

Engineered storage refers to any fully contained building or structure specifically designed for the storage of waste packages. These stores may range from simple constructed enclosures to highly engineered facilities incorporating shielding structures and remote handling equipment, fully serviced with ventilation, effluent collection and instrumented controls.

Waste packages may be stacked or placed on shelves. Free stacking is the most used arrangement for containers and drums. Vertical stacking is usually limited by the load bearing capacities of the bottom-most containers as well as by drop height or seismic requirements. Alternatively, cylindrical packages may be stacked on their sides or grouped on stacked pallets. The principle of segregation involves consolidating waste packages by type to facilitate surveillance and detection, and solution, if possible, of potential problems.

Waste packages may be handled either manually, for small packages with very low surface dose rate, with a lift truck, with a locally-controlled overhead crane, with a remote-controlled crane, sometimes computer assisted, or with a telescopic arm and monitored emplacement devices [1].

Low and intermediate-level radioactive waste Interim Storage Facility in the LOG – Netherlands [25]

Low and intermediate level radioactive waste in the Federal Interim Storage Facility (BZL) at Würenlingen – Switzerland [27]

New low level radioactive waste Interim Storage in Latina – Italy [26]

New low level radioactive waste Interim Storage in Garigliano – Italy [26]

Figure 7 – Interim Storage Facilities

6.2 Monitoring Strategy

As highlighted above, the storage facility should have a monitoring strategy conceived to facilitate the inspection of the structures, systems, and components of the facility and of the waste packages stored in the facility to the extent that they are important for ensuring safety [19].

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.

It is also necessary to define 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 the following figure.

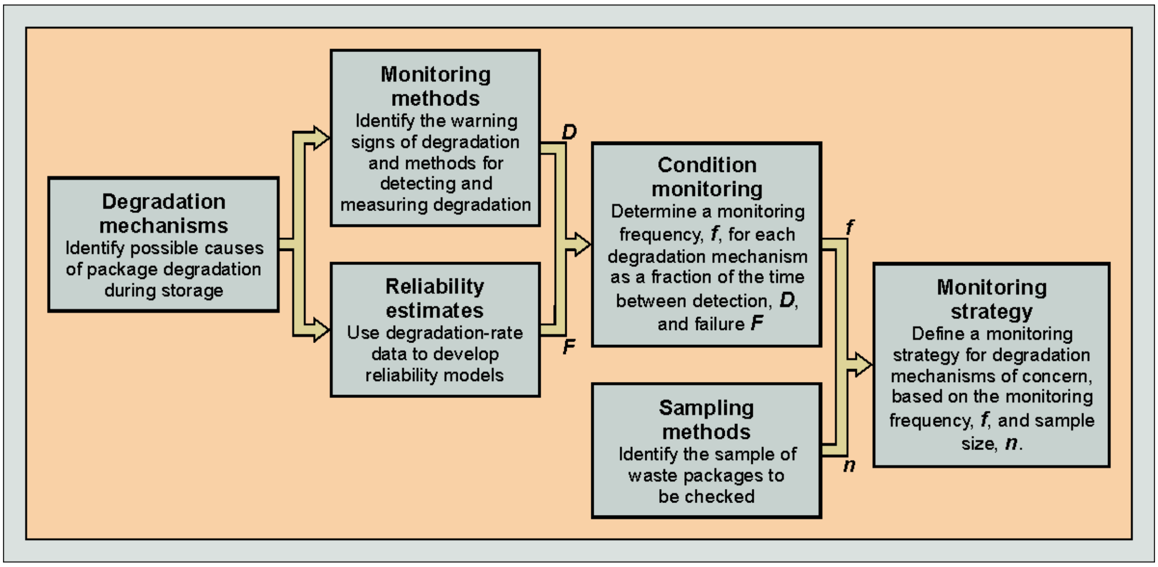


Figure 8 - Key Components of Condition Monitoring Strategies [19]

A condition monitoring strategy may be summarised as:

- Identification of potential degradation mechanisms which lead to changes in properties;
- Identification of monitoring techniques to detect such changes.
- Estimation of package reliability based on degradation rate data;
- Determination of monitoring frequency as a fraction of the time between the point of detection of degradation and the expected time of waste package failure;
- Identification of a means of selecting a representative sample of packages to be monitored.

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 frequency of such inspections should be derived from storage facility safety analyses but may require modification (increase in frequency) as facilities age or as dictated by operational experience. Mechanisms should be established to ensure that corrective action is taken for any deterioration of packages, package identification or cooling/monitoring systems identified during inspections.

The detection of general package degradation may be feasible by means of sample inspection. Consequently, such packages containing the same matrix may be randomly selected for testing their integrity. Obviously, it is necessary to check any change in surface dose rate of the package in order to know the geometric distributions of activity. If abnormal increases in dose rate are detected locally, this means the partitioning of activity is no longer homogeneous and, in that case, repackaging is probably necessary.

Chemical conditions (e.g. concentrations of chloride or of flammable gases, chemical properties of liquids) and non-radiological parameters (e.g. temperature, pressure, humidity, flow rates of water coolant) should also be monitored.

Where high activity wastes are involved, required inspections may be performed remotely by camera, together with air and liquid effluent monitoring.

6.3 Survey and Inspection

Monitoring and inspection of waste package should preferably use non-destructive testing methods. Non-destructive methods for testing waste packages include all tests that can be conducted without penetrating or opening the waste container. Destructive methods generally imply taking samples out of the waste packages; this in turn implies breaking the confinement assured by the container and the wasteform and hence the need of reconstituting such confinement with inevitable cost and dose impacts. Therefore, destructive methods are recommended only on a sample basis for monitoring properties undetectable by means of non-destructive tests (NDT) (e.g. alpha emitting nuclides and small amounts of low energy radiation may not be detected with NDT).

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, including [1]:

- Intensive visual inspection to detect corrosion, mechanical damage, penetrations and internal overpressure;
- Weighing to identify heavy parts, e.g. shielding material;
- Dose rate measurements;
- Radiography to determine contents of packages, void spaces, container wall thickness, presence of liquids, etc.;
- Scanning to measure the spatial distribution of gamma radiation and identify prominent gamma emitters;
- Tomography (with an external gamma source or with an accelerator) to detect any inhomogeneity in density;
- Passive and active neutron counting to detect fissile material.

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. 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.

In addition to the visual inspections of waste packages, a number of other techniques could be used for monitoring and inspecting. These techniques are strictly dependent on the specific typologies of the package including container materials and radiation levels; for instance the surface of stainless steel waste containers could be investigated by a dye penetrant testing for inspecting for presence of surface defects in welds and initiation of stress corrosion cracking, but currently this technique requires close access by the operator and would only be applicable to shielded waste packages and unshielded waste packages with low external radiation levels (e.g. plutonium-contaminated waste).

Where survey, inspection and testing of conditioned packages retrieved from storage whose characteristics are known and documented are involved, even if the waste packages are surveyed during storage, degraded packages may remain undetected until retrieval. However, the implementation of a proper quality assurance programme during conditioning and storage should lead to a very low probability of waste package failure. In this case, the presence of a failed package will be considered extremely unlikely. Therefore, efforts should be made to detect failed waste packages and other situations that increase the risk to personnel safety.

6.4 Quality Assurance System

The recording, review and survey of waste packages normally begins with the review of the waste package records maintained by the storage facility. The waste package records need to be retrieved and reviewed to determine the age of the package, length of time in storage, wasteform container type, unique retrieval requirements and potential package problems. Waste package quality control can be performed by examination of the waste package documentation, which describes the relevant properties of the waste package, and by non-destructive or destructive testing of the waste package itself, when necessary. The decision on which of these procedures would be most suitable for package retrieval is influenced by questions such as:

- How complete is the documentation?
- How reliable is the documentation?
- What is the presumed risk potential of the waste package failure?
- What is the obvious state of the waste package?

Quality control by examination of the documentation is simplified when the waste packages to be inspected have been conditioned by a qualified process. In some countries, thousands of 200 L drums with operational LLW from nuclear power plants have been checked since 1990 before being disposed of in final repositories. Only a small number were controlled by testing waste packages, while the majority were controlled by examination of the documentation. As a result, some packages required certain additional conditioning prior to disposal, and only very few were completely withdrawn.

The implementation of quality assurance procedures and development of conditioning technologies normally leads to a reduction in the proportion of failed packages to nearly zero. When investigation of the records is complete, an initial survey should be performed.

Packages that meet the criteria set for the records search, the initial survey, and the visual inspection may be subject to testing to determine whether the WAC of the continued interim store or the disposal facility have been maintained over the storage life of the package. Whether or not, and to what extent waste packages must be further tested, must be decided taking into account the content of the records and the state of the packages [1].

The following figure illustrates the elements of a management system, including the relationships between quality assurance, quality control and the management system. Quality assurance and quality control are directed towards providing conforming products and services. They are both an essential part of any management system for nuclear facilities and activities [10].

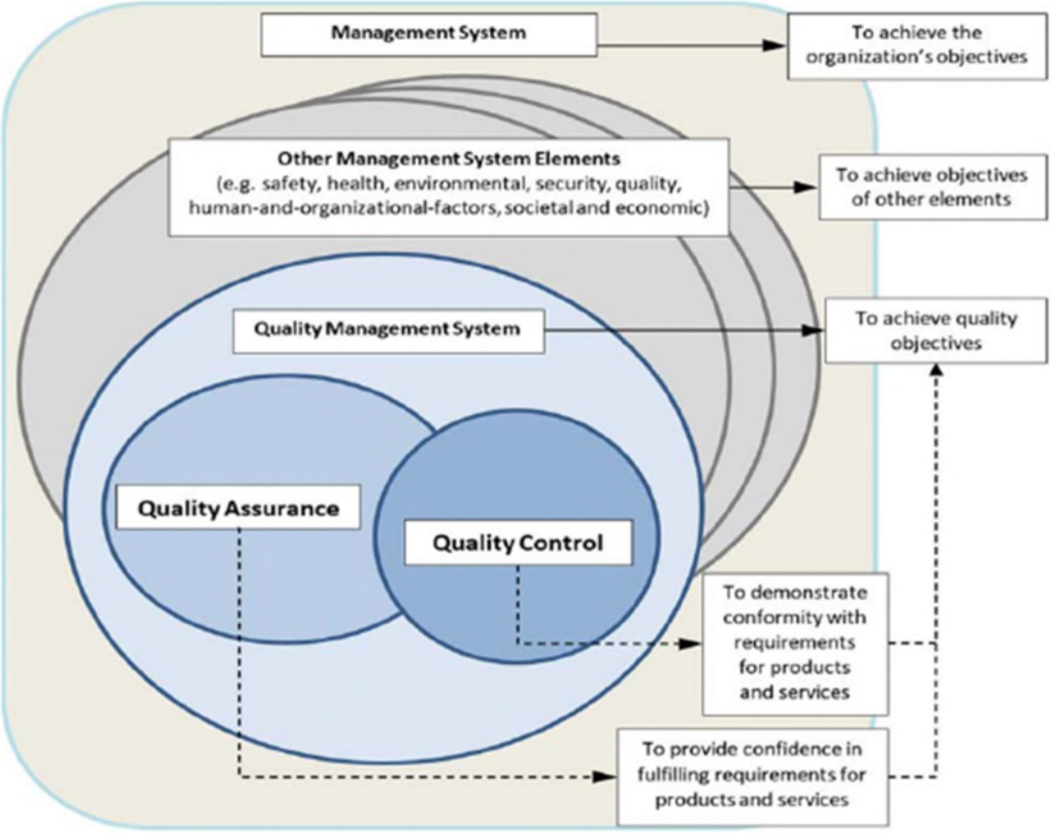


Figure 9 - Quality Assurance and Control framework [10]

7 Overview of current cemented waste packages storage management approaches

The approach originally envisaged for conducting an overview among End Users in order to gather useful information for the SoTA included both visits to the main WMOs storage facilities and the distribution of a questionnaire to these organizations. Unfortunately, the COVID-19 pandemic made the visits impossible and forced the project team to only make use of the questionnaire.

As one might imagine, the unscheduled cancelation of the visits to the storage facilities has undeniably caused the exclusion of the original major source of information for the SoTA. However, the results of the questionnaire do represent a valid instrument for collecting current methods and procedures for cemented waste management. Owing to the lack of information that can only be collected only through direct contact with WMOs and actual survey of the stored waste packages, we plan to update this report in later years of the project, when further information can be gathered.

The questionnaire, which covers all “waste classes” (as defined in [1] and [2]) with the exception of High Level Waste, has been conceived with the following main objectives:

a. Identifying the main common waste package typologies scheduled to be long-term stored, also in view of selecting a reference container/package type to be used in the following tasks of the WP (e.g. the demonstration phase)
b. Exploring the currently adopted storage configurations and waste package handling procedures
c. Deriving the main degradation phenomena observed/considered by store operators and material conditions that may lead to the initiation of ageing mechanisms during the long-term storage conditions in order to drive the selection of the most suitable monitoring technologies/procedures
d. Understanding the current monitoring and data collection systems put in place by End Users to be considered also as the starting point of the gap analysis to be performed within WP2

and is arranged in four sections:

1. **General information on the respondent**
2. **Storage system**: waste streams to be stored (existing and foreseen); description of the main waste package typologies; package handling system, storage configuration
3. **Storage management strategy**: monitoring strategy; long-term storage monitoring strategy
4. **Parameters and data collection systems currently used for monitoring package normal and degradation scenarios**: relevant parameters currently monitored; data transmission/archiving; data analysis; anomalies; quality assurance and control

A copy of the questionnaire is shown in Appendix 1. The results of the questionnaire, presented in the following chapters, consist in the analysis and summary of the answers collected from the respondents, arranged according to the overall questionnaire objectives previously indicated. The questionnaire was distributed to the registered End Users at the end of 2020 and this report captures responses received, as of February 2021, from eleven organizations of the following countries: Belgium, Czech Republic, Denmark, Estonia, Finland, France, Italy, Spain, Sweden, Switzerland.

7.1 Main cemented waste streams

The physical, chemical, and radiological characteristics as well as the amount of radioactive waste have a major influence on the selection of waste management treatment and conditioning processes. Composition, technology, and variation in nature of the input waste (e.g. aqueous waste concentrates, combustible and non-combustible solids, etc.) determine the robustness of the solution for the whole waste life-cycle, and play a role in the potential degradation phenomena.

The questionnaire submitted asked respondents to indicate which are the main waste streams to be conditioned with cement, in terms of waste origin, production process, radiological classes [2], other issues related to the specific main typologies and quantity (volume).

In particular, two groups of cemented waste were identified (as described at §4):

- Homogeneously mixed cemented waste
- Heterogeneous in-container or annular grouted cemented waste

For each group, a separate set of questions and information is required.

7.1.1 Homogeneously mixed cemented waste

The main typologies investigated include liquid waste (organic and nonorganic solutions, etc.) and fluid waste (sludges, fine particulate, resins, etc.). The following *Table 3* summarises a set of these main waste streams. The questionnaire submitted to End Users asked to specify the origin and useful characteristics that might play an important role during the conditioning process with cement and the long-term storage. Note that as the End-Users were asked about their main waste streams, other cemented packages may be produced and not specified below.

Nonorganic liquids (presence of reactive, corrosive, fissile, alpha contaminated materials, etc.)
Organic liquids (presence of chelating agents, oils, complexing compounds, fermentable substances, paraffins, fissile-, alpha-contaminated materials, TBP, etc.)
Liquids from nuclear medicine/research
Other liquids
Sludges
Other fluid waste (e.g., powders, fine particulates, resins, etc.)

Table 3 – Liquid and fluid waste streams

Looking at the results from the answers of the End users on their main streams reported in Figure 10, it can be deduced that:

- All proposed waste stream typologies are present in the inventories of End Users.
- The *sludges* are the main-stream; they are the result of several processes such as evaporation and sedimentation, NPP and research reactor operations, concrete dismantling (sawing sludges, primary and pool water clean-up, hot laundry water clean-up, resins, secondary waste from resins treatment), concentrates from LWR and PWR water treatment systems.
- *Other fluid* waste (powders, fine particulates, resins, etc.) deriving from resins treatment, resins in watery solutions, evaporate concentrates, ashes, fine particulates, metal frit, are present with a large percentage.
- Half of respondents condition *non-organic liquids* with presence of reactive and corrosive chemicals, fissile and alpha contaminated materials, etc..
- A quarter of End Users have *organic liquid* with presence of chelating agents, oils, complexing compounds, fermentable substances, paraffins, fissile and alpha contaminated materials, tributyl phosphate, etc..
- Another quarter of respondents have liquids from nuclear medicine activities and research reactor operations.
- The data highlight the great variety of waste streams in terms of amount, physical and chemical properties, that are processed with a homogeneous conditioning with cement matrix. These data can help to understand which possible degradation phenomena should be taken into account in the simulations of package evolution.

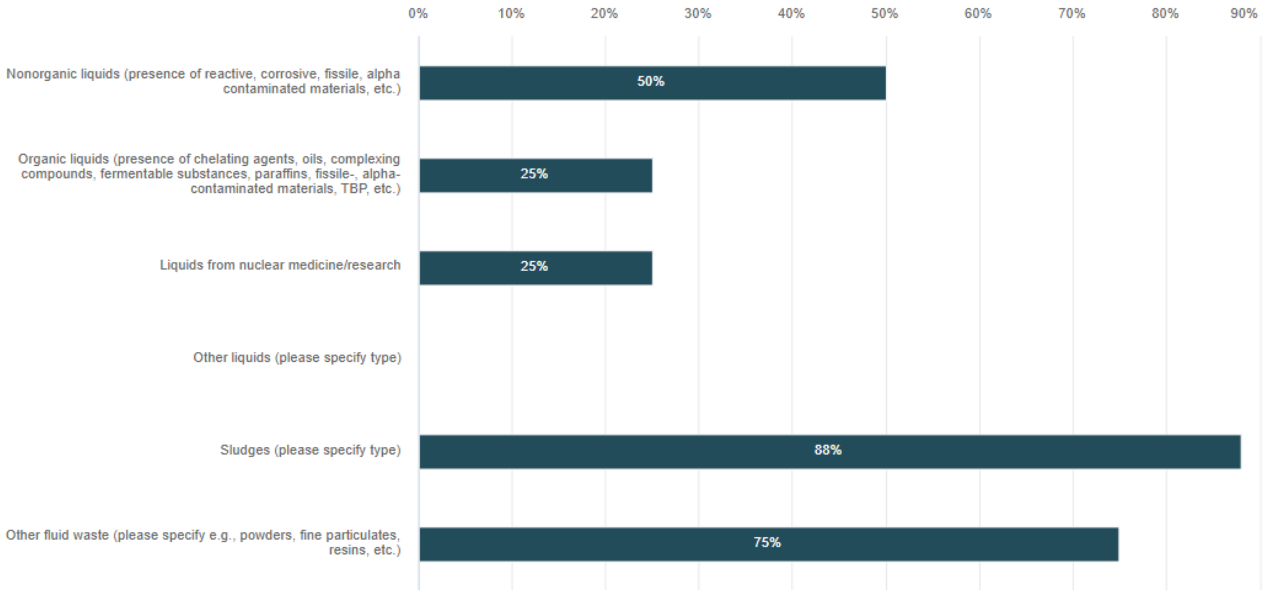


Figure 10 – Homogenous waste stream typologies

Moreover, the respondents indicated the classification of their homogeneous main waste in terms of waste classes VLLW, LLW and ILW, as reported in *Figure 11* (overall estimated quantities). Looking at the results from the answers reported, it can be stated that:

- Most of End Users have liquid/sludge/ashes classified as LLW and 50% have the same stream classified as ILW.
- This means that large quantity of waste (ILW) may need to be long-term stored prior to geological disposal.
- 25% of the End Users also need to manage liquid/sludge VLLW waste.

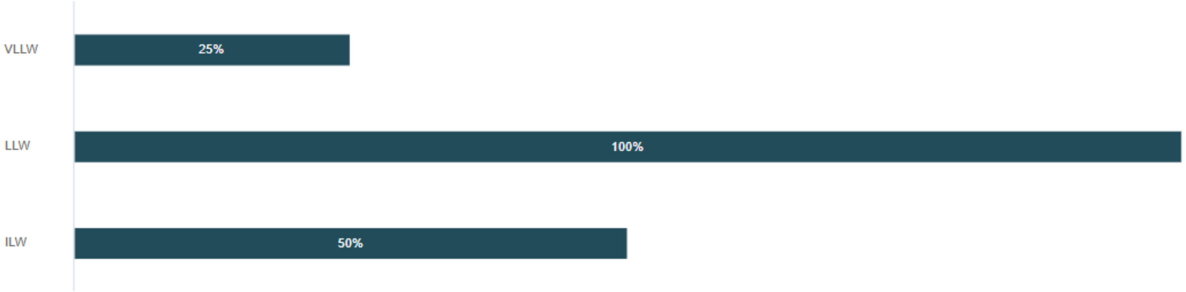


Figure 11 – Homogeneous waste classes

Table 4 and *Table 5* show details about the number and volume of homogeneously mixed waste packages. Regarding VLLW class, only one respondent specified the number of packages and the corresponding total volume (overall estimated quantities). More details are reported for LLW and ILW. The note expressed by some End Users shows that the conditioning of homogeneous waste packages is in progress. The greatest detail in terms of number of packages and overall volume is for LLW class.

VLLW	LLW	ILW
	250	50
	105	3955
	1280 packages already produced + max 120 packages produced each year	
	>100 packages of 200l per year	
	18058	
33600	9900	3600

Table 4 – Number of packages of homogeneous waste (Overall estimated quantities)

VLLW	**LLW**	**ILW**
	60	15
	180	6840
	288	
	>100 packages of 200l per year	
	3864	
14200	4600	1600

Table 5 – Total Volume (m^3) of Homogeneous waste (Overall estimated quantities)

7.1.2 Heterogeneously cemented waste

This section concerns the second group of waste streams, i.e. solid waste conditioned directly in container or in annular grouted containers. There is a wide variety of solid waste typologies to be investigated and reported in *Table 6*, in terms of materials, physical and chemical properties, amount and shape. They consist of small or large components, cementitious rubbles, metal waste deriving from different activities (operation NPP/research reactor, dismantling, maintenance, etc.), plastic materials and radiation sources. In particular the metal and plastic waste can be compacted/supercompacted in pucks or pellets to reduce the volume of conditioned waste. Regarding the plastic waste streams, the End Users specified that they are composed for the most part of PVC, PET, PPE. Other materials are ashes, which in this case require heterogeneous conditioning, glass, cartridge filters of NPP. One End User specified the use of a heterogeneous conditioning process for metal scraps, metal pieces and plastic materials in container with surrounding cement. Note that as the End-Users were asked about their main waste streams, other heterogeneously cemented packages may be produced and not specified below.

Cementitious rubble
Metal scraps/equipment/metal pieces in general from dismantling/maintenance/operation activity/research
Compacted waste in pucks/pellets
Large metal components
Plastic
Rubber
Radiation sources

Table 6 – Heterogeneous waste streams

Looking at the results from the answers reported in *Figure 12*, it can be noted that:

- All proposed waste stream typologies are present in the inventories of End Users.
- Metal scraps, equipment, pieces and components conditioned without pre- treatment are the main part (78%), the remaining 22% being treated for example by means of a compaction process (22%),
- Large size metal waste is reported with a relevant percentage (44%). This value together with the previous one indicates that the main waste streams to be heterogeneously conditioned are metals.
- More than half of End Users have cementitious rubber and other waste like cartridge, filter glass, ashes (67%) to be immobilized,
- Almost half of respondents have to treat plastic materials like PET, PVC, PPE, etc. (44%),
- The radiation sources (56%) are a relevant waste stream among the End Users,
- A smaller amount is constituted by rubber waste (11%).

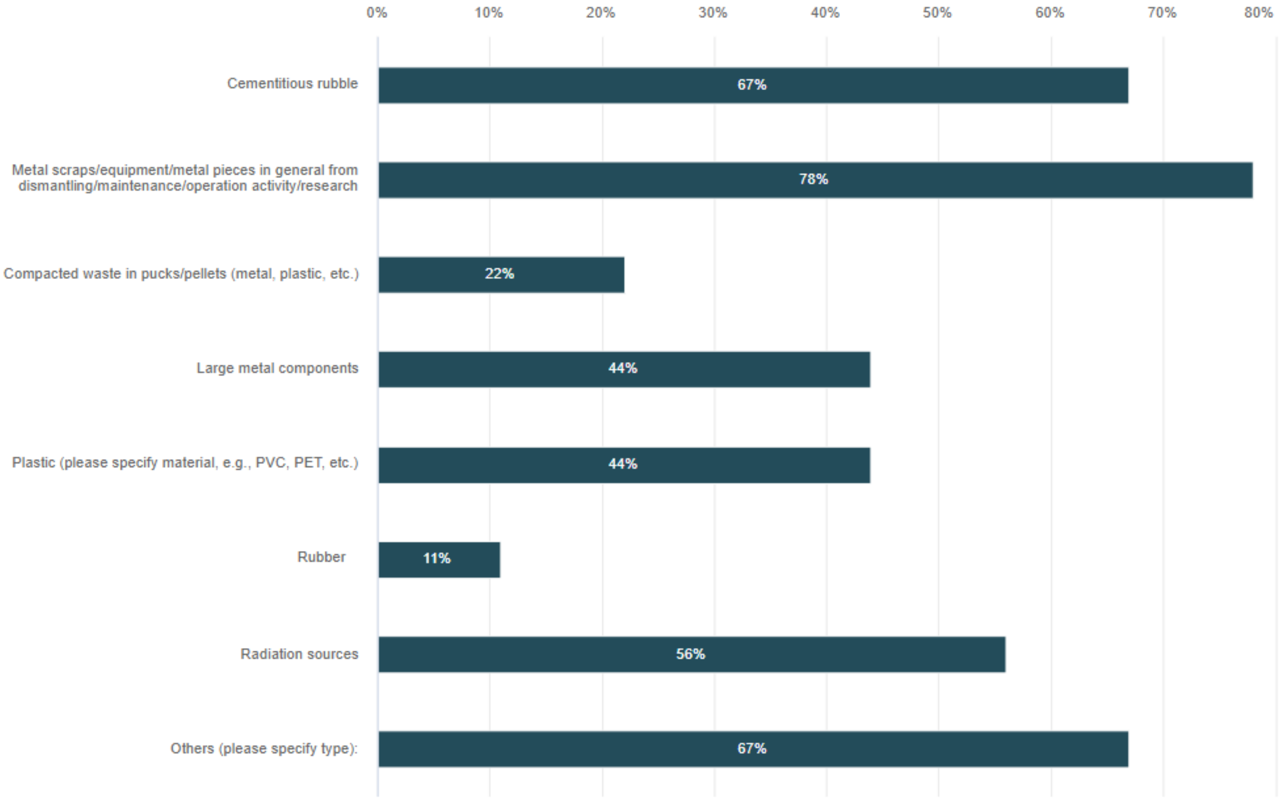


Figure 12 – Heterogeneous waste streams typologies

The respondents indicated moreover the classification of the heterogeneous waste in terms of waste classes VLLW, LLW and ILW, as reported in *Figure 13* (overall estimated quantities). The results from the answers show that:

- 100% of the End Users have solid waste classified as LLW and 44% have ILW solid waste.
- This means that a relevant quantity of waste (44%) may need to be long-term stored prior to geological disposal.
- 33% of the End Users have solid VLLW waste,
- Comparing this distribution by waste classes with respect to homogeneous waste, it is highlighted that LLW remains unchanged, the VLLW class increases and the ILW decreases. This last change could be due to the possibility of treating the metal components (for example through superficial decontamination) and declassifying them to a lower waste class. The LLW class represents the remaining materials from operation and dismantling activities.

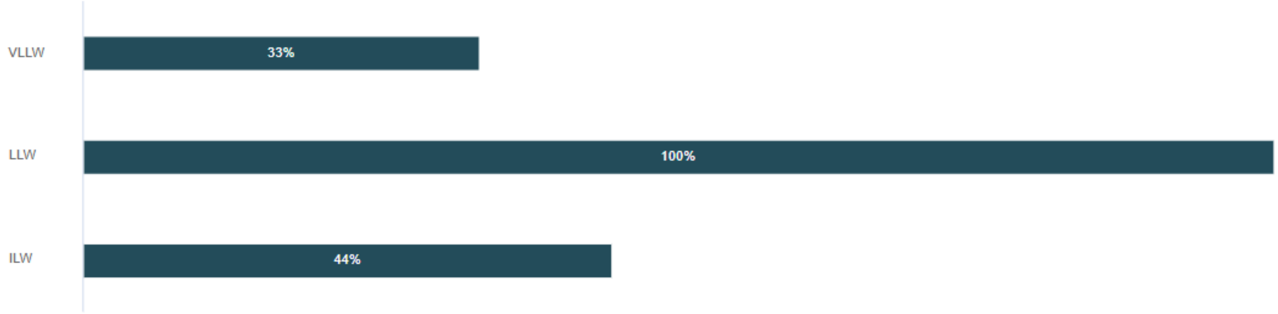


Figure 13 - Heterogeneous waste classes

Table 7 and Table 8 show the number and volume of heterogeneous waste packages. Regarding VLLW class only two respondents specified the number of packages and the corresponding total volume (overall estimated quantities). More details were provided for LLW and ILW. Also, in this case the data suggest that the conditioning of heterogeneous waste packages is in progress. The greatest detail in terms of number of packages and overall volume is for LLW class.

VLLW	LLW	ILW
	120	
	11500	40
	6200 packages already produced + from 50 to 200 packages per year	
	36215 packages (already produced) + from 1000 to 1500 packages per year	
more than 100 packages per year	more than 50 packages per year	
11600	38900	140
	6143	
	40000	5000
	in the order of 4500-5000 drums	

Table 7 - Number of packages for heterogeneous waste (Overall estimated quantities)

VLLW	LLW	ILW
	220	
	3800	13
	30380	
	24000	
metallic boxes of 1500 litres	metallic boxes of 1500 litres	
23500	33400	160
	25740	

Table 8 - Total Volume (m^3) for heterogeneous waste (Overall estimated quantities)

7.2 Main waste packages typologies

7.2.1 General technical data

This section describes the waste package types used to cement the main streams described in the previous section. The respondents indicated for each waste stream the following technical aspects:

- Package name.
- Waste class,
- Shape and external dimensions.
- Container material.
- Waste conditioning process,
- Cement matrix typology.
- Waste treatment process (before conditioning),
- Waste package main design characteristics.
- Package handling system.
- Storage configuration.

This information is fundamental for the research activities of this project, as it provides data on the technical and functional characteristics of the cemented packages that must be monitored over time and for the development of new innovative technologies to achieve this goal.

Table 9 shows some technical data about **37 waste packages typologies** reported by the respondents. Looking at the results it can be summarised that:

- For the homogeneous conditioning packages (32% of the total number of typologies) the cylindrical metallic container is used in 67% of the cases. Just one operator uses cylindrical concrete package with stainless steel reinforcement.
- The homogeneous cemented packages are mostly used for LLW (77% of the total number of typologies) and the remaining for ILW,
- The cement matrix used for homogeneous waste packages is for the most part ordinary Portland cement. The use of sulfate resistant Portland cement with additional zeolites for sorption is interesting for conditioning of sludges and concentrates from power plant water treatment (LLW),
- Different mixes (e.g. special light weight Portland cement, blast furnace slag cement) are also reported for encapsulating scrap and interchangeable parts from reactor operation and maintenance, smaller metal scrap from decommissioning of power plants, etc.
- The liquid/sludge waste streams are pre-treated before the conditioning process by means of evaporation, Cs separation, dewatering, thermal treatment, alkalinisation,
- For the heterogeneous conditioning packages, about 60% of respondents use mainly concrete prismatic containers, but there are some cases of metallic prismatic containers (stainless steel, galvanized steel),
- The heterogeneous cemented packages are mostly used for LLW.

ID	Name	Conditioning process	Material	Shape	Dimensions	Waste class	Closure system	Cement matrix	Pre-treatment	Design life
1	Solidified waste package	Homogeneous	Concrete with stainless steel reinforcement	Cylindrical	Height: 1,3 m; Diameter: 1,3 m; Wall thickness: 105 mm; Inside volume: 1 m^3	ILW	Concrete lid cast after waste solidification	Cement and blast furnace slags	Evaporation, Cs separation	-
2	-	Homogeneous	Steel	Cylindrical	60 l to 216 l	-	Sealed lid	Bitumen	-	-
3	Sludges incorporated to cement matrix	Homogeneous	Stainless steel	Cylindrical	200 l and 1500 l	LLW	Upper lid with a ring plus screw for 200, and upper lid for metallic	Ordinary portland cement	No waste treatment, directly introduction in container and mix with cemen, homogenize by stirring	-
4	Sludges and concentrates from power plant water treatment	Homogeneous	Steel	Cylindrical	Height: 0.9 m, Diameter: 0.6 m	LLW	Lid, screwed or clamping ring	Sulfate resistant portland cement, additional zeolites for sorption	-	-
5	S04	Homogeneous	Sheet steel	Cylindrical	Height: 90 cm Diameter:60 cm (200 l drum)	ILW	Locking clips	Ordinary portland cement	Dewatering and in drum cement mixing	300
6	Ashes incorporated to cement matrix	Homogeneous	Carbon steel	Cylindrical	Diameter: 610 mm, Height: 880 mm	LLW	Double lid	Ordinary portland cement	Thermal	300
7	Resins from power plant water treatment	Homogeneous	Steel	Cylindrical	Height: 0.9 m, Diameter: 0.6 m	LLW	Lid, screwed or clamping ring	Sulfate resistant portland cement, additional zeolites for sorption	-	-

8	Double layer steel drums 115/210 l separated by 5 cm concrete	Homogeneous	Steel	Cylindrical	Height: 88 cm Diameter: 59 cm		Cemented on top, then closed with steel lid	Ordinary portland cement	Mixed waste (metal, plastic, glass, weaker sources etc) compressed into double layer drums. Cemented on top, then closed with steel lid	-
9	CEMEX	Homogeneous	Stainless steel	Cylindrical	Height: 1117mm Diameter: 791 mm	ILW	Bolted lid, metallic gasket	Ordinary portland cement	Alkalinization	50
10	Double layer steel drums 115/210 l separated by 5 cm concrete	Homogeneous	Steel	Cylindrical	Height: 88 cm Diameter: 59 cm	LLW	Cemented on top. Then closed by lid	Ordinary portland cement	Compacting; mixed waste (metal, plastic, glass, weaker sources etc) compressed into double layer drums. Cemented on top, then closed with steel lid	-
11	Solidified waste package	Homogeneous	Concrete with stainless steel reinforcement	Cylindrical	Height: 1,3 m; Diameter: 1,3 m; Wall thickness: 105 mm; Inside volume 1 m^3	LLW	Concrete lid cast after waste solidification	Cement and blast furnace slags	Evaporation, Cs separation	-
12	-	Homogeneous	Steel	Cylindrical	216 l	LLW	Sealed lid with screw	Ordinary portland cement	Solidifying with polymer	-
13	-	Homogeneous	Stainless steel	Prismatic	1 m^3	-	-	Ordinary portland cement	-	-

14	Resins, concentrate, all the information the same as sludges.	Heterogeneous	Stainless steel	Cylindrical	1500 l	-	Upper lid	Ordinary portland cement	No treatment in general, just introduction and blocked by mortar. for LLW is required an internal envelope of 5 cm of mortar in the metallic boxes	-
15	Metallic boxes with rubble	Heterogeneous	Stainless steel	Cylindrical	1500 l	VLLW mainly but some LLW	Upper lid	Ordinary portland cement	No treatment in general, just introduction and blocked by mortar. for LLW is required an internal envelope of 5 cm of mortar in the metallic boxes	-
16	Cementitious rubble from decommissioning	Heterogeneous	Concrete	Prismatic	2.4 m * 2 m * 2 m	LLW	Concrete lid	Special light weight cement	-	50
17	Concrete containers	Heterogeneous	Concrete	Prismatic	1,2 * 1,2 * 1,2 m	LLW	Concrete lid	Ordinary portland cement	Solidifying with polymer	-
18	-	Heterogeneous	Steel drum	Cylindrical	216 l	LLW	Sealed lid with screw	Ordinary portland cement	Sorting	-
19	Double layer steel drums 115/210 l separated by 5 cm concrete	Heterogeneous	Steel	Cylindrical	Height: 88 cm Diameter: 59 cm	LLW	Cemented on top Then closed by lid	Ordinary portland cement	Compacting; mixed waste (metal, plastic, glass, weaker sources etc) compressed into double layer drums. Cemented	-

									on top, then closed with steel lid	
20	-	Heterogeneous	Steel	Cylindrical	216 l	LLW	Sealed lid	Ordinary portland cement	Sorting, fragmentation	-
21	Scrap and interchangeable parts from reactor operation and maintenance. Smaller metal scrap from decommissioning of power plants. Can contain steel, Al, Cu, stainless steel or mixtures of these	Heterogeneous	Steel drums	Cylindrical	Height: 0.9 m Diameter: 0.6 m	LLW	Screwed lid or clamping ring	Sulfate resistant portland cement or special light weight cement	-	-

22	Scrap and interchangeable parts from reactor operation and maintenance. Smaller metal scrap from decommissioning of power plants. Can contain steel, Al, Cu, stainless steel or mixtures of these	Heterogeneous	Concrete containers	Prismatic	1.5 m * 1.5 m * 2 m	LLW	Concrete lid	Sulfate resistant portland cement or special light weight cement	-	-
23	Scrap and interchangeable parts from reactor operation and maintenance. Smaller metal scrap from decommissioning of power plants. Can contain steel, Al, Cu, stainless steel or mixtures of these	Heterogeneous	Concrete containers	Prismatic	2.4 m * 2 m * 1.3 m	LLW	Concrete lid	Sulfate resistant portland cement or special light weight cement	-	-

24	Scrap and interchangeable parts from reactor operation and maintenance. Smaller metal scrap from decommissioning of power plants. Can contain steel, Al, Cu, stainless steel or mixtures of these	Heterogeneous	Concrete containers	Prismatic	2.4 m * 2 m * 2 m	LLW	Concrete lid	Sulfate resistant portland cement or special light weight cement	-	-
25	CP-5.2	Heterogeneous	Stainless Steel AISI 304L	Prismatic	2500 mm * 1650 mm * 1250 mm	LLW	Bolted lid Metallic gasket	Ordinary portland cement	Decontamination, cutting, compaction	-
26	Concrete container	Heterogeneous	Concrete	Prismatic	1,2 m *1,2 m * 1,2 m	LLW	Clean layer on top of steel container or concrete lid for concrete container	Ordinary portland cement	-	-
27	Steel container	Heterogeneous	Steel	Prismatic	1,2 m * 1,2 m * 1,2 m	LLW	clean layer on top of steel container or concrete lid for concrete container	Ordinary portland cement	-	-
28	Steel pellets metal scrap from decommissioning of power plants	Heterogeneous	Concrete	Prismatic	2.4 m * 2 m * 2 m	LLW	Concrete lid	Special light weight cement	-	-

29	Large components, mostly steel, mainly from power plant decommissioning.	Heterogeneous	Concrete	Prismatic	2.4 m * 2 m * 1.3 m (rarely 2.4 m * 4 m * 2 m)	LLW	Concrete lid	Special light weight cement	-	-
30	Sources in packages	Heterogeneous	Stainless steel	Prismatic Cylindrical	200 l in drum 1500 l in metallic boxes	LLW	Upper lid	Ordinary portland cement	Always is required an internal envelope of 5 cm mortar for both drums and boxes, introduction of sources and final block with mortar	-
31	Cartridge filters (all the same as sources)	Heterogeneous	Stainless steel	Prismatic Cylindrical	200 l in drum, 1500 l in metallic boxes	LLW	Upper lid	Ordinary portland cement	Always is required an internal envelope of 5 cm mortar for both drums and boxes, introduction of sources and final block with mortar	-
32	Cubic concrete container	Heterogeneous	Reinforced concrete	Prismatic	4,9 m^3	LLW	Single concrete lid	Ordinary portland cement	None	-
33	Steel 400 l drum	Heterogeneous	Galvanized steel	Cylindrical	400 l	LLW / ILW	Seam folding	BFS cement	Incineration, precompaction, supercompaction	-
34	Cylindrical concrete container	Heterogeneous	Reinforced concrete	Cylindrical	Diameter : 840 mm, Height : 1200 mm	LLW	Single reinforced concrete lid	Reinforced concrete	Compacting	-
35	Steel container	Heterogeneous	Steel	Prismatic	1,2 m * 1,2 m * 1,2 m	LLW	Protective clean layer of concrete	Ordinary portland cement	-	-

36	-	Heterogeneous	Concrete	Prismatic	1,2 m *1,2 m *1,2 m	LLW	Concrete lid	Bitumen	-	-
37	-	Heterogeneous	Stainless steel	Prismatic	1 m^3	-	-	Ordinary portland cement	-	-

Table 9 – Cemented Waste package typologies and main characteristics

7.2.2 Waste package main design characteristics and handling system

To better represent all aspects of waste packages and their behaviour, the questionnaire also asked respondents to provide some information on the design characteristics of the packages and the main performances they have. In this first draft of the document, the number of main waste package typologies reported is 37, but still a first good picture for deriving information in terms of technical issues such as mechanical thermal and corrosion resistance, lifting features, stackablity, use of internal devices.

The following Figure 14 and Table 10 show the questions asked and the average percentage of the responses on the specific characteristics of the packages. Where indicated, the table also reports some added descriptions.

The following observations can be highlighted:

- Most packages are certified for the transport with reference to IAEA standard.
- Almost all packages are stackable, in some cases up to 8 levels with maximum load on bottom package: 25 - 35 t.
- More than 70% of the packages are mechanical stress resistant; some packages are respondent to the mechanical design basis equal to 8x-staple and also resist earthquake loads. Often a simplified calculation of the radioactive release after drop (1.2 m on its lid) is performed. Where concrete packages are used, some cement strength tests are carried out.
- 30% of the packages are thermal stress resistant and precisely for this reason some have a minimum 3 cm outer cover of reinforcement. Simplified calculation of radioactive release during fire is performed.
- The design life of waste packages can be very different: starting from 50 years up to 300 years, covering in the last case both storage and disposal periods.
- Few waste packages are qualified to resist internal and/or external corrosion.

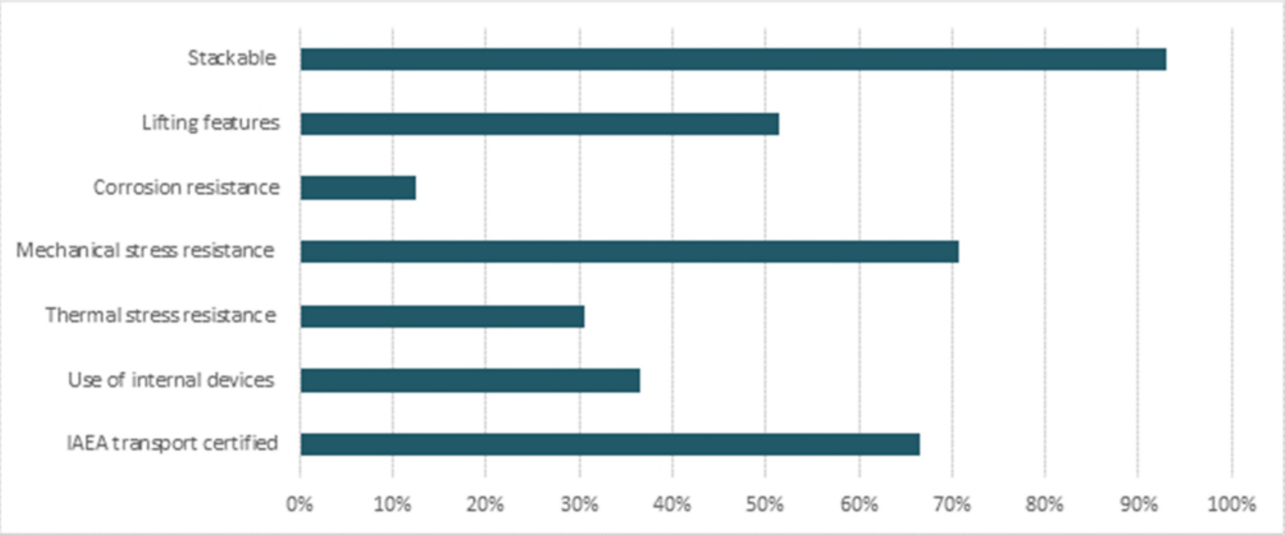


Figure 14 – Package main design characteristics

Packages Design Characteristics	Average percentage*	NOTES from some responses
IAEA transport certified	66%	
Use of internal devices (e.g. disposable mixing paddle, basket)	37%	
Thermal stress resistance (T max (°C) and duration, accepted degradation/leak rate after fire, etc.)	30%	simplified calculation of release during fire; 3 cm minimal outer covering of reinforcement, simplified calculation of release during fire;
Mechanical stress resistance (drop, impact, accepted permanent deformations/leak rate, internal pressure, etc.)	70%	mechanical design basis: 8x-staple and resistance to earthquake loads, simplified calculation of release after drop; mechanical design basis: 5x-staple or 8x- to 10x-staple with resistance to earthquake loads for concrete container, simplified calculation of release after drop; drop of 1.2m on its lid; IP-2 tests; cement strength test
Corrosion resistance internal and external (e.g. mm per year)	12%	
Design life (years)	36%	200 years; Integrity of the waste package without maintenance for 300 years (storage + disposal); 50 years; 75 years
Lifting features (please specify)	51%	ISO edges; iso-edges or ball abutment for concrete container; corner fitting, twist lock for vertical and horizontal lifting; handling from above and transfer by loading pallet or handling crane (according to package); hoist fittings
Stackable (to be placed on top of another similar package) specify max n, of stackable packages and max load on bottom package	93%	altogether 8 including bottom, max load on bottom: 25 - 35 t; 8 x stack

(*) The percentage is calculated on the basis of the number of responses and the number of packages to which the responses refer

Table 10 – Package main design characteristics

To complete the information about waste package technical characteristics, the questionnaire asked questions about handling systems in use. The survey showed that very few use fully automated handling systems, while the majority use semi-automated and remoted operated ones; about 25% use manual handling systems (see Table 11).

Packing handling system	average percentage*
Fully automated (the system functions automatically, without continuous input from an operator)	5%
Semi-automated (the system functions by the combined activities of man and machine)	65%
Remotely operated (the system is operated by a person from a distance)	58%
Manual (the system is operated by a person without machine support)	23%
(*)the percentage is calculated on the basis of the number of responses and the number of packages to which the responses refer	

Table 11- Package handling systems

7.2.3 Main waste packages storage configurations

The waste package behaviour in long-term storage will be influenced by the storage time and configuration. A suitable storage facility and equipment system are important for both short- and long-term waste management strategies. Therefore, it is clear how the technology and efficiency of monitoring systems and the knowledge of the long-term waste packages behaviour is crucial to the success of the overall storage strategy.

The specific waste package storage configuration is an integral part of the monitoring and inspection system. The questionnaire therefore investigated some main aspects of the storage facilities currently used for those types of waste reported by the respondents. The survey specifically asked for package identification, arrangement of the packages, the needs of shielding walls, the presence of maintenance areas, ventilation system and other issues.

As the following Table 12 reports, here are the main conclusions:

- Almost all the packages in storage are identified individually.
- About 70% of the packages are stored in a stack; some reported cases indicated vertical stacking up to 8 levels.
- 80% of the packages are stored in areas with forced ventilation and/or air conditioning systems.
- Many storage areas are accessible by the operators during the operations.
- Some storage areas use shielding walls to separate areas at higher doses.
- Presence of packages maintenance areas in the storage facilities is declared in about 30% of the cases.
- Some waste package typologies are not placed into storage facilities or are stored outside pending their imminent disposal (some months).

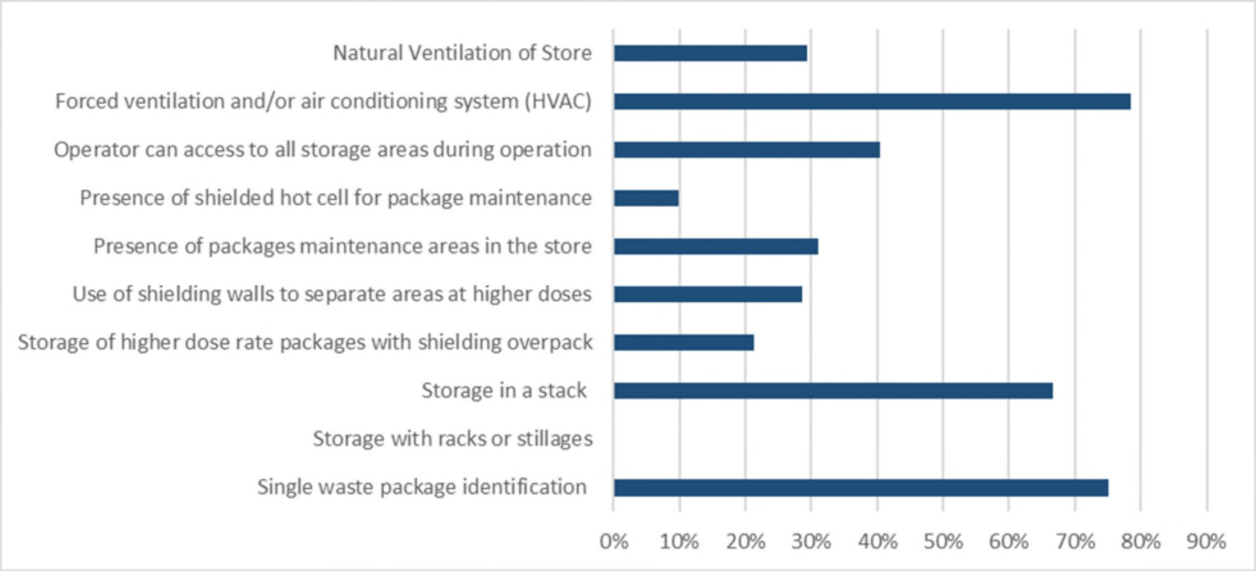


Figure 15 - Waste packages storage configurations

Storage configuration	average percentage*	NOTES from some responses
Single waste package identification (labelling and storage position)	75%	
Storage with racks or stillages	0%	
Storage in a stack (specify stacking configuration, e.g. horizontal/vertical stacking of drums)	67%	Vertical; triangular vertical stacking 4 drums on one tray, max 8 layers in height; Max stacking height: 4 drums; vertical stack of 5 levels (1+4);
Storage of higher dose rate packages with shielding overpack	21%	
Use of shielding walls to separate areas at higher doses	29%	
Presence of packages maintenance areas in the store	31%	
Presence of shielded hot cell for package maintenance	10%	
Operator can access to all storage areas during operation	40%	
Forced ventilation and/or air conditioning system (HVAC)	78%	
Natural Ventilation of Store	29%	Forced ventilation is in operation. Some natural ventilation
Others storage configuration details you would like to add	0%	
(*) the percentage is calculated on the basis of the number of responses and the number of packages to which the responses refer		

Table 12 - Waste packages storage configurations

7.3 Monitoring strategy

Degradation of waste packages has been observed to occur faster than expected in some cases. The possible mechanisms of package degradation, factors affecting the evolution of the packages and their performance during interim storage and preceding final disposal must be considered.

For the scope of the present report, monitoring can be defined as *continuous or periodic observations and measurements of specific parameters/indicators which reveal changes in the conditions of a waste package over time*. For example, metal containers will tend to corrode, cementitious materials will undergo hydration and conversion reactions leading to the formation of different mineral phases and the waste packages will undergo a variety of physical and chemical changes, such as gas production or porosity changes for example.

The questionnaire asked respondents to indicate the types of monitoring activities undertaken during storage of waste packages by proposing one or more choices from the following options:

Monitoring of all individual waste packages
Monitoring of accessible waste packages
Monitoring of a sample of waste packages/material
Monitoring waste packages at specific storage positions
Handling and monitoring waste package in dedicated area or in hot cell
Monitoring waste packages by portable instruments or by remote monitoring system
Instrumented waste packages (external and/or embedded)
Monitoring of relevant environmental conditions (e.g. temperature, humidity, etc.)

Table 13 - Monitoring options

Looking at the results from the answers reported in *Figure 16*, it can be deduced that:

- None of the End Users who answered the questionnaire employ a monitoring strategy based on sampling waste packages/material. for their main streams.
- None of the End Users who answered the questionnaire employ a monitoring strategy based on instrumented waste packages (external and/or embedded).
- More than half of the respondents monitor all the individual and accessible waste packages (56%).
- Monitoring is only partially carried out at specific storage positions (33%) while some End Users handle and monitor waste packages in a dedicated area: in a building or in a hot cell, outside/inside of the interim storage (22%).
- Many respondents monitor relevant environmental conditions such as temperature and humidity (44%).
- Almost a quarter of the End Users monitor waste packages by portable instruments or by remote monitoring system (22%).

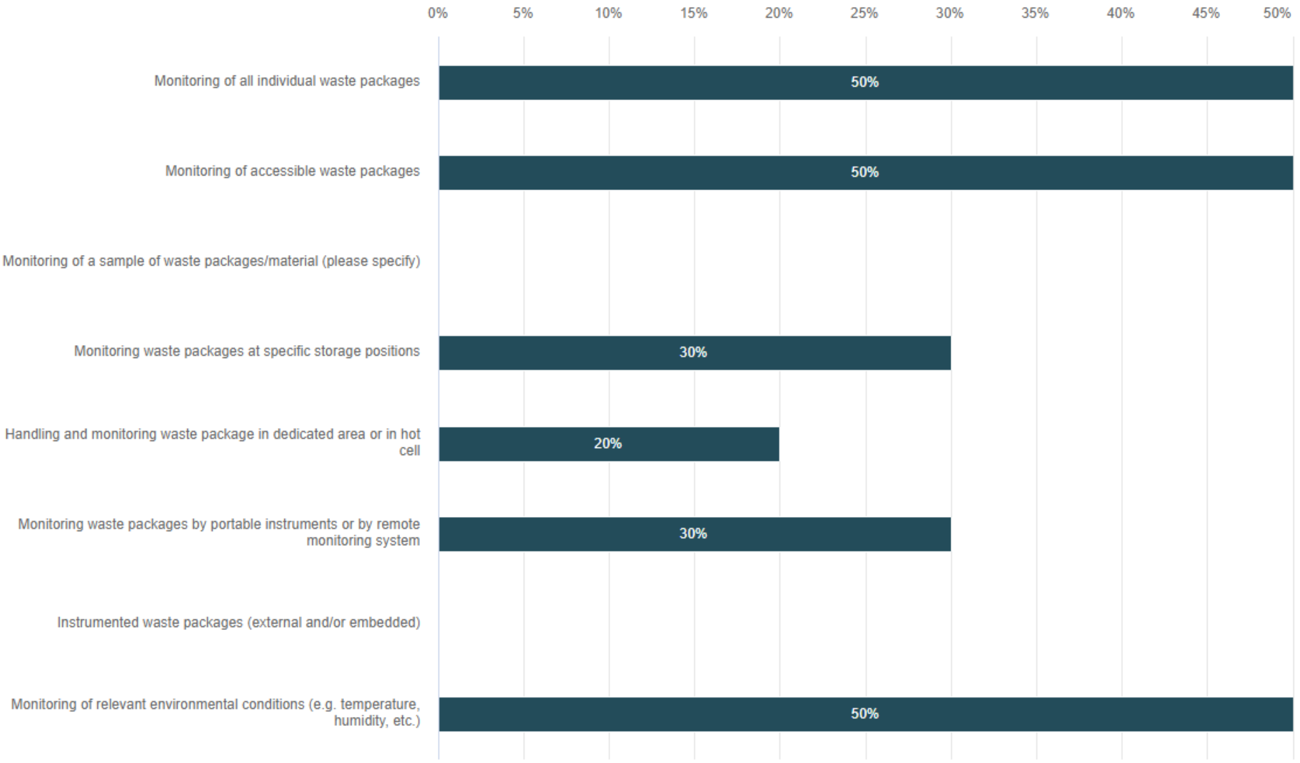


Figure 16 - Types of monitoring activities undertaken during storage of waste packages

7.4 Long-term storage strategy - ageing and degradation phenomena expected

Long-term interim storage is becoming an important issue in countries where the implementation of disposal facilities is postponed. Consequently, suitable long-term storage is an essential enabling component of decommissioning programs while providing confidence that packages will be disposable at the end of the storage period.

The questionnaire asked the respondents about the approach to the long-term management of cemented waste packages storage and investigated on the following aspects:

Long-term management plan in place (good practice, enforced by law, authority prescription, generalities, etc.)
Ageing and degradation phenomena expected
Options in place for remedial actions to be taken in case of degrading packages
Declassification of “old waste packages” thanks to extended interim storage and related decay time
Other

Table 14 - Long term management approaches

Looking at the results from the answers reported in Figure 17 together with some added information from the respondents, it can be deduced on the mains waste streams that:

- Most of the respondents manage the long-term storage putting in place some options for remedial actions to be taken in case of degrading packages (63%) and by adopting good practices, requirements enforced by law or authority prescription, etc. (50%). In some cases, a long-term management plan is currently under development alongside the preparation of a new upgraded storage facility. The new storage facilities are declared to be designed for an operating life of up to 50 years.

- More than a third of the respondents expect some ageing and degradation phenomena (38%); e.g. cracks have been observed in some packages. They are often linked to the handling of the packages.
- Some End Users do not have a long-term storage strategy and declare that:
    - final disposal is expected within a few decades.
    - interim storage lasts approximately one month for quality control. After that period the packages are transported to the final repository.
    - maximum long-term storage period is limited by law to 2 years,
    - package monitoring is made twice during interim storage: when the package is produced before its entrance in the interim storage and before it is sent to final disposal when it leaves the storage area.

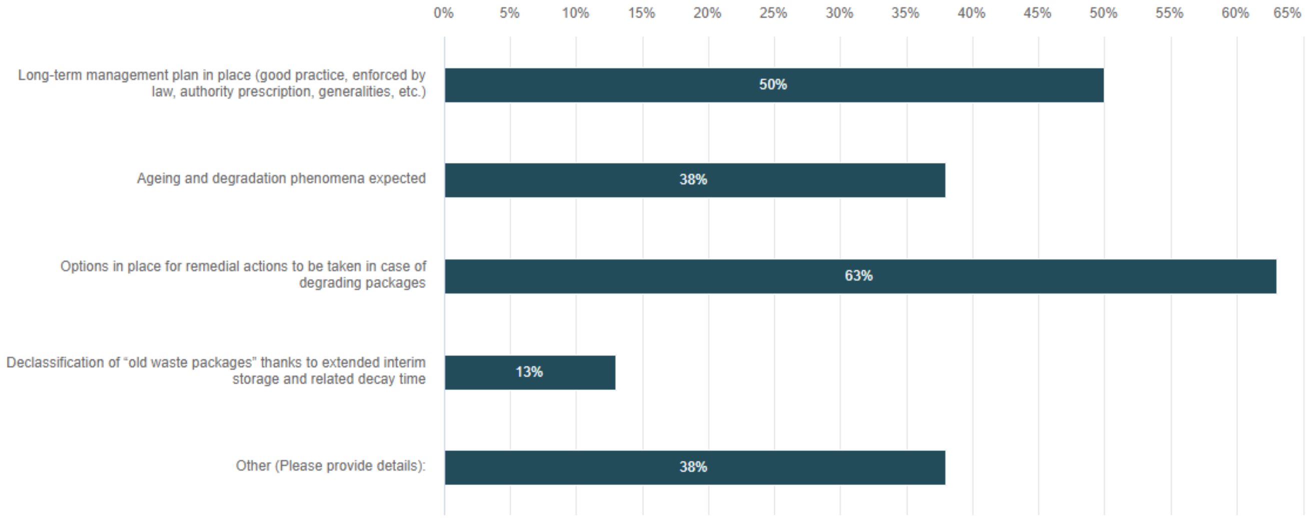


Figure 17 - Approaches to the long-term management of cemented waste packages

7.5 Parameters and data collection systems used

The possible mechanisms of package degradation, factors affecting the evolution of the packages, and their performance during interim storage and preceding final disposal must be considered. These degradation mechanisms have been and continue to be explored in the relevant research fields, with the aim of minimizing or completely avoiding package degradation, through adequate conditioning processes, appropriate design of waste packages and suitable waste storage management.

Therefore, it is crucial that the accuracy in predicting the behaviour of waste packages in stores, through the monitoring of suitable parameters, is improved.

A list of relevant parameters is captured below for monitoring waste package evolution and degradation processes.

7.5.1 Relevant parameters currently monitored

The questionnaire asked the respondents about the relevant parameters currently monitored into their own storage facilities on their main streams described previously to obtain some information about the following aspects:

- Identification
- Metal corrosion

- Chemical reactions
- Leakage
- Lifting feature deformation
- Swelling
- Cracks
- Condensation
- Contamination
- Fissile content
- Other

Looking at the results from the answers reported in *Figure 18* together with some added information from the respondents, it can be highlighted that:

- Almost all of the respondents manage and monitor the identification, metal corrosion, cracks and external contamination of their waste packages (88%).
- About three-quarters of the respondents monitor the presence of swelling and leakage (75%).
- More than half of the respondents check for lifting feature deformation (63%).
- Half of the respondents monitor the presence of chemical reactions (50%).
- Several respondents monitor condensation (38%) while some do check for other unspecified parameters (13%).
- Nobody checks for fissile content.

Figure 18 - Relevant parameters currently monitored on cemented waste packages

7.5.1.1 Waste Package Dimensional Variation

Among the parameters controlled, 6 respondents out of 11 answered that they collect information about the variation of some container dimensions, as requested by regulatory requirements, law or with the purpose of optimizing storage conditions.

They mostly monitor dimensional parameters by visual periodic inspections (100%).

40% of the respondents check the entire surface of the packages, while 60% monitor on a sampling basis and according to the accessible percentage of the packages and their reachable surface.

All of them collect data exclusively by manual systems.

7.5.1.2 Waste packages gas emissions

Among the parameters controlled in monitoring cemented waste packages, 5 respondents out of 11 answered that they collect information about gas emission from packages, as requested by regulatory requirements, law or with the purpose of optimizing storage conditions.

They check gas emission by real-time tritium monitoring with inert gas radon compensation and by monitoring aerosols.

Monitoring of gas emissions is mostly continuous and in a real time manner (67%). The rest of the respondents collect data periodically and manage them by manual systems (33%)

67% of respondents check the whole store area of the packages, while 33% monitor single waste packages.

7.5.1.3 Waste package dose rates

Among the parameters controlled in the monitoring of cemented waste packages, 9 respondents out of 11 answered that they collect information about dose rates, as requested by regulatory requirements, law and with the purpose of optimizing storage conditions.

They use different techniques among which manual dose rate meters and on-line monitoring and ionisation chambers. Monitoring is performed directly when packages are placed in store.

They monitor dose rates mostly during periodic inspections (86%).

57% of the respondents check all the cemented waste packages stored, while 43% monitor on a sample basis using ‘reference package’ representative of the sample.

The monitored data are collected mostly by manual systems but also by automated and real time systems.

7.5.1.4 Wasteform internal conditions

Some of the parameters controlled in the monitoring of cemented waste packages from 4 respondents out of 11 are linked to information about wasteform internal conditions, as requested by regulatory requirements, law and with the purpose of optimizing storage conditions.

The technique used by the respondents is RTR (X-ray imaging).

Monitoring is performed directly when packages are placed in store.

They monitor wasteform internal conditions with both periodic (50%) and continuous (50%) inspections.

50% of the respondents check all the cemented waste packages stored, while the remaining 50% monitor sampled waste packages based on technical judgement.

The monitored data are collected mostly by automated and real time systems.

7.5.2 Monitoring techniques used

The questionnaire asked the respondents about the main techniques put in place to perform monitoring of relevant parameters during the storage period of the cemented waste packages. The survey proposed the following multiple options:

- Identification
- Metal corrosion
- Chemical reactions
- Leakage
- Lifting feature deformation
- Swelling
- Cracks
- Condensation
- Contamination
- Fissile content
- Other

Looking at the results from the answers reported in *Figure 19* together with some added information from the respondents, it can be concluded that:

- All respondents use visual monitoring (100%) and half of them do it through TV cameras (50%).
- Half of the respondents check external contamination by taking swabs (50%).
- Up to a quarter of the respondents put in place destructive testing (25%).
- One respondent integrates visual inspection with digital image correlation (13%) and some others use techniques such as RTR (X-ray imaging).
- None of the respondents use digital scanners.

Figure 19 - Cemented waste packages monitoring used techniques

7.5.3 Monitoring Frequency and Monitoring of other Parameters

As regards the frequency of the monitoring performed, the questionnaire asked respondents to indicate how frequently they perform the inspections and controls on their cemented waste packages.

33 % of the respondents perform monitoring continuously (see Figure 20). The rest of the respondents implement the monitoring on a periodic basis (67 %) using one of the following different manners:

- Annually
- Twice for each package: after its production and before the package is sent to final disposal
- case dependent
- twice a year

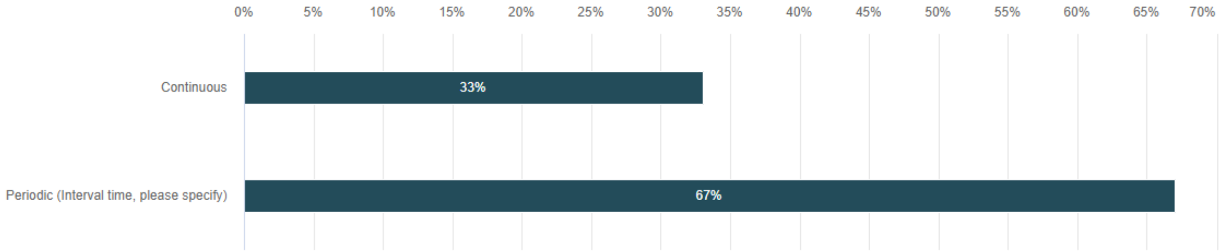


Figure 20 – Monitoring frequency

7.6 Observed Degradation phenomena

Most of the respondents replied that they have observed degradation phenomena, while 25% of them never detected particular degradation phenomena.

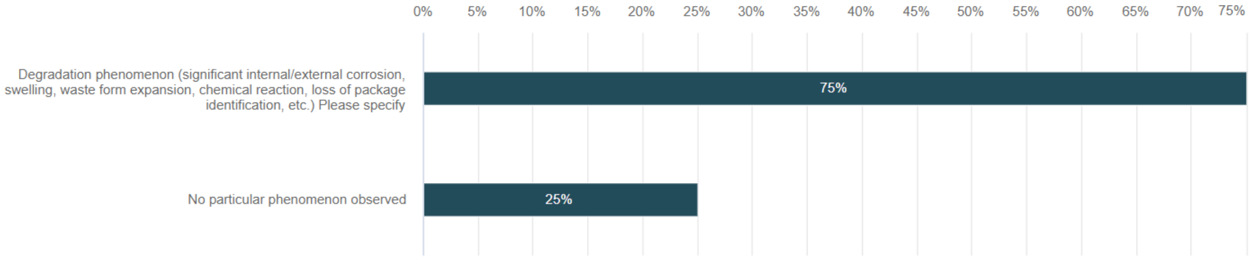


Figure 21 - Cemented waste packages degradation phenomena observed

Among the phenomena detected, the following cases were indicated by 6 out of 8 respondents:

- Significant internal and external corrosion.
- Cracks linked to the handling of the package.
- Alkali–silica reaction (ASR) gel formation.
- Leakage of liquids.
- Swelling.
- Chemical reactions.

7.7 Data management

7.7.1 Data collection, transmission and archiving

The respondents were asked about the methodology used to collect monitored data and waste package information on the basis of the following options:

Manual
Automated
Semi-Automated
Real-time
Parameter monitoring at regulator requests (current law)
Parameter monitoring for storage optimization

Table 15 - Data management methodology

Looking at the results from the answers reported in *Figure 22*, it can be underlined that:

- Almost all respondents manually collect the monitoring data (88%).
- Half of the End Users use semi-automated collection systems (50%) and only 13% automatic ones.
- Some of the respondents perform real-time collection of the monitored data (13%).

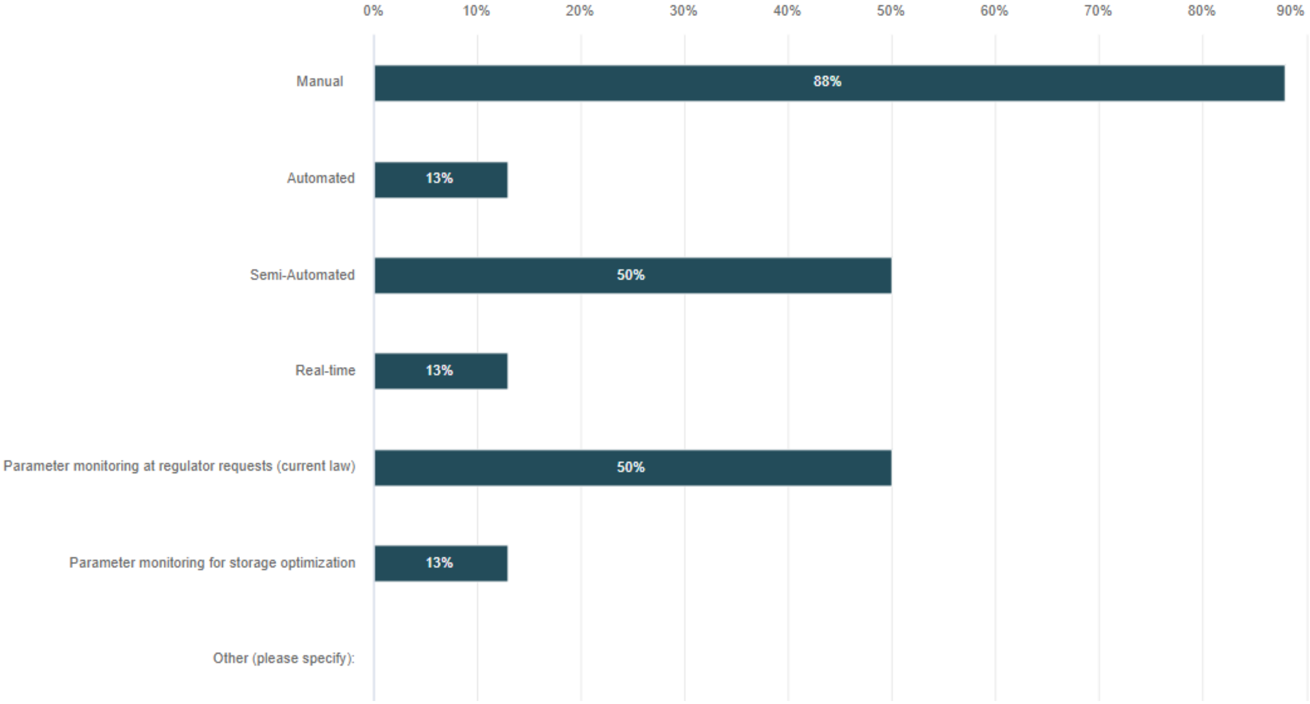


Figure 22 - Cemented waste packages monitoring techniques

The questionnaire also asked some questions about the methods used to manage data collected from cemented waste package monitoring systems. Referring to the collection and archiving of the data, the respondents reported on the basis of the following options:

Paper Based	25%
Digital	63%
Other (both)	12%

Table 16 - method of data collecting

Looking at the results from the answers reported in *Figure 23* and *Figure 24*, it can be seen that:

- No one uses only paper-based systems for data archiving.
- Most respondents use digital transmission and archiving systems (62% - 75%).
- About 25% of the respondents adopt paper-based data transmission-systems.
- Some respondents use both digital and paper-based systems for the transmission and archiving of the monitored data (12% and 25%).

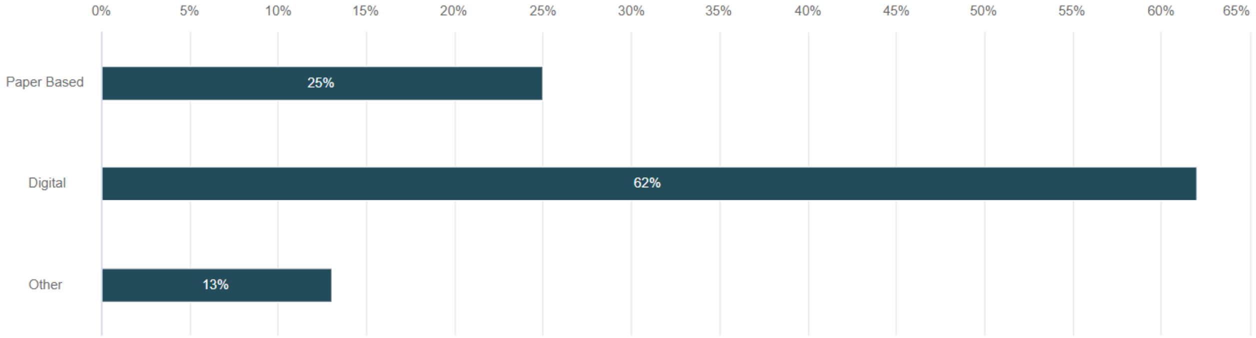


Figure 23 - Cemented waste packages monitoring data transmission systems

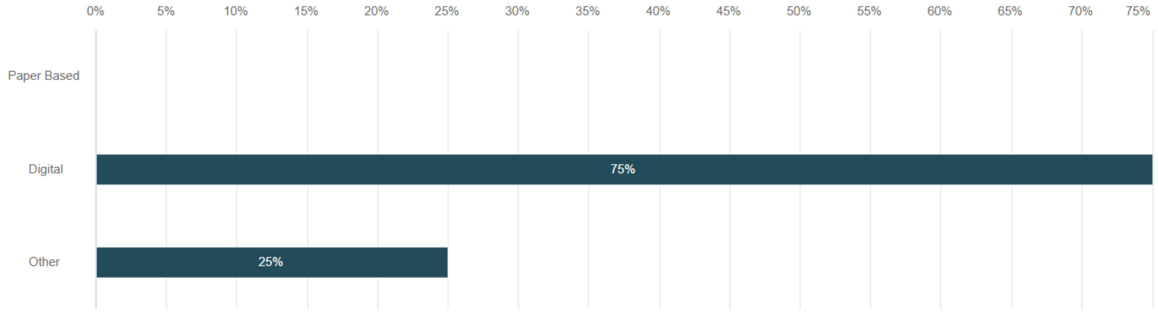


Figure 24 - Cemented waste packages monitoring data archiving systems

7.7.2 Data analysing

Regarding the analysis of the cemented waste packages monitoring data, the questionnaire asked for information about the methods used to manage data collected from monitoring systems; the respondents reported on the basis of the following options:

Expert System	57%
Digital Twin	14%
Other systems	28%

Table 17 - Data analysis system

As *Figure 25* represents, the results from the questionnaire lead to the following conclusions:

- More than half of the respondents adopt Expert System data analysing application (57%).
- some respondents use a Digital Twin system (14%).
- about 30% of the respondents use some other customized integrated systems.

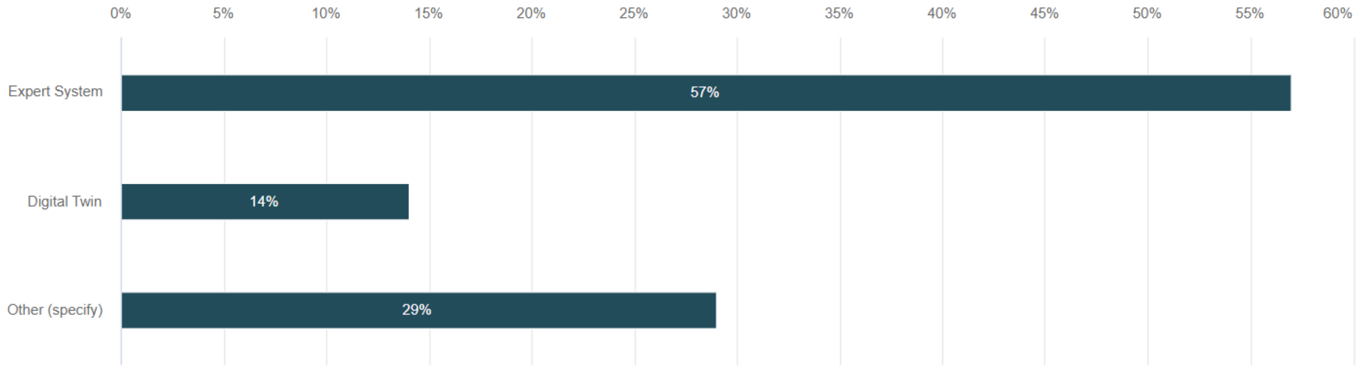


Figure 25 - Cemented waste packages monitoring data analysing systems

7.8 Quality assurance and control

All respondents noted that they employ their own Quality Assurance and Control System.

8 Innovation Technologies

Innovation technologies applied in *cemented waste package monitoring* during the short or long-term storage periods will have significant impacts for all waste producers in terms of improved storage operations, including cost and safety (for example, in reducing intervention and repackaging) and an improvement in understanding the characteristics of waste prior to final disposal. These technologies will be relevant to End Users aiming to:

- Understand the evolution and improve accuracy in predicting the behaviour of waste packages, during the storage period through store monitoring, package condition monitoring, modelling and decision frameworks.
- Identify packages in need of remedial treatment and options for treatment,
- Automate operation of waste stores using digital and robotics technology.

PREDIS WP7 aims to provide the following outcomes and innovations:

- Innovative NDE tools for evaluation of package integrity, including, but not limited to visual methods, muon tomography and ultrasonic techniques.
- Innovative sensor technologies for instrumented packages, including, but not limited to fiber optical techniques and methods for wireless power supply and data transmission,
- An approach for developing and maintaining individual digital twins of packages, including a package evolution model based on inventory and monitoring data.
- Application of machine-learning algorithms, trained on digital datasets, to produce a fast and accurate description of the geochemical evolution and the geo- and thermo-mechanical integrity of radioactive waste packages during pre-disposal.
- A digital twin of a radioactive waste package based on machine-learning algorithms that can offer advanced information for waste package inspection protocols and, thus, contribute to safety of storage facilities,
- Large digital database to train the machine-learning algorithms.
- A decision framework model that is based on existing knowledge, data from measurements and predictions from digital twins.

The following sections outline the main innovative techniques to be used in this project. These are some examples and preliminary approaches to be developed in the coming years.

Additional techniques will be considered also by means of fruitful information exchange with other Euratom funded R&D projects as these projects report their results.

It is worth mentioning for example the CHANCE project which aims to address the characterization of conditioned radioactive waste by means of NDA techniques and methodologies like calorimetry, muon tomography and cavity ring-down spectroscopy (https://www.chance-h2020.eu/) and the MICADO project whose goal is to propose a modular and transportable system for the complete radiological characterization of cylindrical waste packages with techniques such as gamma spectroscopy, active/passive neutron measurement, photo fission and long term monitoring system based on scintillating optical fibers (https://www.micado-project.eu/).

8.1 RFID Sensors

The aim of this technology is implementation of wired, wireless, and passive radio frequency identification (RFID)-based sensors embedded into waste packages to detect acoustic emissions, which are indications of crack initiation, and to monitor relevant parameters, such as temperature, pressure, humidity, pH-value, gas concentration of O_2 and N_2, internal corrosion rate, and radiation. For many of these parameters, RFID technologies enable battery-less implementation of the embedded sensors and thus, long-life maintenance-free operation.

Figure 26 and *Figure* 27 show the technology concept which uses contactless powering and communication in concrete and a typical sensors system under development.

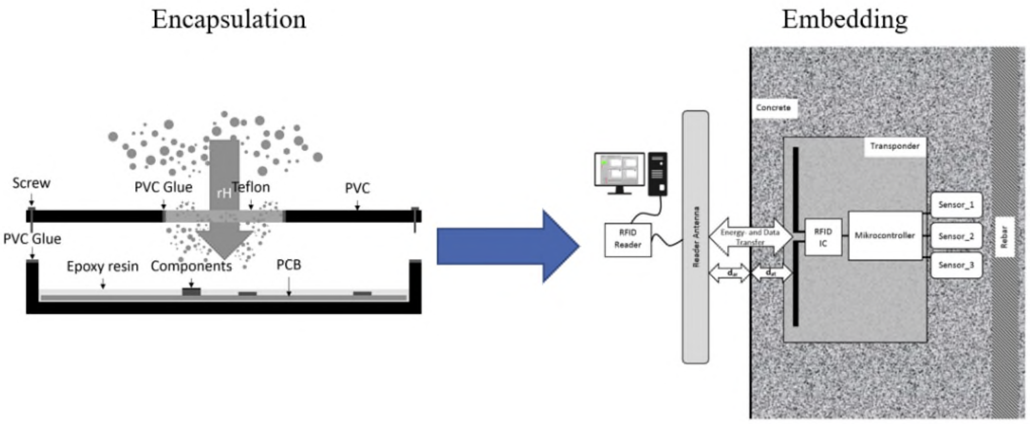


Figure 26 - Embedded monitoring of waste canisters - Technology concept (Source: BAM)

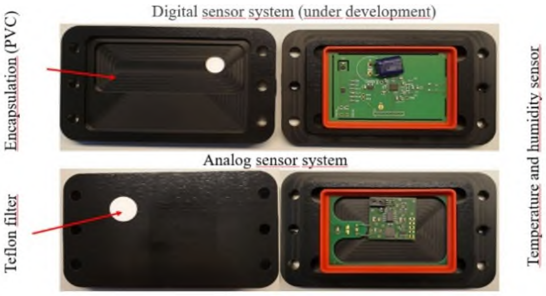


Figure 27 – Sensor system (Source. BAM)

Regarding the technology concept for communication and energy supply (*Figure 28*), research is ongoing with two approaches:

- Option 1: Inductive RFID
  - Based on loop antennas at the opposite sides of the wall.
  - Standard inductive RFID technologies cannot penetrate through metals => Customized solution with remarkably lower operation frequency necessary
  - Performance depends on the wall thickness and material electromagnetic properties => work will start with feasibility study (experiments, simulations)
- Option 2: Acoustic (ultrasonic) link
  - Piezoelectric elements bonded at the opposite sides of the wall.
  - Critical issue: bonding technology
  - no commercial technologies available

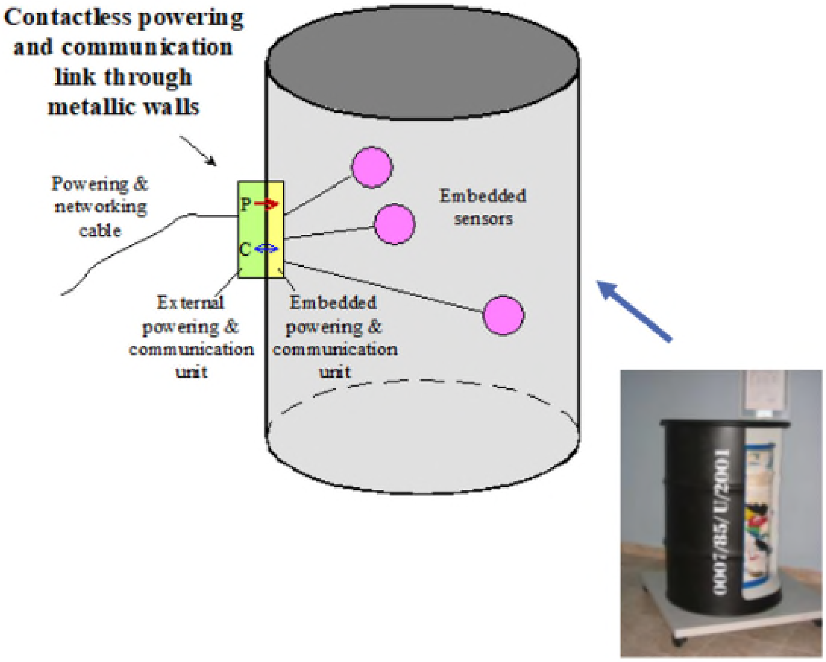


Figure 28 - Embedded monitoring inside metallic waste canisters - Technology concept for communication and energy supply (Source: VTT with picture from UJV)

8.2 Fiber optic sensing system

The aims are development of a fiber optic sensing system, either on surfaces or integrated into materials, that provides remote long-term monitoring of temperature, strain, pressure, humidity, variation/acoustics and radiation distribution around the package as well as detection and localization of cracks.

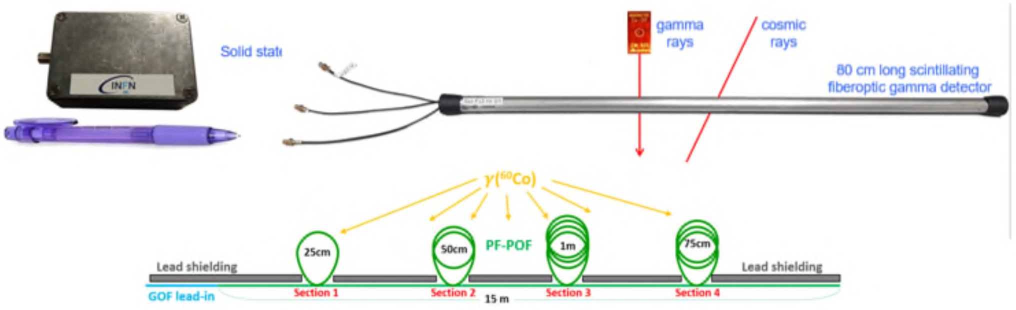
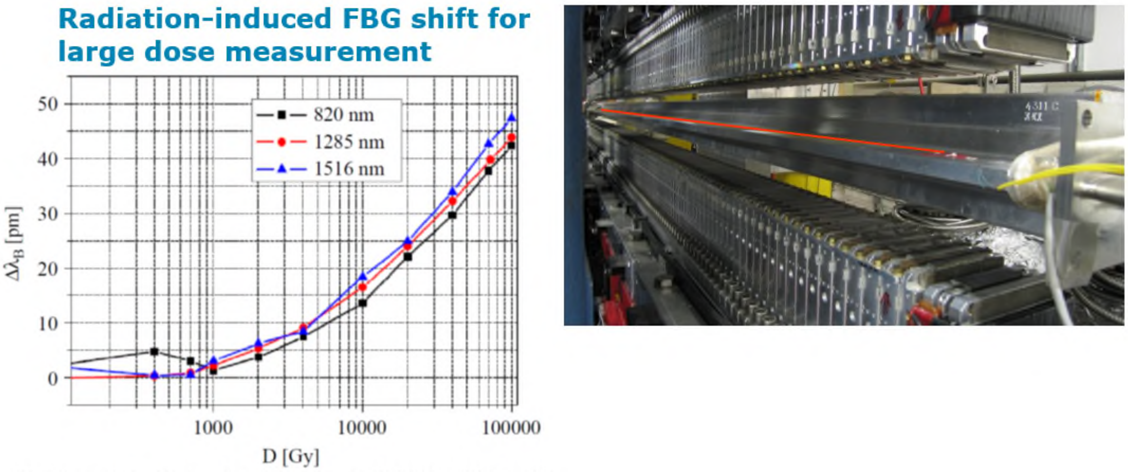


Figure 29 – External sensing technology. Top left: compact solid state neutron counter. Top right: scintillating fiber gamma ray counter for dose rate measurement. Bottom: optical fiber for total dose measurement.

The main advantages to using this technology are electromagnetic immunity, small footprint and remote monitoring, real-time (online) monitoring and distributed sensing. The physical concept behind measurements concerns detecting change of light in terms of intensity, wavelength, phase and polarization or direct measurements of single photon counting rate. In *Figure 28* (top right side) is shown a detector used for gamma-ray dose measurements based on scintillating fiber and using this single photon detection technology. In the top left side of the same figure is shown, for completeness, a system based on solid state detectors LiF^6-Si capable to detect neutrons coming from fission materials. Both these apparatuses can be read out with a new-conceptual smart electronics appositely developed to be modular, easily configurable, not expensive and suitable for the use in different scenarios (inside and outside a storage site, during waste transportation and for a more general environmental monitoring).. In *Figure 30* and *Figure 31*, an example of fiber optic radiation measurement, suitable for dosimetry up to 100 KGy, and two examples for radiation induced attenuation for two different radiation-sensitive silica fibers are shown. It can be highlighted that sensitivity of the radiation sensors can be influenced by the choice of dopants in the silica fiber core.



Krebber et al., Meas. Sci. Technol. 17 (2006), 1095-1102.

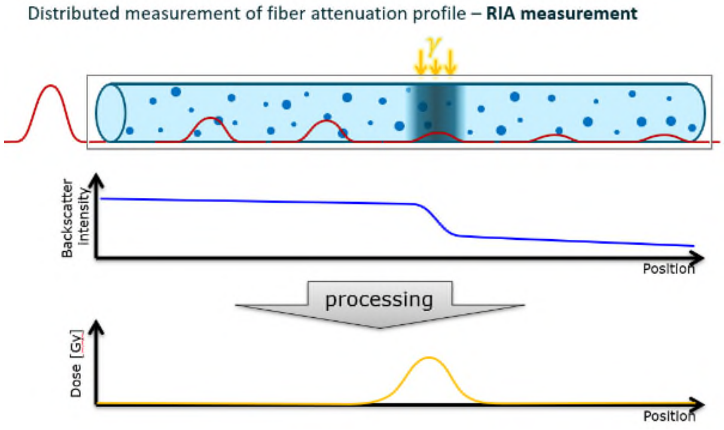
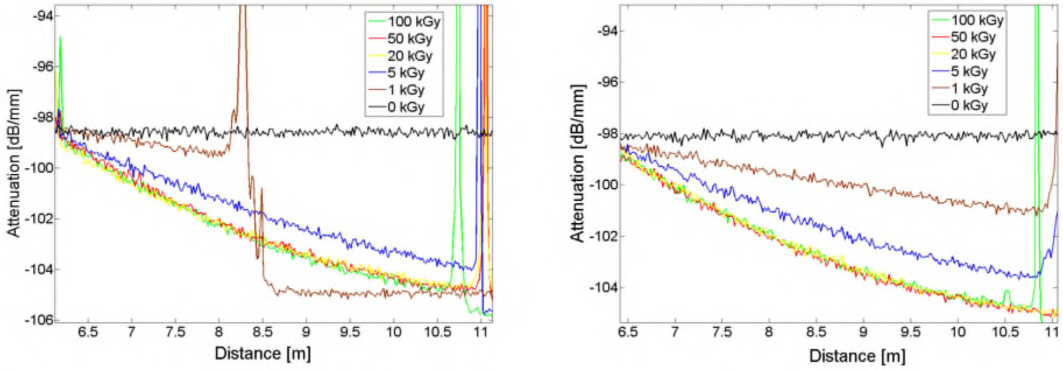


Figure 30 – Example of fiber optical radiation measurement – Fiber Bragg Grating



A. Wosniok et al., Proc. of SPIE. 9916 (2016) 99162J-1 – 99162J-4.

Figure 31 - Radiation-induced attenuation for two different radiation-sensitive silica fibers

8.3 Muon Imaging

Muon tomography (MT) is a technique that uses the muons, elementary particles produced by the interactions of primary cosmic rays from outer space with the Earth atmosphere, to reconstruct an image of the inner structure of large object (see *Figure 32*). objects. While X-rays, used in radiographs, cannot cross more than a few tens of centimetres of material, muons can pass through large thickness, even a few kilometres (see *Figure 32*). This feature can be exploited to create three-dimensional images of large structures from the outside and in complete safety [28].

The MT technique exploits uses the multiple Coulomb scattering (MCS) that the muon undergoes when it passes inside a material. Since MCS is related both to the material density and to the atomic number, the technique is able to detect and classify materials inside an inaccessible volume, such, for example, of a container. It involves the measurement of the muon direction and impact point when it enters the material under investigation, and the direction and exit point when it exits the material.

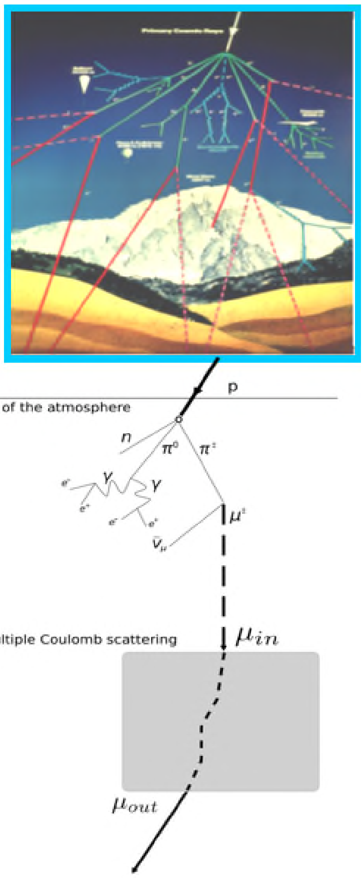


Figure 32 – Muon production in the Earth atmosphere (top figure) and muon behaviour when it passes through a material.

The identification of the material is based on the statistical analysis of the scattering events occurred in the volume under investigation. Because of its stochastic nature, MT requires that a sufficiently high number of events is collected. The exposure time is a relevant parameter, which influences the discrimination capability of the technique, and depends strongly on the elemental composition and density of the body, and on its shape and size.

An experimental setup for muon tomography, previously assembled for studying the technology, could be applied for nuclear waste case. The demonstrator [29] consists of two muon chambers, producing a the Compact Muon Solenoid (CMS) experiment at CERN [30] installed in the barrier. The demonstrator detector consists of two 300 cm×250 cm dimension, placed horizontally, and with a vertical separation of about 160 cm, as shown in Figure 32.*Figure 33*. The chambers enclose an inspection volume of more than 11 m^3, one of the largest for MT test in the world (see *Figure 33*).

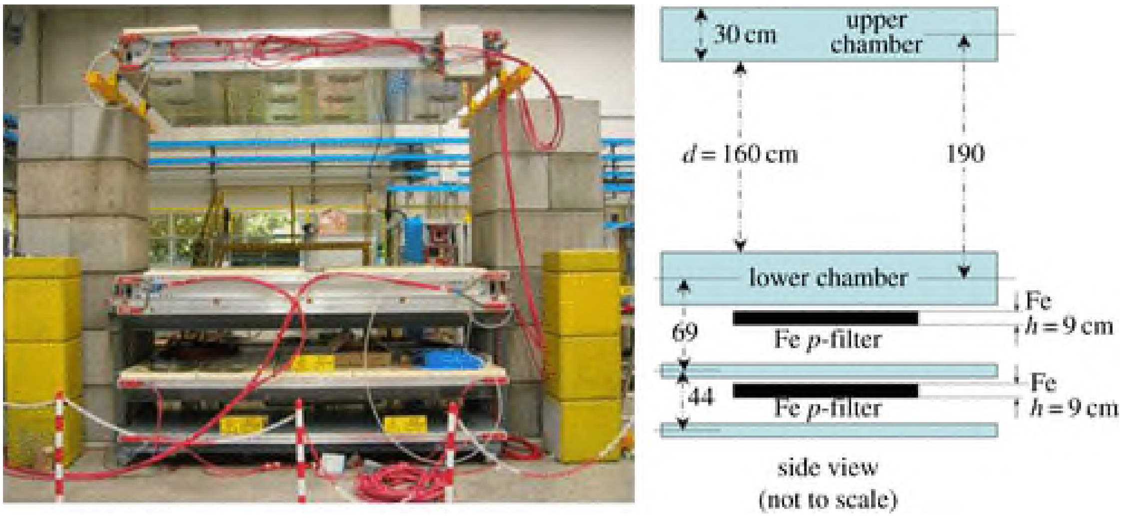


Figure 33 – INFN Muon Tomography demonstrator

A preliminary activity concerned a concrete block (50x50x17 cm^3) with some iron objects of different dimensions on the mu-tomography system. The technology managed to clearly distinguish iron inside the concrete block. This can be useful also for other applications in terms of scanning of cemented nuclear waste or studying the content of inaccessible volumes (for example for legacy cemented waste)

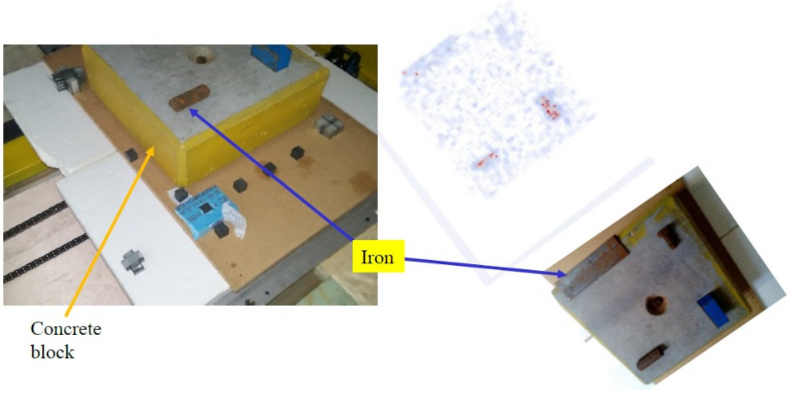


Figure 34 – Test with iron objects on a concrete block: pictures of the layout and outcome of the test.

8.4 Digital Twin

A digital twin in the context of PREDIS WP7 refers to the representation of a cemented radioactive waste package using digital means (e.g. a computer model). The "digital twin" is planned to be a toolbox based on machine-learning algorithms and neural networks which will be trained with data produced by numerical tools for geochemical and mechanical integrity modelling. These numerical tools will be validated and calibrated with information from NDE data, existing experimental data and experimental data obtained from the experimental characterization of real radioactive waste packages (*Figure 35*).

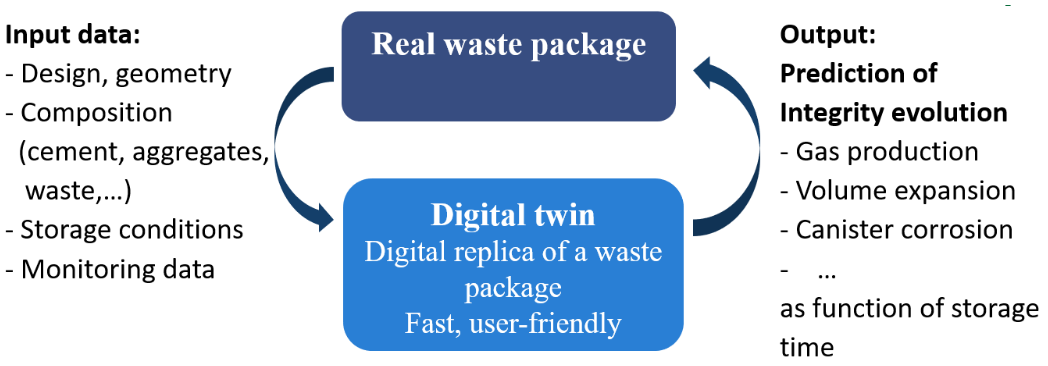


Figure 35 - Digital twin process for cemented waste package [32]

For this development it is necessary to perform the following activities (*Figure 36*):

- Identify and describe dominant chemical processes as well as chemo-mechanical and thermo-mechanical processes influencing the evolution of wasteforms during pre-disposal
- Set-up and application of predictive geochemical evolution models. The models should be adaptive to the waste package design, initial inventories, and available NDE/monitoring parameters
- Set-up and application of predictive models for mechanical integrity of waste packages. Full thermal-hydrological-mechanical-chemical (THMC) coupling is not foreseen
- Application of reduced-order and data-driven modelling to decrease the computational cost of numerical models
- calibration and validation of the numerical models based on experimental chemical and mineralogical characterisation of existing waste packages (for instance, 35 year-old cemented wasteforms at PSI), data from mock-up experiments of real-scale waste packages at Belgoprocess in collaboration with SCK•CEN, and from a large set of data on long-term evolution of cement materials (UJV). Calibration will be done in a Bayesian framework to quantify uncertainty associated with measurements and model errors. To make it tractable, machine learning emulation of the physics-based models will be explored.
- Deep neural networks will be trained to describe the evolution of waste packages using a large digital database generated from the output of sophisticated geochemical, chemo-mechanical and thermo-mechanical models.

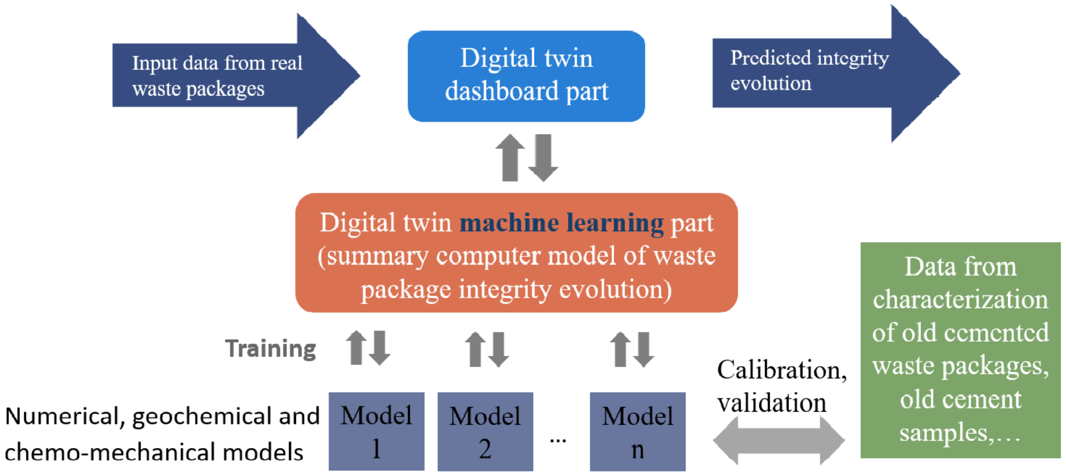


Figure 36 – Digital twin approach

8.5 Data handling, processing, and fusion

The modern monitoring methods and sensors can produce ample data. The more you measure, the more you know and decrease uncertainty. The amount of data can be so vast that humans cannot utilize the full extent without the proper tools. So, it is important to develop and research tools for monitoring cemented waste packages to better understand and utilize the available data, with the possibility to detect and even predict important features from the measured data: how long will the concrete last, what measurements are truly relevant and what is the current condition (*Figure 37*).

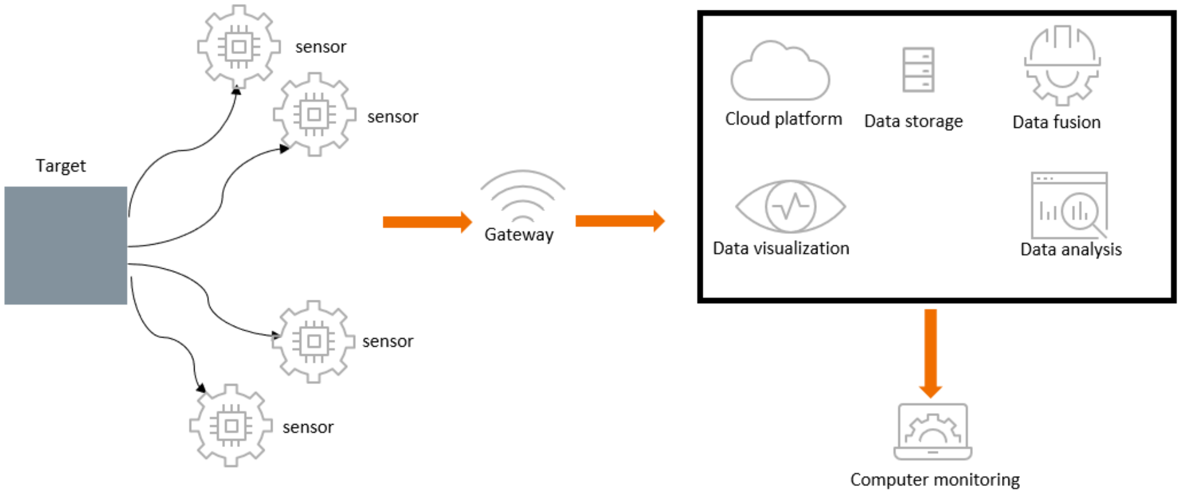


Figure 37 – Data handling, processing, and fusion approach

For the development of this methodology, it is necessary to:

- Provide a conceptual model for secure and persistent data handling and storage, both for measured and simulated data
- Develop models and methods to translate NDE and monitoring data into engineering parameters
- Develop approaches for fusion of multi-method monitoring and other data to obtain adequate input for the decision framework
- Implement a plan for ensuring data integrity
- Provide a database and software prototype for demonstration
- Develop a platform that will foster the seamless connection between devices and sensors from different manufacturers, including those used in the monitoring system
- Implement a configurable Human Machine Interface (HMI) into the platform, which provides the real-time status of field sensors, time trends, alarm thresholds, etc. and is safely accessible to third parties (i.e. safety authorities, fire brigades, etc.)
- Develop a “dashboard concept” for the platform that enables model predictions of event evolution (i.e. concrete waste package evolution and/or deposit) to be assessed alongside real-time sensor measurements
- Develop a reference-database for the platform containing waste-condition information from various stages throughout the waste lifecycle, starting at the acceptance of the (often unconditioned) waste and including the impact of the conditioning (i.e. cementation) and the evolution of the waste during pre-disposal storage
- Implement improved data processing (e. g. denoising by use of Convolutional Neural Networks), combination (data fusion based on Dempster-Shafer-theory), and interpretation/parameter translation (general machine learning) approaches
- Develop advanced signal processing methods that emulate certain processes observed within the numerical models in to save computational time
- Use data learning strategies and methods to digitize and automate selected operations necessary for creating and maintaining a digital twin of a radiological waste store

- Implement advanced information and communication technology (ICT) for data mining and predictive forensics (e.g. vision systems and neural networks)
- Design a decision framework that utilizes Statistical Decision Theory to combine available data, computed results, predictions from the digital twin, and expert knowledge and to convert this information into recommendations and semi-automated decisions for the End User
- Implement a prototype decision support platform for integrating data from monitoring with the scheduling of preventive maintenance actions in order to optimize maintenance strategies and assessment of safety and condition
- Develop strategies for optimization of the package arrays with regard to store requirements using the digital decision framework.

9 Conclusions

The first objective of the PREDIS-WP7 project is the issue of the present document which reports the State of The Art (SoTA) in current methods and procedures used for *cemented waste management* with specific focus on *monitoring during preparation, handling and long-term storage*.

The conditioning processes by cement grouting currently adopted by many organizations have been explored and categorized in two main classes: ‘homogeneous conditioning’ for liquid/fluid waste and ‘heterogeneous conditioning’ for solid waste.

A thorough analysis has been performed which considered the normal and abnormal thermo-mechanical-hydro-chemical processes occurring within the waste package possibly leading to degradation phenomena during extended storage conditions. These processes include hydration, degradation of organic materials, carbonation, Alkali Aggregate Reactions (AAR), sulfate attack, corrosion of metals. The possible interactions of the external environment with the waste package have been described together with the relevant geo-chemical and geo-mechanical modelling for estimating the chemical impact on the evolution of stiffness, strength and crack initiation and propagation, which may additionally impact fluid and chemical transport processes.

How can the storage system impact on the waste package degradation scenarios? This question has been the driver for the following detailed analysis performed in the SoTA on the current storage configurations and monitoring strategies. The storage system may negatively impact on the waste package behaviour impairing their required isolation from the external environment and preventing the correct monitoring actions during the storage period.

The core of the document is the overview of current cemented waste package storage management approaches, carried out through the administration of a specific questionnaire submitted to registered End Users in the PREDIS project. The results of the survey, from eleven respondents, represent a very first picture of the main aspects related to the storage of cemented waste packages, degradation phenomena and monitoring systems currently employed. The data highlight that the conditioning process by cementation of both liquid/fluid and solid waste is largely employed for a great variety of waste streams. Waste streams often conditioned using cement include sludges, fine particulates, rubbles and metals, with a high percentage classified as ILW meaning that such waste may need long-term storage while waiting for the availability of a geological disposal facility.

Many different containers are widely used for storing waste conditioned by cement grouting, with preference for metallic drums for liquid/fluid waste and prismatic concrete containers for solid waste. Most waste package typologies are certified for transport and almost all are stackable, in some cases up to 8 levels, while more than 70% are mechanical stress resistant. Regarding the handling approach, the majority of the organizations use remotely operated and semi-automated systems.

Waste packages are often identified by single labelling and mostly stored in ventilated and controlled areas. For VLLW, LLW and ILW, the survey on current monitoring strategies revealed that no End Users employ an approach based on sampling or instrumented waste packages. The majority employ visual monitoring (either in person or using TV cameras) on a periodic basis to identify metal corrosion, cracks and external contamination, swelling, leakage, lifting feature deformation, and external dose. Almost half of the respondents collect information about gas emission from packages checking in real-time the whole storage area. It is interesting to note that 4 respondents out of 11 monitor by means of RTR the internal condition of wasteforms and package by means of X-ray imaging. Just a quarter of the respondents use destructive testing of samples for monitoring purposes.

Data collection is mainly manual with about half of the respondents using semi-automated collection systems and only a minor percentage perform real-time monitoring. Data transmission and archiving on the contrary is implemented often by means of digital systems with the following phase of data analysis performed by the majority with Expert System applications.

Most of the respondents have observed degradation phenomena in the past such as internal and external corrosion, damages linked to the handling of the package, Alkali–Silica Reaction, leakages, swelling and are therefore putting in place options for preventive or remedial actions to be taken in connection with the extended storage of the waste packages.

Innovation technologies applied in *cemented waste package monitoring* during short or long-term storage will have significant impact for all waste producers in terms of improved storage operations, including cost and safety. The following main innovative techniques will be explored by PREDIS WP7: RFID sensors and Fiber Optic Sensing Systems for continuous monitoring of many parameters of waste packages, Muon Imaging, and a Digital Twin process based on machine-learning algorithms and neural networks which will be trained with data produced by numerical tools for geochemical and mechanical integrity modelling.

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Appendix 1 – Questionnaire format