TESTS FOR PROCESS CONTROL DURING CEMENTATION OF LAW AND MAW

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ABSTRACT

The state-of-the-art of a running project on radioactive waste management is described. The partners in this European project are The Netherlands, Germany and Belgium. The object is to develop test methods and procedures for process quality control during cementation of radwaste from nuclear power stations. The findings may form a basis for recommendations and harmonization in the field of waste management.

Up till now inventories were made of processes and test methods. Based on these inventories, selections were made with respect to the development of adequate chemical, radiological and mechanical/physical test methods. Some preliminary results are given as well.

INTRODUCTION

Adequate management of low and medium radioactive waste that will be formed during operation of nuclear power stations, is an absolute necessity to warrant the protection of man and environment. Therefore the total waste treatment process from waste release up to interim and final storage has to be controlled. Continuous process control is preferable above verification just before storage, because of its higher reliability, traceability and the possibilities for system corrections.

Decisive elements of such a process control are tests in order to check if the criteria formulated by the authorities are met. Therefore it is necessary to determine which tests and procedures are appropriate.

In order to focus the research programme on realistic conditions, first typical (to be cementated) low and medium radioactive wastes from power stations and their routes during conditioning up to disposal, were studied (see Fig. 1).

The results of this research programme will be used to define recommendations for test procedures and measuring techniques which may form the basis for standardisation of specific quality systems of radwaste management.

This project is being performed jointly by order of the electricity production companies in the Netherlands and in the framework of the European Communities Programme on Management and Storage of Radioactive Waste by KEMA, KFA Jülich and Laborelec.

PROCESS DESCRIPTIONS

The development of a quality control system for an actual process needs adequate description of this process, as well as application of the specific governmental regulations. A typical example of such a cementation process is schematically shown in Fig. 2.

For the Belgian, German and Dutch situation typical processes and approaches concerning cementation of radwaste have been studied (2).

With respect to the Belgian situation the nuclear waste treatment system of the Doel power station was described with emphasis on liquid waste and encapsulation. The main treatment process is evaporation although flocculation facilities are also available. Boric acid is recovered as much as possible. Non recoverable liquid effluents can be divided in chemical waste, miscellaneous waste and regeneration effluents. The main types of solid wastes are filter cartridges, ion-exchange resins and solids (equipment parts). All these types of wastes are cementated. The formula's used to calculate the composition of concrete are based on pH, density and boron content. The acceptance criteria in Belgium are formulated by a body called NIRAS/ONDRAF.

In Germany the waste producers and conditioners must demonstrate that waste forms or waste packages of adequate quality are produced if certain operating conditions, which have to be specified in a handbook, are observed. They have to show that the instrumentation is appropriate and that the control measures assure the observance of the operating conditions so that the fulfilment of the acceptance criteria can be guaranteed. The acceptance requirements, specified by BfS for the Konrad repository include requirements on activity inventory and package properties and consequently product properties. Activity inventories and product properties are usually verified by a combination of analyses and tests at the primary waste, observance of certain process parameters and checks at product samples. During examination of the process and procedures for process qualification, it has to be shown that fulfilment of the repository requirements is guaranteed by the range of measures for normal operation.

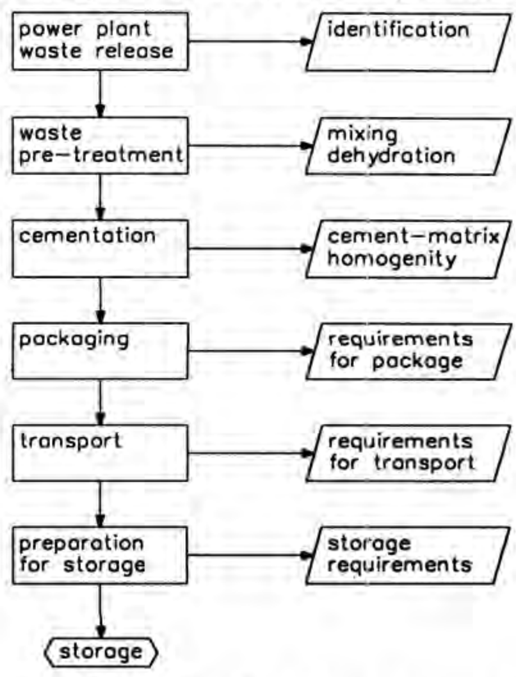

Fig. 1. General flow chart of waste treatment process.

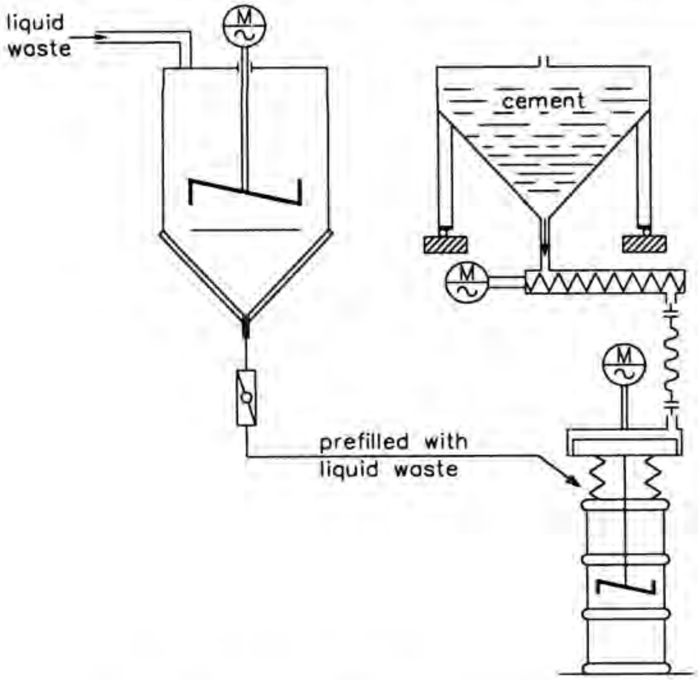

Fig. 2. Typical cementation process (1).

In The Netherlands two nuclear power stations are operated, a 60 MWe BWR and a 475 MWe PWR. The wastes are cementated by in line and in drum mixing respectively. The cementated waste is packaged in 220 litre steel drums which may be placed in 1000 litre concrete containers. The transport and interim storage is organized by COVRA, which also defines requirements and procedures. Standard tests are included for process control during conditioning as well as qualification tests on strength, stability and leacheability for the wastes to be cementated.

CHEMICAL TESTS

The research project is focused on test methods and procedures which can be applied during the operation of cementation. On-line test methods are preferable. However, if these are not available other test methods have to be introduced which do not disturb the continuation of the process (3).

For the chemical characterization it was recognized that it is important to determine the following properties and components:

Determination of acidity or alkalinity. Measurements of pH-value is necessary for the control and adjustment of alkalinity with respect to the removal of ammonia and to the reaction temperature. Measurements can be carried out by test papers or by using glass electrodes.

Inorganic constituents of the radwaste such as PO43-, SO42-, F⁻, NO3-, BO33-, NH4 +, Ca^{2+}, Mg^{2+} and complexing agents can be determined by photometry and atomic absorption spectometry (AAS).

The above-mentioned species are known as cement poisons, which influence the cement hardening process. Some typical effects are given in Table I. Depending on their concentrations, these cement poisons have to be determined more or less often. For this purpose photometry and AAS are well proven test methods.

TABLE I
Effect of Cement Poisons

Species	Effect on Cementation
NH_4^+	bad influence on thermal characteristics of evaporator feed solution; retards cement setting
BO_3^{3-}	influences cement setting
PO_4^{3-}	influences cement setting
Mg^{2+}	influences cement setting
NO_3^-	negative influence on thermal behaviour of feed solution during evaporation process
C	higher concentrations of organic C retard cement setting
Cl^-	higher concentrations retard cement setting
SO_3^{2-}	influences mechanical stability of cement
$Ca^{2+}SO_4^{2-}$	influences mechanical stability of cement

Higher concentrations of organic carbon may cause problems during the conditioning process, especially in the presence of nitrates. Adequate determination methods are TOC (Total Organic Carbon determination) or thermogravimetry (MS).

In this project specific test methods were selected for further research. Therefore well defined mixures are being examined qualitatively for cement poisons. The ions to be determined are: NH4 +, Mg^{2+}, Ca^{2+}, BO33-, PO43-, SO42- and NO3-. The test methods chosen are:

- ICP and IC by Laborelec
- photometry by KFA
- selective electrode and ICP by KEMA.

Special attention will be given to dissolution techniques.

RADIOLOGICAL TESTS

With respect to radiological tests several measurements are important such as:

- dose measurements
- surface contamination
- total alpha, beta and gamma activity using proportional counters
- beta and alpha/beta determination by scintillation counting
- qualitatively alpha measuring in an alpha chamber, after extraction and electro deposition.

The methods to be used will depend on the nuclides to be determined. With an adequate measurement system, gamma radiation detection can be performed on-line during the cementation process. Alpha and beta measurements, however, require sampling from the waste and chemical separation.

In the project special attention is given to alpha, beta and gamma spectroscopy. The partners will exchange procedures on which bases alpha activity will be determined of a well defined sample. With respect to Sr-90 and T procedures will be exchanged for beta spectrometry. The gamma activity of a cementated waste sample will be determined by gamma spectroscopy.

Furthermore a computer simulation programme (DENSITY) developed by KEMA, will be applied for quick measurements of gamma radiation and homogeneity of the cementated waste. Findings of preliminary calculations are presented in Fig. 3. It can be seen that the best source detector geometry for nuclide inventory control is the top or bottom centre of the vessel. The best place for homogeneity measurements is the side centre because of the maximum effect of the waste density (3).

MECHANICAL AND PHYSICAL TESTS

In this research project the emphasis lies on non destructive on-line determination of strength development of cementated waste forms. Besides the importance of this property, strength is well correlated to other parameters like durability. Three methods for strength prediction were selected for further research being viscosity, maturity and pulse velocity. These methods are fundamentally different. Waste sludge viscosity is linked to its water content. Maturity is a measure of the degree of hydration of the cementated waste, while ultrasonic pulse velocity is a function of waste form density and Young's modulus.

In a preliminary experimental programme the feasibilities of these test methods were investigated. It could be concluded that especially viscosity and maturity are appropriate for strength prediction (4).

Maturity is a widely accepted test method in the concrete building industry. This concept basically involves integrating temperature development over time for the curing cement and correcting for factors such as type of cement used. By means of a correlation function, early strength gain can be derived from maturity. In Europe standard computerised equipment is available for these tests. The method is economically adaptable by simple thermocouple temperature measurements in the cementated waste. Some typical relations between maturity and seven days compressive strength are shown in Fig. 4. It can be seen that a measuring time of about six hours was needed to obtain acceptable sensitivity.

CONCLUSIONS

The main object of this European project is to define procedures and test methods for on-line process control during radwaste cementation. Being half way in this ongoing project no solid conclusions can be formulated yet.

In the project selections were made for chemical, radiological and mechanical/physical test methods and procedures, which will be further developed.

With the simulation programme DENSITY, activation inventory and homogeneity determination of 220 litre waste vessels could be optimized.

Promising test methods for cementated waste strength prediction turned out to be the maturity concept and sludge viscosity.

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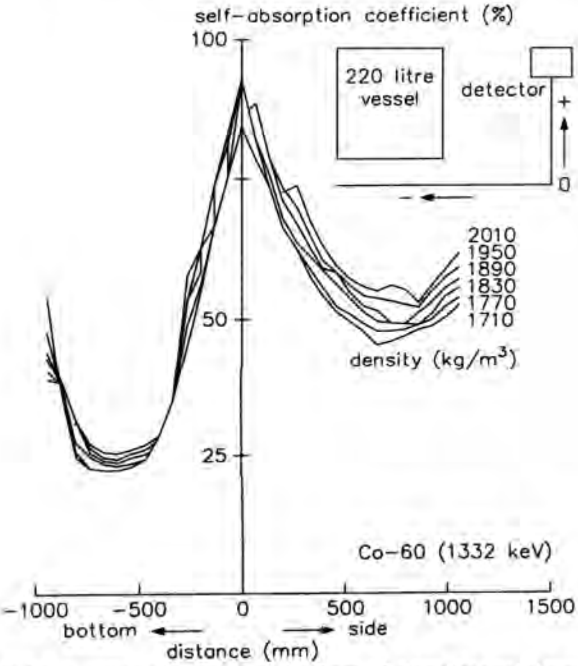

Fig. 3. Computer simulation of effect of density and detector position on the efficiency of measurements on 220 litre vessels.

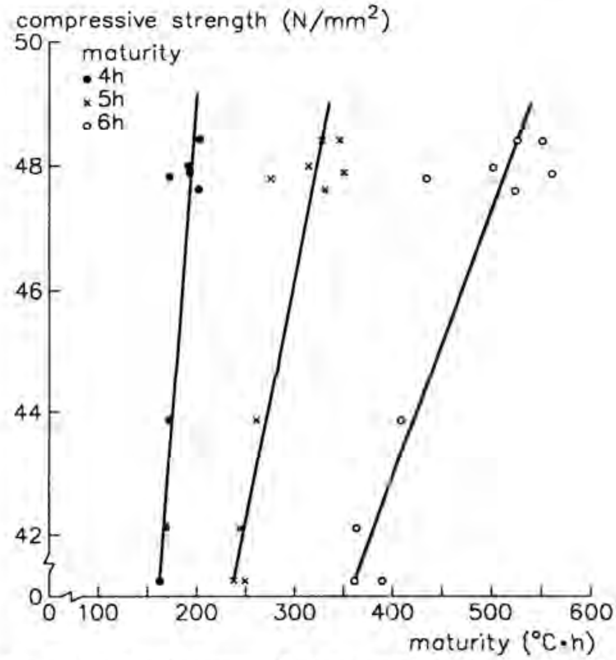

Fig. 4. Maturity versus 7-days compressive strength of cementated waste (4% waste; Portland cement (4).