CEMENTATION OF RADIOACTIVE WASTES IN THE FEDERAL REPUBLIC OF GERMANY

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ABSTRACT

The cementation of solid and liquid raw wastes as well as of waste concentrates to produce solid products is a well established technique for many years. Cementation will also be the method for the fixation of cladding hulls, dissolver residues, evaporator low level and intermediate level waste concentrates and solid wastes arising from the planned 350 MTHM/year reprocessing plant. The cementation techniques used are discussed briefly. They include indrum mixers, rotating containers with pebbles or mixing installations and continuously operating cementation mixers. The influence of organic coumpounds in the waste solutions on the hardening process is discussed. Basic data on product properties like mechanical stability, chemical stability (corrosion, leaching) and radiation stability are presented on the basis of laboratory and full scale unit investigations. Main objective of the work is to establish source term formulations as input functions for safety analysis for the radionuclide mobilization via gas phase after mechanical or thermal impacts. In order to evaluate source terms for the mobilization of relevant radionuclides via liquid phase as a function of time due to leaching and corrosion, detailed experimental and theoretical investigations of processes occuring when cemented waste forms are in contact with salt brines were carried out. Recent developments concerning improvements of existing cementation methods and the increasing significance of waste container application along with a newly developed standardized container system are presented. The conclusion can be drawn that the present FRG cementation technology is adequate for the wastes from nuclear power reactor operation and the solid and liquid LL and IL wastes from the reprocessing plant. There is a demand to improve waste products due to economic and safety considerations especially for wastes of higher alpha- activity like dissolver residues or burnable materials. Consequently, the current ROD is concentrated on optimizing grout formulations and conditioning processes.

INTRODUCTION

In the Federal Republic of Germany the waste management concept is based on disposal of all radioactive wastes in repositories in deep geological formations. In the repository the wastes are isolated from the biosphere by a system of multiple engineered and natural barriers.

The raw wastes have to be transferred into an appropriate physical and chemical form to produce waste packages which satisfy the requirements of transport, handling, interim storage and disposal. Waste packages shall have high chemical and mechanical stability and low volumes relating to the primary waste volume.

From the great number of different low level (LL) and intermediate level (IL) waste types this paper focuses on wastes from operation and decommissioning of nuclear power plants and from reprocessing of spent LWR-fuel. These wastes can be roughly grouped into the following categories:

- evaporator concentrates and chemicsl sludges
- ion exchange resins from reactor coolant clean-up and from storage pond clean-up
- solid compactible wastes, e.g., components from ventilation systems, failed equipment, contaminated trash, cladding hulls
- non-compactible and non-combustible wastes, e.g., concrete rubble, failed equipment, contaminated soil.

The amount of wastes to be conditioned can be illustrated by the volume of about 8200 cubic meters of conditioned wastes in the Federal Republic of Germany in 1983. This figure is based on actually used techniques and 11.6 GWe installed nuclear power [1].

STATUS OF CEMENTATION TECHNIQUES AND WASTE FORM PROPERTIES

From 1967 to 1978 all low level wastes and from 1972 to 1977 all intermediate level wastes were disposed of in the abondened salt mine Asse. Consequently, radwaste treatment methods were developed which first of all satisfied the acceptance criteria of the Asse.

Liquid wastes generally were solidified in cement, minor amounts also with bitumen or polymeric materials. Depending on primary waste properties pretreatment steps like evaporation, incineration, compaction or drying were employed.

Cementation of solid and liquid wastes is a well established conditioning method for many years. According to the conceptual design of the 350 mtU reprocessing plant for LWR fuel, cementation will be employed in this plant for solidification of evaporator concentrates, insoluble dissolution residues, cladding hulls and solid wastes. For the great number of different waste types to be solidified different cementation systems have been developed. Basic advantages of waste treatment by cementation are:

- simplicity of the process
- non-inflammability of the matrix
- low process temperatures
- high process and matrix flexibility.

A negative aspect generally is the relatively large waste form volume after cementation especially of liquid wastes.

In the Federal Republic of Germany mainly planetary mixers and tumbling mixers are used for cementation of liquid radwastes from nuclear research facilities and from operation of nuclear reactors.

In the Karlsruhe Nuclear Research Center (KfK) evaporator concentrates and spent ion exchange resins from laboratories and from the pilot reprocessing plant Karlsruhe (WAK) are fed into the drum which is prefilled with cement. In the drum the liquid waste is mixed with cement by a planetary mixer. The waste solids content in the waste form is up to 15 wt%. The throughput is about 2 drums per hour. A representative composition of ILW concentrates from a reprocessing plant with Purex flowsheet for LWR fuel is given in Table I.

TABLE I

ILW-Concentrate From a Purex Reprocessing Plant
(LWR fuel, burn-up 30 GWd/mt H.M., U 235 3.5%, cooling time 5 a.)

specific Beta-Activity $\leq 10^{13}$ Bq/m³
specific Alpha-Activity $\leq 10^{10}$ Bq/m³

main activity carriers:
Cs 137/Ba 137m; Ru 106/Rh 106; Ce 144/Pr 144; Sr 90/Y 90; Sb 125/Te 125; Cs 134

solid content: 25-35 wt% ($\geq$ 90% $NaNO_3$).

(see Ref. 2.)

For the different nuclear power stations the use of mobile conditioning units has been enhanced in the last few years. The mobile cementation facility MOWA (NUKEM) is utilized for treatment of liquid wastes in nuclear power plants and will be described in a separate paper of this session.

A tumbling mixer is used in the mobile plant FAFNIR (Gesllschaft fur Nuklear Service, GNS) for cementation of evaporator concentrates, filter sludges and slurries. PWR evaporator concentrates may also contain borates. Mixing is carried out at reduced pressure in a drum which is rotating around its logitudinal and lateral axis. Blades are welded into the drum mixer prior to filling the drums with cement. In one eight hour shift up to 5 cubic meters of evaporator concentrates can be solidified[3].

Normally cement waste forms contain between 10 wt% and 20% solid residues, the water to cement ratio is in the range between 0.4 and 0.6. Basic waste form properties like:

- mechanical stability
- mechanical and thermal impact behavior
- chemical stability (corrosion leaching)
- radiation stability.

Required for safety analyses were investigated in detail in laboratory and full scale experiments. The objective of these investigations is to deduce source terms for release scenarios via the aqueous pathway and via the atmospheric pathway (release of respirable fines after mechanical or thermal impacts)[4,5].

Typical cemented evaporator concentrate waste form properties are listed in Table II.

TABLE II

Typical Waste Form Properties
(Cemented Evaporator Concentrate Waste Form)

Matrix: Ordinary portland cementstone (OPC)
Main components of concentrate: $NaNO_3$
solid load in the waste form: 5 - 15 wt.%
Water content: 20 - 30 wt.%
Density: 2 g/cm³
Porosity: 25 Vol.%
Air porosity: 2 - 4 Vol.%

Pressure Resistance:	$\sim$ 15 N mm^{-2}
Considerable water release:	T $\geq$ 105°C (p = 1 bar)
Heat conductivity:	0.5 $W \cdot m^{-1} \cdot K^{-1}$

Integral leach rates:
$10^{-3} - 10^{-4}$ $cm \cdot d^{-1}$ for Cs, Sr
(1 Year, T = 25°C)
$10^{-5} - 10^{-7}$ $cm \cdot d^{-1}$ for Co, TRU-Elements

Radiation resistance $\leq 10^{10}$ rad

Radiolysis gas formation: H_2 : 0.3-0.8 ml/kg·10^6 rad
O_2 : 0.1-0.2 ml/kg·10^6 rad

(See Ref. 6)

For the aqueous pathway radionuclide releases from cemented waste forms have been investigated in detail in water and salt brines. The leachability of, e.g., Cs 137-tracer amounts in saturated NaCl brine from a simulated ILW concentrate cement waste form in laboratory scale using the IAEA leach test is shown in Fig. 1.

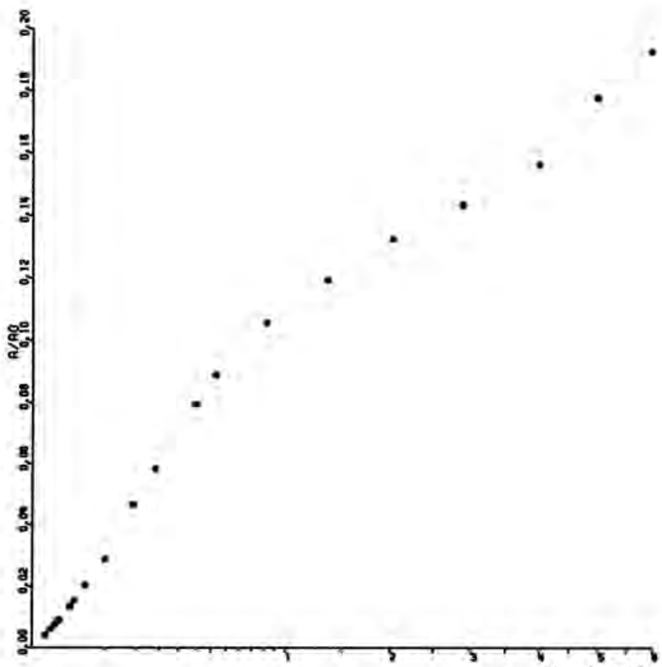

Fig. 1. Cs release from laboratory scale ILW-OPC waste forms in sat. NaCl-solution.

The volume of the leachant is ~ 10 times the sample volume. From this curve a diffusion constant can easily be calculated. In a brine rich in $MgCl_2$ (Q-brine) - which has to be considered for safety analysis as possibly attacking the waste form - the release of Cs cannot be described by a simple diffusion process, as can be seen in Fig. 2. The kinetics in this case are determined by three corrosion processes:

- leaching of soluble compounds
- exchange reactions ($Ca(OH)_2 + MgCl_2 \rightleftharpoons CaCl_2 + Mg(OH)_2$)
- formation of new phases causing swelling.

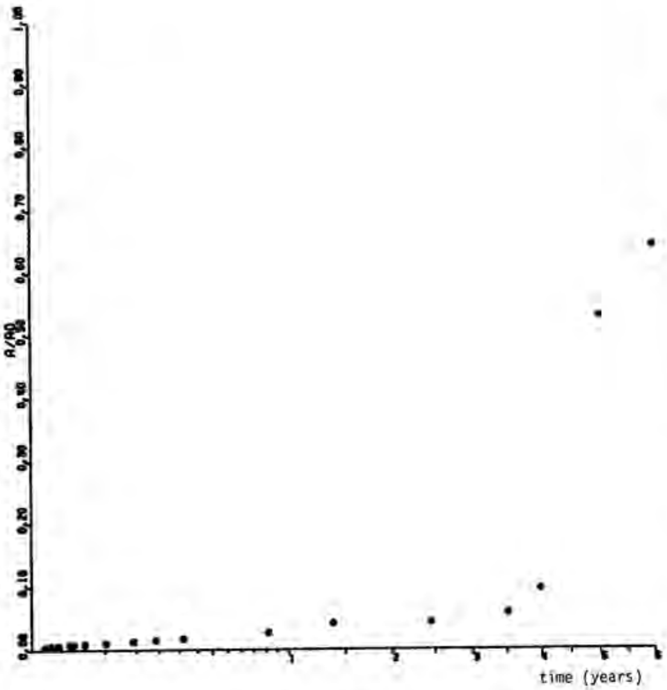

Fig. 2. Cs release from laboratory scale ILW-OPC waste forms in Q-brine. (waste form contains 10% natural bentonite as Additive)

Leach experiments, x-ray analysis of phase composition and determination of element concentration profiles by electron microprobe analysis in the cement stone sample as a function of time and distance from phase boundary were carried out. These data have been integrated into a theoretical model using finite difference techniques to establish an improved basis for longterm predictions[7]. A comparison between measured and calculated element concentration profiles is shown in Fig. 3.

In summary it can be stated that the developed techniques have been employed successfully for conditioning the wastes arising in different facilities. However, the increasing importance of volume reduction factors and the need of conditioning TRU containing wastes such as insoluble dissolution residues and cladding hulls promoted the development of improved techniques and matrix materials.

RECENT DEVELOPMENTS

General Situation

In 1978, the operating licenses for disposal of wastes at the Asse have expired and have not been renewed so far as a result of a changed rule in the 4th amendment of the German Atomic Act, creating a new situation for waste management technology. Since no repository was in operation and will not be in the next few years, all the conditioned radioactive wastes have to be stored in above-ground interim storage facilities.

Minimizing the waste volume therefore got an increasing incentive, creating new waste processing techniques and packaging procedures. In addition, originally the waste form was considered the major barrier against radionuclide release. In the last few years safety analyses were based on radionuclide release from the whole package (waste form plus packaging), supporting in general the significance of the barrier function of containers. At the same time the established and successfully employed techniques have been improved.

Improvement of Existing Methods.

In general the tendency to condition the wastes from nuclear power reactors in mobile units has increased. A continuously mixing unit with a dry premixer, followed by a wet mixer "DUMA" for cementation of LL and IL wastes has been developed by Kraftwerk Union (KWU). The compact design allows an easy replacement of a spent mixer which fits into 200 2/400 1 drums[8].

In the Kernforschungszentrum Karlsruhe a continuously working cementation facility for LL/IL waste concentrates and ion exchangers (throughput 0.25 m^3 concentrate/hour) will go into operation in 1985 in addition to the approved in-drum mixing unit. Figure 4 shows the cementation unit which is installed parallel to the bituminization unit with a common filling station.

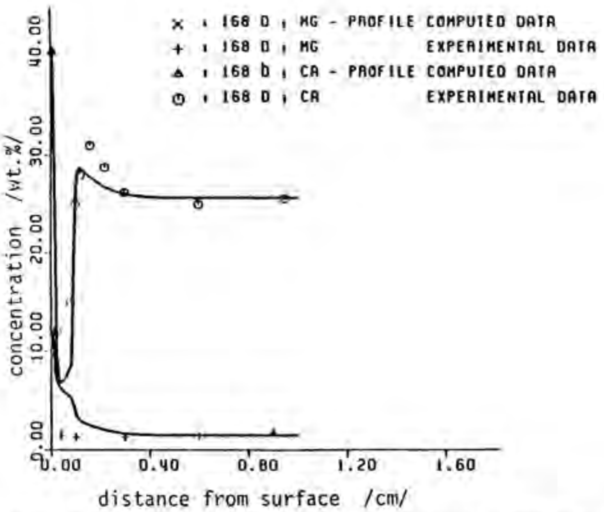

Fig. 3. Comparison between experimental and computed Ca- and Mg-concentration profiles in slag cement corroded in quinary brine.

In addition to the process developments improvements have been made concerning the waste form itself. This includes cement type selection, and optimization of grout mixtures to improve workability, control of setting behavior and long-term stability against ground water or salt brines[9]. Figure 5 shows as an example the influence of phosphates and organic compounds on the setting time of the ILW/cement mixture. This organic compounds may occur especially in decontamination waste solutions[10].

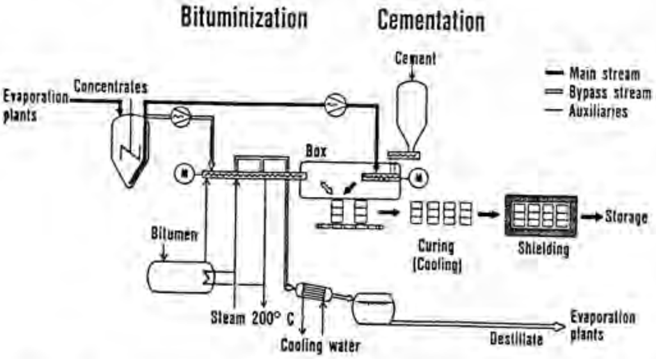

Fig. 4. Simplified flowsheet for liquid waste treatment by cementation and bituminization.

In order to increase waste loadings in the final product while maintaining low w/c ratios, investigations in KfK and NuKem are being pursued. The idea is to concentrate the waste solutions by evaporation directly prior to mixing and to condition the product in continuous mixing machines with the help of liquifiers[11].

Waste Packages and Standardized Container System

Considerable improvements have been made in the design of high integrity waste packagings which can take a barrier function in the repository, especially for short-lived wastes. Families of high integrity waste casks, made of cast nodular iron with or without an inner lead liner, are currently being used in nearly all German nuclear power plants for storage and transportation of medium level wastes.

An example of a typical waste cask is shown in Fig. 6. The high cask integrity guarantees a tight containment and may make an additional fixation of the waste in the cask cavity dispensable.

With respect to the planned disposal of waste in the Konrad mine in the near future, including wastes from nuclear reactor decommissioning, recently there has been developed a technical concept for a flexible standardized container system with easy handling covering all the LL and IL wastes.

The following container types are proposed:

1. Cylindrical containers, made of concrete or cast iron up to 3.1 m^3 gross volume
2. Box type containers, made of sheet metal, concrete or cast iron up to 10.5 m^2 gross volume
3. Standard 200 and 400 1 drums in sheet metal containers.

Quality Assurance Concept

Since 1980 considerable efforts have been initiated by the Physikalisch-Technische-Bundesanstalt (PTB) to establish a quality assurance system for radioactive waste packages. The basic idea is the qualification of different conditioning processes for different wastes. The conditioning process and relevant instrumentation shall guarantee the final waste package quality, which meets the disposal demands. Further input parameters for the process

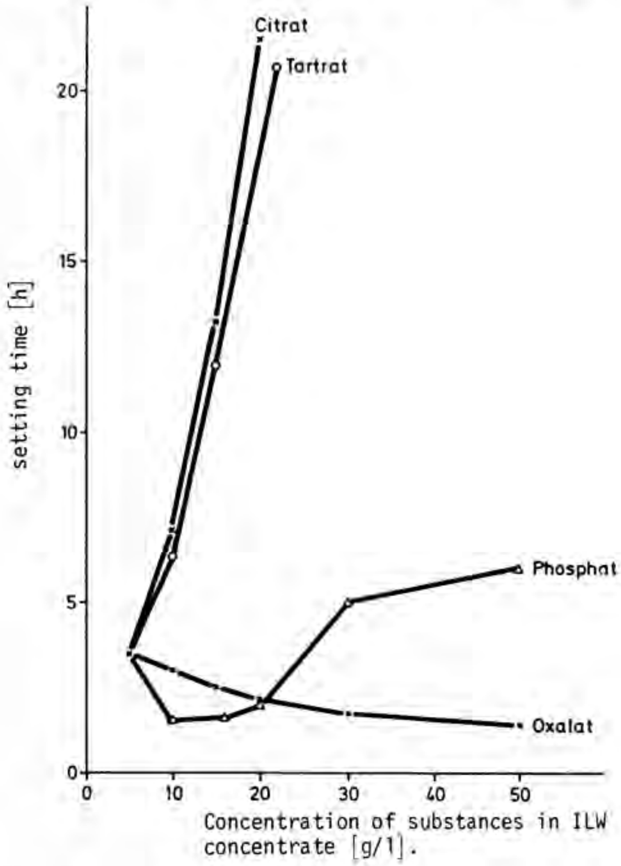

Fig. 5. Influence of substances interfering with the setting of ILW-cement-grouts.

qualification are raw waste data, quality of solidification agents, quality of containers. Quality control efforts shall be minimized and shall be limited to incidental inspections, random tests should be carried out non-destructively if possible.

CURRENT R & D ACTIVITIES

The conditioning methods have attained a high technical standard and a high degree of reliability. Based on these methods, the current R & D program in the Federal Republic of Germany focuses on the objectives:

1. Improvement of product properties
2. optimization of process steps
3. recycling of materials
4. reduction of waste management costs.

Insoluble dissolution residues and cladding hulls are being characterized in detail with respect especially to Tc and Pu contents and heat production rates. Cladding hulls and the *corresponding* cemented waste form are being investigated with respect to the possible release of H-3 and Kr-85[12].

The use of $CaO \cdot SiO_2 \cdot H_2O$-free ceramic cements with improved chemical stability against magnesium containing brines for conditioning of cladding hulls is investigated. Compaction techniques with or without additives like lead fines are being developed, realizing a high volume reduction while maintaining a low process temperature to retain the gettered tritium.

R & D work is going on to tailor waterfree composite ceramic waste forms to incorporate particularly wastes with higher TRU contents together with corresponding process developments including the steps mixing, drying, calcination[13].

Work is being carried out to eliminate the salt contents of IL concentrates by using electrolytical methods instead of chemicals and hydrazine carbonate instead of sodium carbonate in the Purex process.

Separation of fission products with high gamma energies and actinides from IL waste concentrates from reprocessing plants, e.g., by precipitation, is being investigated[14].

Especially recycling of metallic components from decommissioning or conventional disposal of concrete rubble should be intensified. At the same licensing procedures should be simplified by establishing general permissible contamination limits for components to be recycled.

The in-situ concept with containerless transport of preconditioned LL and IL waste granules into a non-accessible underground cavern seems to have a high technical potential to manage the wide variety of wastes in a simple and safe manner provided a suitable site is available[15].

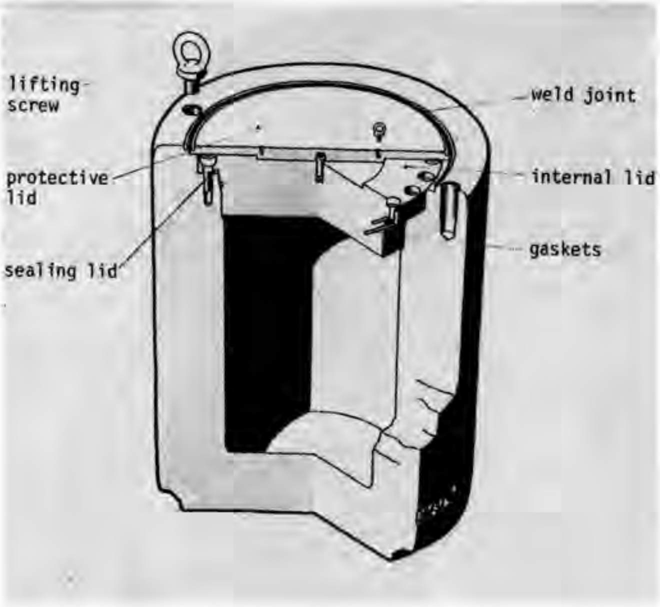

Fig. 6. Cast nodular iron container for storage, transport and disposal.

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