LONG-TERM INTERIM STORAGE IN GERMANY SAFETY REQUIREMENTS FOR WASTE PACKAGES WITH LOW AND INTERMEDIATE WASTE AND THEIR CONVERSION RELATED TO PRACTICE

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ABSTRACT

In Germany the supervision of the storage of radioactive waste is subject to state and federal authorities and is regulated by laws and guidelines for the protection of human health and environment. The storage of low and intermediate waste is based on the waste acceptance requirements for the Konrad repository (a former iron ore mine) as well as for existing interim storage facilities. The implementation of posed safety requirements for waste packages is supervised on behalf of the relevant authorities by independent associations of technical experts. On the basis of examples specific waste product and container characteristics are given from a regulatory viewpoint, which are necessary to meet safety requirements for waste packages with low and intermediate wastes taking into account long-term interim storage and the state of the art for conditioning and disposing radioactive wastes.

INTRODUCTION

In Germany special requirements for waste packages - waste products and waste containers - are needed due to the current legal situation for disposing low and intermediate waste. At present the types of radioactive waste, solid wastes (mixed wastes, scrap irons, building debris, core scrap iron, resins), liquid wastes (sludge, evaporation concentrates, waste water), arising from nuclear power stations have to be stored after their conditioning in interim storages, since in Germany no repository is in operation. Among others, the interim storages Gorleben, Würgassen, Unterweser and Greifswald are available for storage, whereby their supervision takes place via the state authorities. The beginning operation of a repository, which is subject to the supervision of federal authorities (the Federal Office for Radiation Protection), is not exactly foreseeable at the moment. The final court decision concerning the Konrad repository for the final dispose of low and intermediate radioactive wastes is yet not given. Therefore from today's view a long-term interim storage has to be taken into account for already produced and in the future arising waste packages.

While examining the requirements for waste packages special attention must be given to the effects of long-term interim storage.

SAFETY REQUIREMENTS

Radioactive wastes have to be conditioned with the objective of ensuring a safe inclusion of the radioactive substances. This can be achieved through integrating the waste into a waste matrix, inclosing the waste in waste containers or if necessary taking credit from further barriers (building, ventilation systems with hold up mechanisms). The safe inclusion can be achieved technically depending upon the selected concept by one or by a combination of several barriers.

Due to the temporary storage, which cannot be avoided in Germany at present, radioactive wastes have to meet the requirements of the existing interim storages before disposal. The temporary storage facilities in Germany are appropriate only for the handling and storage of enclosed radioactive substances. Therefore the waste containers have to secure the activity retention for the entire storage time and thus ensuring a safe interim storage.

The waste containers should be constructed in a way that monitoring measures can be kept as small as possible for securing safety objectives during interim storage, such as minimizing the radiation exposure for the employed personnel handling the waste packages. Therefore the waste packages should be maintenance-free. Taking this into account requirements for waste products and waste containers result, which are partially more restrictive than the requirements demanded for final disposal.

The requirements for waste products and/or their chemical/physical form of the waste matrix result in particular from their behavior during specified normal operation of interim storage facilities and repositories as well as during assumed incidents. For final disposal the following safety relevant characteristics have to be regarded:

- total activity of the waste package,
- activity of relevant single nuclides,
- dose rate at the waste package surface as well as in a distance of 1 and/or 2 m,
- surface contamination of the waste package,
- chemical composition of the raw waste,
- quality of the fixing material,
- quality of the waste container,
- quantitative proportion: waste/fixing material/water/aggregates,
- mixing (consistency),
- mass,
- tying condition of the waste matrix,
- water content and/or residual moisture,

- thermal behavior and
- stackableness.

In principle these characteristics have to be considered for long-term interim storage also. Beyond that however intermediate and final waste products have to be produced using suitable conditioning processes so that requirements for the safe handling, storage and transport are fulfilled during the period of long-term interim storage also. Thus additional characteristics have to be regarded apart from the above-mentioned relevant characteristics for waste disposal. Possible changes of the waste package characteristics have to be observed, caused by reactions between waste product and waste container and/or within the waste product for the period of interim storage.

In the following sections it is shown through examples which specific waste package characteristics and measures are necessary to fulfill the requirements of long-term interim storage. Requirements for conditioning processes for radioactive wastes as well as criteria for evaluating waste package characteristics are presented.

CONTAINERS

Due to the long-term interim storage of waste packages the long-term stability of container materials have to be regarded for the duration of the storage securing the posed requirements. Therefore the physical and chemical characteristics of the waste products as well as the atmospheric conditions of the temporary storage facilities have to be considered also. Possible impairments of the container integrity are to be expected by effects arising from the container inside and from the outside.

In the following, relevant processes occurring inside the container are discussed.

On the basis of packed mixed wastes in polymer coated containers of carbon steel the requirements for the container materials are illustrated using investigations for describing the corrosion behavior of container materials considering physical and chemical characteristics of mixed wastes done by the University of Berlin, Department of Radiochemistry [1].

In Germany low active and intermediate wastes - mostly mixed wastes - are filled up into coated carbon steel containers after conditioning procedures and/or the waste is directly conditioned in the aforementioned containers. Beside drums with a volume of 200 and 400 liters increasingly containers in units of cubic meter are used. These containers are manufactured from carbon steel species (e.g. material number 1.0330) followed by a surface coating.

This type of container is used in particular for the following types of wastes:

- gate valves   austenitic steels
- apparatus pieces   ferrous steels

• engine pieces	ferrous steels (galvanized, lacquered)
• vessels	copper, zinc
• plumbing	aluminum, Al-Mg-alloy, plastics
• ventilation ducts	austenitic steels
• work on scaffolding	ferrous steels (galvanized, lacquered)
• cantilevers	aluminum
• coverings	plastics
• electric installations	copper, brass, aluminum, plastics
• filters	glass fiber, mineral wool
• isolation material	cellulose, plastics, wood, aluminum
• ashes	silicates, phosphates, sulfates, oxides, fluorides, carbon (carbon black, unburnt organic substances), metals (aluminum, iron)
• pulps, plastic films,	cellulose dry or moistened with: clothes from water, acids, oils, fats, hydraulic fluids, solvents, decontamination cleaning substances works plastics, cotton wool
• packaging materials	oxides, silicates, carbonates, cellulose (wood, paper, construction waste, cardboards)

To implement requirements for long-term interim storage the problem of determining the lifetime of such waste packages has to be considered. Possible remainder substances inside the waste affect the lifetime of waste packages. These substances can lead to a substantially increased corrosion of the waste container. As seen above the spectrum of residual substances is extensive and non-specific, since the most diverse wastes have to be disposed. Among other things corrosion-promoting acid residues and halides as well as organic solvent remainders and oils must be counted on strongly.

For the evaluation of corrosion processes therefore different residual categories of substances as well as waste compositions (e.g. regarding electro-chemical element formation) have to be considered.

The cartouches of compacted waste are manufactured from uncoated material. Therefore crevice corrosion and stress corrosion cracking have to be regarded additionally.

Furthermore damages of the inner surface of the container coating have to be assumed, which can occur for example while loading the container. Mechanical processes (scratches, flaking of corroded material) and chemical reactions (swelling and/or dissolving of the surface coating by organic materials) can cause further damages.

In addition the stability of plastic coatings as well as corrosion processes at welding seams have to be considered.

Testing the Behavior of Corrosion of Carbon Steel in Contact With Mixed Wastes

According to the described investigations in the literature coated and uncoated carbon steel was examined for specifying requirements for waste packages as well as waste containers regarding its suitability for waste packages for low and intermediate radioactive wastes [1].

For the modeling of different waste systems "model electrolytes" were used. The different model systems were composed of individual components of possible radioactive waste, which essentially consist of metal parts, plastics, cellulose and ashes. For coating the carbon steel a polymer film was used, which had the structure of a three-layer epoxy resin coating with a dry coating thickness of 150 µm.

The investigations showed that uncoated carbon steel is unsuitable for the use of waste containers because of its corrosion-susceptibility. Surface erosion rates of almost 10 $mm \cdot a^{-1}$ can occur. In crevices and cracks of uncoated carbon steel corrosion processes with even higher corrosion rates were found. In sour or salty liquids crevice corrosion of uncoated carbon steel can lead to rates twice as high compared to the surface erosion rates of uncoated carbon steel in contact with sour liquids. The integral rates of corrosion for welding seams are in the same order of magnitude compared to the one found for the surface erosion processes. However, the range of the heat influence zones of the welding seams proved to be very sensitive to corrosion processes.

Using coated carbon steel the corrosion resistance improves substantially. The examined corrosion rates ($< 0.1\ \mu m \cdot a^{-1}$) show, that coated carbon steel is in principle suitable as packing material for compacted mixed wastes for long-term storage. However, if the coating is damaged, within the range of the damage corrosion is increasing, which can lead to fast processes of rusting all the way through the container wall. Carbon steel appears completely unsuitable in the presence of sour solutions, even if a coating is present. Herewith corrosion rates of almost 1 $mm \cdot a^{-1}$ can occur.

Examining crevice corrosion, stress corrosion cracking and corrosion of welding seams showed as well that attention has to be focused carefully on the constructional container implementations for a long-term stability. In particular unprotected crevices have to be avoided by sealing these areas with appropriate materials.

Due to the results for corrosion processes at damaged surface coatings of the aforementioned containers highest care is necessary to avoid damages inside the container and at the external walls of the container while handling them.

Requirements for the Conditioning of Mixed Wastes to Avoid Corrosion of Carbon Steel Containers

With respect to the various compositions of the mixed waste sour liquids or strongly salty solutions cannot be excluded as part of the raw waste. On the basis of past experiences the elimination of liquid to a reasonable amount represents a technically important practice for minimizing and/or preventing processes of corrosion. Conditioning procedures with special requirements for mixed wastes became generally accepted. In these procedures a substantial step of treatment was introduced. After compacting the mixed waste with a super compactor for those pellets, which show after compaction a release of liquid, an additional drying step was added.

In Germany the drying procedures used normally for mixed wastes are based on the principle of drying the waste products via a vacuum, e.g. using the so-called PETRA plant of the Gesellschaft für Nuklear-Service mbH (GNS). For this treatment the waste products are placed into drums. After closing the drums by means of a special cover adjustment the drums are placed into the drying oven of the plant. The drums are connected with the vacuum equipment of the drying unit using flexible lines. To support the drying process the drying oven can be heated up to 150 °C. Air removed over the vacuum unit is cooled down and the humidity, removed from the waste product, is separated in a condenser. During the drying process all relevant data such as the temperature of the drying oven, the system pressure of the vacuum unit as well as the resulting volume of condensate are recorded. The drying process is considered to be terminated successfully, if at an oven temperature above 100 °C and a system pressure smaller than 5 kPa in the thermal equilibrium per drum less than 100 ml condensate per hour of operation result. Other systems, drying without a vacuum unit, are also used in Germany.

Requirements for the Conditioning of Evaporation Concentrates from Pressurized Water Reactors to Avoid Corrosion of Waste Containers

Evaporation concentrates from pressurized water reactors consist of an aqueous solution of different salts with a small portion of insoluble solids. The main parts of the soluble salts are boric compounds, which originate from borating the primary water circuit. The collected liquid waste of pressurized water reactors is neutralized with sodium hydroxide before or during the evaporation process in the power station. Thus the compounds of boric acid in evaporation concentrates are essentially a mixture of boric acid, lithium and sodium borates. Other components of evaporation compounds are e.g. suspended matters from the laundry, particles of corrosion products, surfactants, products from decontamination processes and inorganic salts.

Evaporation concentrates can be conditioned via a process, where these liquid wastes are dehydrated for example with the FAVORIT plant of the GNS. The liquid wastes are brought into a drum, heated from the outside and concentrated using a vacuum. Additional evaporation concentrates replace the evaporated water, until the drum is filled with the dried waste product. For the completion of the drying process the yield of condensate is measured; the process of drying is finished, as soon as less than 1000 ml condensate per hour and container are caught while the pressure in the drum is less than 50 hPa and the temperature of the container wall is at least 100 °C.

After the drying process a solid sample is taken out of each charge of the FAVORITE plant for investigations. According to the requirements for final disposal the conditioned waste product has to show a melting point > 70 °C and it has to be inspected regarding an occurrence of free liquid. Isolated cases in the past have shown, that oil or not definable organic liquid phases were discovered. Using additional conditioning steps (addition of oil binding compounds and/or further drying) these liquids can be eliminated. Further examinations have to be done to show, that the conditioned waste packages can fulfill the requirements for long-term interim storage. Therefore samples have to be examined with respect to their residual moisture.

A collection of determined water contents in FAVORIT products of conditioned wastes of pressurized water reactors is shown in the following table.

Table I Residual Moisture of Evaporation Concentrates and Mixtures of Evaporation Concentrates and Resins from Different Conditioning Campaigns.

Project-Number	Date of Report	Water Content [Wt%]	Waste Products
494	12.07.1999	4.2	Evaporation Concentrates
495	04.05.1999	3.3	Evaporation Concentrates
495	04.05.1999	5.7	Evaporation Concentrates
495	21.07.1999	2.5	Evaporation Concentrates
495	21.07.1999	3.5	Evaporation Concentrates
494	08.02.2000	3.5	Evaporation Concentrates
494	18.10.2000	1.9	Evaporation Concentrates
582	30.10.2000	4.5	Evaporation Concentrates
491	10.03.2000	21	Evaporation Concentrates / Resins
491	22.03.2000	22	Evaporation Concentrates / Resins
491	10.04.2000	4.8	Evaporation Concentrates
491	10.04.2000	8	Evaporation Concentrates / Resins
491	10.04.2000	2.9	Evaporation Concentrates

Table II Water Contents and Melting Points of Selected Boric Compounds [2].

Compound	Water Content [Wt%]	Melting Point [°C]	Remarks
B_2O_3	0	577	
$B_2O_3 \cdot H_2O$	43.7		Decomposition in B_2O_3 and H_2O
H_3BO_3	43.7	185	Decomposition in B_2O_3 and H_2O (Intermediate Stage HBO_2)
$Na_2B_4O_7$	0	741	
$Na_2B_4O_7 \cdot 5H_2O$	30.9		
$Na_2B_4O_7 \cdot 10H_2O$	47.2	75	Melting in Crystal Water

The FAVORIT products show a content of residual moisture, which is relatively low in comparison to the data of boric compounds (cf. table II). It is to be assumed that other borates, e.g. lithium borates do not have substantially different characteristics. Thus the drying criteria guarantee a sufficient elimination of free water and crystal water. On the basis of the specified data the occurrence of unbound aqueous moisture, which can cause corrosion processes as an electrolyte, has not to be assumed. Therefore the substantial requirement, the avoidance of corrosion processes of the waste container, is fulfilled.

WASTE PRODUCTS

Waste products have to be sufficiently stable regarding their chemical and physical characteristics with respect to long-term interim storage. Changes of the waste characteristics are to be minimized, since such procedures lead to a change of the gas composition of the container atmosphere frequently. In addition these processes can produce a pressure build-up in the container and it is possible that explosive gas mixtures are formed. In both cases the barrier function of the waste container can be impaired. Furthermore the production of chemically/physically stable waste products have to be demanded, in order to ensure handling of the waste product/waste packages at a justifiable expenditure after a longer lasting storage. Such later handling can become necessary due to a change of waste container types planned for disposal, the use of containers with less shielding due to the decay of radionuclides or because of segregating and exempting wastes.

Study of Gas Formation Processes in Waste Packages

In the years between 1985 and 1990 in a large quantity of waste packages with low radioactive waste a pressure build-up was observed in Germany. Due to the relatively low inventory of activity in these waste packages the formation of gas could not be explained by radiolysis. Gas formation was found mainly in waste packages with uncompressed and compressed mixed wastes, incineration residues and cemented metals in 200-liter drums. To explain the formation of gas the pressure and the portions of N_2, CO_2 and H_2 in the inner atmosphere were analyzed in a large number of waste containers. Table III exemplifies some results of the analysis [3].

Table III Components of Gas in Waste Packages with an Overpressure.

Waste Package	Closure Time	Pressure Absolute	Volume of Gas	Gas Components		
				H_2	O_2	N_2
	[days]	[bar]	[liter]	[%]	[%]	[%]
KKW 002	1569	2.90	88	72	0.4	23
KKW 003	929	2.80	70	58	2.5	36
KKW 005	1416	3.55	83	74	0.6	21
KKW 006	495	1.10	~ 75	22	1.1	73

The measured pressures in the sampled waste packages varied over a range from 200 hPa negative pressures and in individual cases up to a positive pressure of approximately 0.5 MPa.

Experiments showed that a pressure build-up up to pressures in the range of 0.5 to 0.6 MPa is possible without influencing the stability of the 200-liter drum. With higher internal pressures the drum seal fails.
The pressure build-up was basically caused by the formation of hydrogen and as shown by further studies to a minor degree by carbon dioxide and methane. Furthermore a decreasing concentration of oxygen was noticed in the waste packages.

The time dependent alteration of the composition of the interior atmosphere of the container showed, that after closing the container gas tight the pressure in the container decreased relatively fast. According to further examinations the initially observed decrease of pressure is caused by the reaction of enclosed oxygen with the waste components [3, 4]. After the development of oxygen-poor ranges inside the waste product the anaerobic reaction of metals with aqueous moisture began under formation of hydrogen. A pressure build-up in waste packages could be observed already after 14 days.

An alteration of organic materials was investigated predominantly in waste packages with uncompressed mixed wastes. At the beginning of the decomposition of organic materials a formation of carbon dioxide was observed, while oxygen dissipated. Therefore this process led to no pressure change in the waste package. After the consumption of oxygen in many cases a further decomposition of organic materials was determined. During this following micro-biological process methane was formed. This process can lead to a small pressure build-up in the waste package.

The investigations revealed different processes for the formation of gas. In summary the main processes are:

- chemical reaction between water and metal components of the waste product,
- decomposition of organic compounds caused by micro-biological activities,
- reaction of amphoteric metals with alkaline water in concrete,
- reaction of water with metal carbides of incineration residues.

Requirements for the Conditioning of Radioactive Wastes

As described above, on the bases of different processes gases are formed in radioactive waste products. In most of the cases the presence of water causes an increasing formation of gas. Therefore, it is the objective to remove water as completely as possible while processing radioactive wastes. During the compaction of mixed wastes this can be achieved as mentioned before by means of segregating and vacuum drying those pellets, which showed a release of liquid after compression. With respect to the conditioning techniques used today the conditioning parameters already specified are minimum requirements to be satisfied.

Requirements for Waste Packages Due to the Demand of Chemically and Physically Stable Waste Products

To ensure a safe inclusion of radioactive wastes the following requirements are necessary according to the claim of chemically and physically stable waste products:

- To ensure the integrity of the container a pressure build-up in the waste container has to be avoided.

- A sufficient stability of the waste product has to be ensured.

- The formation of explosive gas mixtures has to be avoided in the waste container and/or in the overpack.

We will exemplify from our view - as a consultant for the regulatory body – on the basis of which criteria the compliance with the formulated requirements can be proven.

The limitation of the pressure build-up in the container results from the design of the container and can be taken from the documents of the licensing procedures.

For the evaluation of the stability of the waste product the information on the production of gas inside the waste container can be used. The formation of gas is an indication for a lack of stability of the waste products. It has to be limited to a quantity that is harmless with respect to safety using processes of engineering.

For specifying an assessment criterion for the stability of mixed waste a permissible gasification rate has to be defined, so that with the help of this value an evaluation of the stability of the waste product is possible. The formation of gas was examined in approximately 500 waste packages conditioned with today's technologies with mixed wastes, incineration residues and cemented metals. The following figure

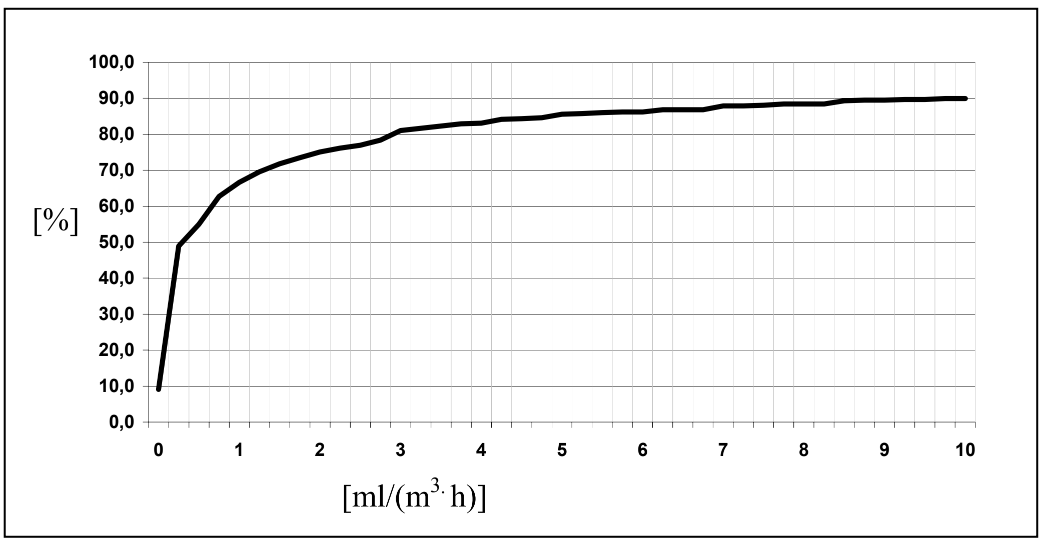

Fig. 1 Fraction of Waste Packages in Dependency of their Gasification Rate Regarding Approximately 500 Drums with Mixed Wastes.

shows, that about 90 % of all waste packages exhibited a gasification rate under 10 ml/(m^3 h) (H_2 and CH_4). In approximately 66 % of the waste packages gasification rates of less than 1 ml/(m^3 h) were found. 75 % of all waste packages exhibited gasification rates below 2 ml/(m^3 h). Further evaluations showed, that for gasification rates up to 2 ml/(m^3 h) chemical and physical changes of the waste product can be neglected during long-term storage. Therefore a gasification rate of 2 ml/(m^3 h) kept by 75 % of the waste packages can be regarded as an acceptable target for conditioning methods according to the present state of the art.

Exceeding this value significantly demonstrates, that the produced waste products were not optimally conditioned. For this case the conditioning method should be changed in a way that increased requirements for the conditioning method have to be adopted or further treatment steps have to be introduced. Among other things this can be done by means of an assortment and/or a preliminary drying of the raw wastes, improved controls and more extensive subsequent treatments of the compacted waste.

Explosive gas mixtures can develop in waste packages by the formation of hydrogen and - to a subordinated extent - of methane while atmospheric oxygen is present. The lower ignition limit of a mixture of hydrogen with air amounts to 4 volume percent of hydrogen. On the basis of this value in areas of nuclear installations 2 volume percent of hydrogen was derived as a limiting value for the maximally permissible hydrogen concentration. If one takes this value as the base criterion for the formation of explosive mixtures in waste packages, this value has to be kept for the entire time of temporary storage for the case, that the formation of a mixture with oxygen is subordinated. The formation of explosive mixtures can occur through reactions of incineration residues with moisture or through reactions of amphoteric metals with alkaline moisture (pore moisture in cemented wastes). If the adherence to the limiting value specified above cannot be proven for example by measurements of the gasification rate, free cavities in the waste package have to be filled by adding inert material, for example quartz sand. The same measures have to be taken for airtight overpacks.

CONCLUSIONS

Due to long-term storage additional requirements for waste packages, radioactive wastes and waste containers, have to be fulfilled. During long-term storage the safe inclusion of radioactive substances in the waste container has to be ensured. Additionally it is necessary that the waste product conditions enable the handling of the waste products directly before the final disposal. Therefore impending changes of known waste characteristics caused by reactions within the waste product and/or between the waste product and the waste container have to be avoided. Accepted conditioning methods have to be used to produce chemically and physically stable waste products.

To guarantee a safe long-term temporary storage the following general requirements have to be fulfilled.

- Container materials have to be selected in such a way that due to the chemical characteristics of the container materials and of the waste product corrosion processes can be neglected.
- The design of the container has to be selected in such a way, that crevice corrosion and stress corrosion as well as corrosion processes at welding seams can be avoided.

- Waste containers have to be handled with highest care during their handling and in the case of the transport of the containers, in order to avoid damages. Damages of waste containers can lead to local corrosion processes and therefore to processes of rusting all the way through the container wall.

- Radioactive waste has to be conditioned with the help of approved conditioning methods with defined conditioning parameters, so that due to the waste product characteristics corrosion processes of the container can be avoided.

- A pressure build-up in the container has to be limited maintaining the container stability via the conditioning of stable waste products.

- The waste product has to be sufficiently stable.

- The formation of explosive gas mixtures in waste containers and/or in overpacks has to be avoided.

If the adherence to one or several of the requirements specified above is not possible, additional treatment steps and/or regular controls of the waste containers have to be introduced to guarantee the security of long-term storage for waste packages.

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