SOLIDIFICATION BY CEMENTATION OF LIQUID RADIOACTIVE PRIMARY WASTE MIXES

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ABSTRACT

Up until 1987, the residues arising in the decontamination of aqueous waste were solidified by mixing with cement powder. Those residues were evaporator concentrates with activity concentrations of a few 10^{10} Bq/m^3, which had arisen in the evaporation of aqueous residues from research facilities, test plants, and operating systems. Some 70 - 90 % of the total dry residue of those concentrates was made up of nitrates, which lent themselves well to cementation. In addition, there were evaporator concentrates arising in the treatment of liquid effluents from the reprocessing plant, with activity concentrations of up to a few 10^{13} Bq/m^3. As these consisted mainly of nitric acid neutralized with caustic soda solution, they were mostly made up of sodium nitrate, which could easily be solidified with cement. For reasons of handling and for cost reasons, these concentrates were blended and solidified with cement powder in an in-drum mixing plant. The product had to have set without having produced any freely movable liquids (supernatant water) and the complete packages had to satisfy the criteria for transports of hazardous goods. There were no criteria other than these.

THE KARLSRUHE NUCLEAR RESEARCH CENTER

The Karlsruhe Nuclear Research Center was established in 1956. It has since been active not only in fundamental research, but also in working on specific aspects of research into, and development of, reactors, the nuclear fuel cycle, and waste conditioning. Experimental facilities in these fields are still operated on a technical scale, such as

- the Institute for Hot Chemistry,
- the Hot Cells,
- the Institute for Radiochemistry,
- the Institute for Nuclear Waste Management,
- WAK, the German prototype reprocessing plant,
- KNK, the German prototype sodium cooled fast breeder reactor,
- the European Institute for Transuranium Elements.

The waste management for all these research and experimental facilities is ensured by the Central Decontamination Plants Operating Department, the largest conditioning operation for radioactive wastes in the Federal Republic of Germany.

THE CENTRAL DECONTAMINATION PLANTS OPERATING DEPARTMENT (HDB)

All radioactive residues arising in the Center, which cannot be reused by institutes and departments, are transferred to HDB. All other residues not fit for reuse are converted into a state allowing them to be stored in a repository. For this purpose, there are facilities for scrapping and compaction, combustion and incineration, decontamination of solid and liquid residues, residue solidification, laboratory facilities for analytical control of these processes and for checking the products for final storage, and a documentation system. In this report, only the solidification of residues arising in the decontamination of liquid waste will be described.

PRESENT SITUATION

When the "Preliminary Repository Storage Criteria for the KONRAD Mine", the planned repository in the Federal Republic for non-heat-generating waste, were published this meant more extensive criteria which had to be met by the waste packages to be stored. These criteria are either of a more general nature or result from studies of technical safety in the following areas:

- Normal plant operation,
- design basis accident conditions,
- thermal impact on the host rock,
- criticality safety,
- long-term radiological effects.

All these studies were conducted for the planned repository. In addition, the "Codes on Transports of Dangerous Goods on the Road and by Rail, respectively" must be observed.

As far as the cemented waste produced in our cementation plant is concerned, the following criteria must be met which result from the basic requirements, the additional requirements, and the criteria to be met by the waste package:

- Observation of the nuclide inventory limits.
- The waste forms must be present as solids or in a solidified form.
- The waste forms must not start digesting or fermenting.
- Except for reasonably attainable and unavoidable

residues, the waste forms must not contain

- any freely movable liquids, or release such liquids under the usual conditions of storage and handling,
- self-ignitable or explosible substances.

- Waste forms may contain materials fissible by thermal neutrons only in mass concentrations of up to 50 g/100 l of waste form.
- The immobilizing agent used must have set completely or must be fully solidified.
- Immobilization must have been achieved in such a way that
  - the activity is distributed in the cement stone uniformly and completely,
  - the compressive strength of the waste form is > 10 N/mm^2.
- The waste container must not be damaged by the waste form.
- The waste container should be filled as completely as possible.
- The local dose rate of any waste package at the time of delivery to the KONRAD repository is limited to a mean level on its surface of $2x10^{-3}$ Sv/h and to a local maximum of 10^{-2} Sv/h; at 1 m distance from the surface of cylindrical waste packages, and at 2 m distance in the case of containers, the local dose rate must not exceed 10^{-4} Sv/h.
- The non-firmly adhering surface contamination averaged over an area of 100 cm^2 must not exceed, at any point on the surface of a waste package, the limits of $3.7x10^{-1}$ Bq/cm^2 for alpha-emitters for which a clearance limit of $3.7x10^3$ Bq has been defined, and of 3.7 Bq/cm^2 for other radionuclides.

In addition to these considerably more stringent requirements, part of the liquid residues arising in the treatment of organic waste solutions from reprocessing is to be added to the concentrates and to be solidified jointly with this mix. These are carbonate solutions arising in the carbonate washing stage and tributylphosphate as well as diluted phosphoric acid, all saturated with kerosene. These primary wastes have meanwhile begun to be solidified in a cementation plant because, as a result of a change in the permit, the planned and already built bituminizing facility could not be started up and was dismantled again. The feed tanks and the drum transport system of that facility were retained, and the cementation plant has meanwhile been installed in the filling cell of that facility.

CEMENTATION PLANT FOR LIQUID PRIMARY WASTE

Brief Process Outline

On the basis of the analytical results obtained on the primary waste, product specific data of the primary waste batch to be solidified are defined, namely the amount of cement and the amount of primary waste per 200 l drum. The amount of cement is filled into the 200 l drum, while the amount of primary waste is weighed in a dosage container and then discharged into the drum. Inside the drum the components are mixed homogeneously by means of a planetary mixer and then reference samples are taken. Lids are put on the drums and, depending on the activity inventories they hold, the drums are moved to the interim storage site either unshielded or shielded.

Plant and Process Descriptions

The primary waste to be solidified (evaporator concentrates, residues arising in the treatment of organic waste solutions from reprocessing) are transferred to a feed tank of 4 m^3 useful volume and homogenized in the light of the quantitative ratio determined on the basis of the results of the radiological and chemical analyses. The feed tank is equipped with an agitator able to keep even residues of approx. 200 l in a homogeneous state.

Representative samples are taken from feed tank and analyzed. When the analytical findings have been made available (alpha-, beta-activities, content of fissile materials, dissolved and undissolved dry residues, pH-level), the primary waste contained in the feed tank is cleared for conditioning jointly by the plant manager and the laboratory manager. The amount of cement specific to the respective batch is weighed into the drum and the associated amount of primary waste is set in the balance of the feed tank. When the preset limits have been reached, both balances stop dosing. Now a sample drum is prepared. For this purpose,

- the drum with the cement in it is transported to the filling position on a roller conveyor,
- the drum is docked to the filling cell by means of a double-lid system,
- the dosage vessel is filled,
- the content of the dosage vessel is emptied into the drum step by step and agitated simultaneously,
- the primary waste and the cement are mixed thoroughly for at least six minutes,
- the drum is removed from the docking position.

The drum closed with a double lid and the drum lid is now moved into a holding position. Over a period of at least twelve hours, the reaction temperature is measured and recorded. Then the drum is returned into the filling position and docked to the cell. The plant manager now checks for

- the state of binding,
- freely movable water,
- demixing,
- a normal development of reaction temperature,
- other optically recognizable deviations from the normal case.

The result of the check is recorded.

If there are no deviations from the normal case, the entire batch is solidified with these amounts of cement and primary waste. At least one drum per workday, normally the drum produced last on the previous day, is checked by the plant manager before further processing is started. In addition, three samples are taken of each batch and after each modification of the formulation. One of these samples is subjected to a compressive strength test after at least 28 days. The other two samples are reference samples made available on request to the product control unit of the operator of the repository.

Under off-normal conditions, the causes are determined and the resultant data are employed to prepare another sample drum until the product has all the required properties.

Products which do not meet the full set of criteria are put into higher-grade repository storage containers in line with the "Preliminary Repository Storage Criteria". In this way, it is ensured that the part of the safety assessment of the repository is taken into account which refers to the quality of the final storage package, i.e., the uniformity of product quality and of the final storage container. While the batches are processed further, the amount of cement and the amount of primary waste used for each drum is entered into a computer system. The associated bookkeeping system calculates for each drum the relation between the dry matter of primary waste and cement as well as the total activity inventory and the inventories of relevant single nuclides. These are filed under the respective drum number for retrieval at any time.

Process Monitoring

All process parameters relevant in observing the "Preliminary Repository Storage Criteria" are monitored by means of instruments. In case of deviations from the preset limits, plant operation is interrupted. The following items are monitored:

- Agitators of the feed tanks,
- amount of primary waste,
- depth of immersion of the mixing tools,
- speed of the mixing tools,
- planetary movement of the mixing tools.

For safety reasons, the following items are kept under surveillance:

- Temperature of primary waste in the feed tanks,
- docking of the drum to the double-lid transfer lock,
- position of the radiation protection lifting gates of the drum transfer lock
- below the filling cell.

Also these measurement stations act on interlocking systems, which interrupt plant operation.

In addition, there are other instruments required for process operation, such as the control of the roller conveyor, temperature measurement points, dose rate measurement points, etc. In addition, the entire process is monitored optically. In this way, also irregularities which do not act on the interlocking systems can be recognized quickly and the proper reactions can be taken. Moreover, a dose rate measuring station is used to check, by random sampling, activity distributions over the drums and within a drum, and the full drum is weighed in order to determine the amounts of individual components it contains. Any changes in formulation or inhomogeneities, which cannot be recognized by means of the general instruments, will be found out quickly in this way.

Product-related Operational Defects

These include the following cases:

- Power failure:

If the normal power grid fails, all systems required to continue the ongoing mixing step will be supplied electricity from a standby power grid after a maximum of two minutes.

- Failure of the lifting mechanism of the mixing tool:

The mixing tool is equipped with an emergency lifting device.

- Failure of the automation equipment:

In case of failure of the automation equipment, manual intervention is possible. However, in that case some of the interlocks will not function.

- Failure of the primary waste dosage system:

If the primary waste dosage system fails, the missing quantity can be fed as water through a separate dosage line; in this way, the water/cement ratio necessary to attain the minimum compressive strength can be maintained.

In all these defects it is ensured by means of auxiliary systems that a conditioning step already begun can be concluded in line with product specifications. The conditioning step must be halted in case of other defects, such as

- failure of the mixing tool drive and
- damage to the mixing tool.

In that case it will be seen whether the product can be assigned to another group, in the light of its activity inventory, or whether a higher-grade package needs to be chosen in order to offset the reduction in quality.

Documentation

A documentation is compiled of the finished products, from which the origin, the composition, and the treatment of the primary waste can be seen from the source through intermediate treatment up to conditioning for repository storage. This documentation is composed of the data compiled by the deliverer of the primary waste, the conditioner, the laboratory monitoring conditioning, and the data supplied by the manufacturer of the cement as well as those provided by the manufacturers of the inner liner and the repository storage container, respectively. The data of the primary waste supplied are taken from the accompanying delivery documents. They are not used to describe the final waste, but serve only for guidance. Whether the criteria spelled out in the "Preliminary Repository Storage Criteria" are actually met is checked on the basis of the data determined by the laboratory from samples of the primary waste to be solidified. These data are interconnected with other product-related data on the materials, preliminary treatment, conditioning, and packaging; this is achieved in the KADABRA bookkeeping system, and the data are then filed away in a database. This database is able to provide information on any question specific to a product.

PROCEDURE ADOPTED IN DEFINING THE BATCH COMPONENTS, THE PRIMARY WASTE/CEMENT RATIO, AND THE AMOUNT OF CEMENT

Determining the Conditioning Criteria

As mentioned above, the product to be stored in a repository must meet a number of criteria. No difficulties arise from the observation of nuclide inventories and the dose rate on the outside of the package. The analytical results available on each individual component to be added to the mixture are used to determine, by means of the bookkeeping system, the maximum possible amount of each component per package still meeting the criteria. As we know from non-radioactive tests prior to hot commissioning, also ensuring homogeneity poses no difficulties. Also the observation of compressive strength levels has not been difficult so far. Minimizing the residual void volume has not so far been attempted, as this is problematic and, in addition, has not yet been requested. The cost advantage arising from minimization of the residual void volume were given up in favor of smooth operation. There was hardly any experience on this point and in additing primary waste from other facilities. Merely the addition of tributylphosphate had been tested on a laboratory scale in order to determine the maximum amount that could be added without giving rise to bleeding. It was also known that the water/cement ratio should be at least 0.4, so as to ensure complete hydration, and should not exceed 0.64 in order to minimize the capillary water fraction. As the low-level aqueous primary wastes to be evaporated may vary in chemical composition, also the concentrates produced from them may contain larger or smaller quantities of substances delaying, accelerating or even preventing hydration. This applies also to the other primary wastes. For this reason, the hydration characteristics of primary waste mixes can be predicted approximately only by full- scope chemical analyses. Cementation tests carried out on a laboratory scale cannot actually be extrapolated to technical-scale conditions in each case, but at best reflect a trend.

As full-scope chemical analyses are very expensive and not really feasible for reasons of time, we tried to solve the problem by means of similarity assessments based on the evaluation of similar primary wastes processed earlier or mixtures of such wastes.

The following existing data and findings, respectively, were used as a basis:

- A water/cement ratio of 0.45 is to be achieved. At this water/cement ratio, a compressive strength of 10 N/mm^2 is normally ensured, and there is still a sufficient margin for change without underrunning compressive strength.
- LLW and ILW concentrates arise in a 3:1 to 4:1 ratio. For cost reasons (ordinary concrete shields instead of high-density concrete shields, or high-density concrete shields instead of nodular cast iron shields, respectively) and also because of limitations of the nuclide inventory per package in the Preliminary Repository Storage Criteria, this is the mixing ratio which should also be employed for solidification.
- Tributylphosphate and mixtures of tributylphosphate-phosphoric acid (adduct), respectively, with a

small fraction of kerosene must not exceed 5 % of the mixes.

As time went on, the following additional findings were made:

- A sodium carbonate solution from the soda washing step improves hydration behavior.
- Concentrated phosphoric acid from adduct formation causes the hydration behavior to deteriorate.
- At pH-levels > 11, the hydration behavior is affected negatively.
- Determining only the total dry residue is not sufficient, as the dry residue affects not only the cementing capability but also the degree of drum filling, depending on the type and fraction of dissolved and undissolved components. In the case of sodium chloride and sodium nitrate, e.g., all the water is available for hydration. The salts behave in a way which does not affect the volume, whereas sodium phosphate and sodiumsulfate crystallize out and thus add to the volume.
- The sludge content must be determined because it may bind up to 50 % of the water content, depending on age, thus making this water unavailable for hydration.

A pragmatic approach was used to achieve predictions of cementability, on the basis of compressive strength and drum filling level criteria, which could be managed in practice. For the most frequent primary wastes occurring in our case we determined evaluation factors based on our accumulated operating experience. These factors indicate the relationship between the cementability of the corresponding primary waste and the cementability of a primary waste easily processed after solidification with a water/cement ratio of 0.45 and attaining a compressive strength of 10 N/mm^2 without any supernatant water and without any unusual heat evolution. Solidification of mixes prepared with these factors has shown that they apply only if the composition of primary waste does not change profoundly, and if the mixing ratio of LLW concentrate to ILW concentrate is within the limits of 3:1 to 4:1, and not more than 4 % of adduct is added. This may even cause the influences of certain components to act in the very opposite way. Thus, it has happened that phosphates and carbonate solution, each of which separately improves the binding characteristics, caused the binding characteristics to deteriorate drastically when present simultaneously and in higher concentrations. This fact is taken into account by a correction factor when changes in composition of different types of primary waste or of the mixes are encountered.

As more and more experience was accumulated, various evaluation and correction factors were added, e.g. those for the pH-level, the content of caustic soda solution or the content of boric acid. Meanwhile, also assays for the amounts of lime required as an additive to compensate for various cement poisons, such as borates have worked out quite well.

After we had produced more than 3000 drums of cemented products, it became more and more obvious that the influence exerted on the hydration behavior by fluorides, phosphates, nitrates, borates, and the fractions of dissolved and undissolved dry residues had to be taken into account in mixing the primary waste. We have therefore begun, in the meantime, to consider this factor in defining the mixing ratio of primary waste; in addition to the pH-level and the total dry residue we determine also these components. In processing the last 600 drums it has been found that we are now on the right way. Where formerly we often had to cement five or six sample drums, we now can do with two sample drums as a rule, provided that the individual components or mixes are not extremely different from those processed previously.

We have developed a computer program for simple conversion of the evaluation factors determined empirically. In this way, we are able to react quickly to chemical changes in the composition of our primary wastes and take those changes into account by entering different evaluation factors.

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