CEMENTATION - A SOLUTION FOR FINAL DISPOSAL?

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ABSTRACT

During the past 10 years NUKEM performed intensive R&D- activities concerning the cementation of radioactive waste and the control of the resulting products. Purpose of the work was to ensure the final disposal of cemented waste forms. Many of our results were used for the safety analysis for the German projects for final disposal (KONRAD and GORLEBEN). The activities covered the following items:

- types of commercial available cements and additives
- recipes including bandwiths for liquid and solid radioactive wastes
- mechanical properties (curing, bending/compressive strength)
- release of radioactive elements (e.g. Cs, Sr) in case of:
  - leaching with brines, simulating host rock liquids
  - fire (underground accident)
  - mechanical impact (underground accident)

This presentation is giving the summarized main results of this work.

INTRODUCTION

During the years 1979 - 1989 NUKEM performed intensive R&D-work concerning the cementation of radioactive waste. This work was partially supported by the German government as well as by the Commission of the European Community. Purpose of our activities was to ensure the ability of cemented waste forms for final disposal in Germany. The work was performed in cooperation with other German R&D- institutions (e.g. Karlsruhe Nuclear Research Center, KfK) as well as the federal institutions responsible for the final disposal in Germany (up to 1989 Physikalisch-Technische Bundesanstalt, PTB; from 1990 Bundesanstalt f r Strahlenschutz).

Many of our results were used for the safety analysis for the German disposal projects KONRAD and GORLEBEN (1, 2). The results were partially published elsewhere (3 - 6). This presentation gives the summarized results in connection with their influence to the safety of final disposal.

EXPERIMENTAL

Our work was performed in lab scale as well as in full scale (200 l-drums up to 5 m^3-containers). The facilities and techniques used for our work in the laboratories and workshops are common described in the following sections:

Materials

For most of our experimental work the wastes were simulated inactively. The composition were derived from analyses performed by Nuclear Power Plants or the KfK (concentrates), or we used materials comparable with the real radioactive wastes (solid wastes like ashes, fuel element hulls, liquids like ion exchange resins). Single waste simulates are listed in Table I. The detailed compositions are listed in (7 - 8). For full scale experiments, the liquid simulates were composed and mixed in 10 m^3 tanks, containing stirrers and pump circulation.

TABLE I

Waste Types experienced at NUKEM

- Evaporator concentrates (BWR, PWR, Reprocessing)
- Filter sludge
- Ashes
- Powered resins
- Bead resins
- Pyrolysis ash
- Shreddered polymer material
- Decontamination effluents

As binders commercial available cements and additives were used. One of our items was to use materials with controlled and standardized quality. The materials are listed in Table II.

Mixers

For lab products a standardized mixer was used (Hobart Co., Ohio, USA), according to the German Industrial Standards (DIN 1164, part 7).

The mixing sequence was normally to add the solids (cement, additives) to the liquids (concentrates etc.). For the technical production we used first a series of commercial in-drum, batch- and continuous mixers:

- planetary mixer, Bahnsen Co., Hamburg (in-drum)

- AMK, AMK Co., Aachen (batch)
- Gipsomat, Putzmeister Co., Stuttgart (continuous)
- Estromat, Uelzener Maschinenfabrik, Uelzen (continuous)

TABLE II

Binders used for radioactive waste solidification

- Ordinary portland cement
- Sulphate resistant portland cement
- Blast furnace slag cement
- Puzzolanic cement
- Additives (zeolithes, liquifiers, stabilizers)

The test experience resulted in an own development of cement mixers, specially designed for the nuclear use (9 - 11):

- DEWA (Demountable Waste Unit), an in-drum mixer based on the planetary mixing principle)
- MOWA (Mobile Waste Unit), an in-drum mixer with a complete new design
- Continuous Mixing System, with a specially developed feed system

The mixing sequence was for the batch mixers to add the solids to the liquids. The continuous mixers worked in the opposite way, they feeded the liquids to the (premixed) solids.

Samples

The lab products were produced normally in the 1 l-scale (cylindrical). After hardening (28 days) they were cut in smaller sizes by a dry diamond saw. The technical products had the 200 l- and 400 l-size. After hardening, the drums were used in full size, e.g. for leach tests or we took samples by core drilling (dry, core drilling facility by Nasovia, Weilburg). The cylindrical cores were cut like the lab samples. Fort the tests described below we used:

- prismatic samples, 2 x 2 x 8 cm (standard)
- cubic samples, 10 x 10 x 10 cm (partially)
- cylindrical samples, 10 x 10 cm (partially)
- full scale samples, 200 l/400 l

Leach Tests

The leach tests were performed according to the ISO-Standard 6961. The samples used for these tests werde mainly the 2 x 2 x 8 cm-prisms as well as 400 l-drums for full scale leaching.

As leachant we used "realistic" liquids, i.e. beside deionized H_2O the so-called Q-brine ($MgCl_2$, $MgSO_4$), simulant for expected liquids in a salt dome (GORLEBEN; ASSE), and saturated NaCl-solution, which can also be seen as simulant for the host rock liquid in the KONRAD-mine. The temperature range was 20°C - 90°C.

Containers for the lab leach tests werde closable glass cylinders resp. polypropylene boxes, for the full scale samples 1 m^3 polypropylene tanks, which were supplied with a temperature regulation.The leached elements were analyzed by AAS (inactive) resp. Ge(Li)-detectors (active).

Mechanical Tests

The products were characterized by the following properties:

- density
- curing time
- bending strength
- compressive strength

The test methods used were performed according to German Standards (DIN 1164).

Fire Tests

The fire tests were performed in a field test facility (see Fig. 1) with 200 l- and 400 l-drums. The drums were opened and contained the cemented waste simulate. They were exposed to an isopropanol fire of 30 - 60 min duration. During the experiment the temperature distribution inside the drums and products was measured by thermocouples. The off gases were suctioned directly above the surface of the products and filtered by a sand particle deep bed filter unit. The sand was analyzed for the content of doted elements by neutron activation analysis (Cs, Sr, J, Eu as Pu-simulant), the drums were controlled for the weight loss.

Fall Tests

The mechanical impact (see Fig. 2) was applied by dropping the waste package from a defined height on to a reinforced concrete target (2 x 2 x 3 m, 20 tons) covered by a 80 mm thick steel plate. Different mechanical impacts could be realized using a crane with a maximum lift height of 65 m. Based on the package weight of about 500 kg and applied drop height of 60 m the mechanical impact yields $3 \cdot 10^5$ Nm. This impact corresponds to the maximum mechanical impact considered for the safety assessments for the repository.

To establish a closed system for the collection of the released dust, (under undisturbed conditions) the concrete basement was surrounded by a mechanically stable cage with mobile ceiling. For collecting a part of the airborne fines, a total of 30 filter units with microfilters (nucleopore 0.2 μm) were placed on the inner sides of the cage. The arrangement of the filter units was selected in accordance with the Institut of Filter- and Aerosoltechnik (LAF) of the

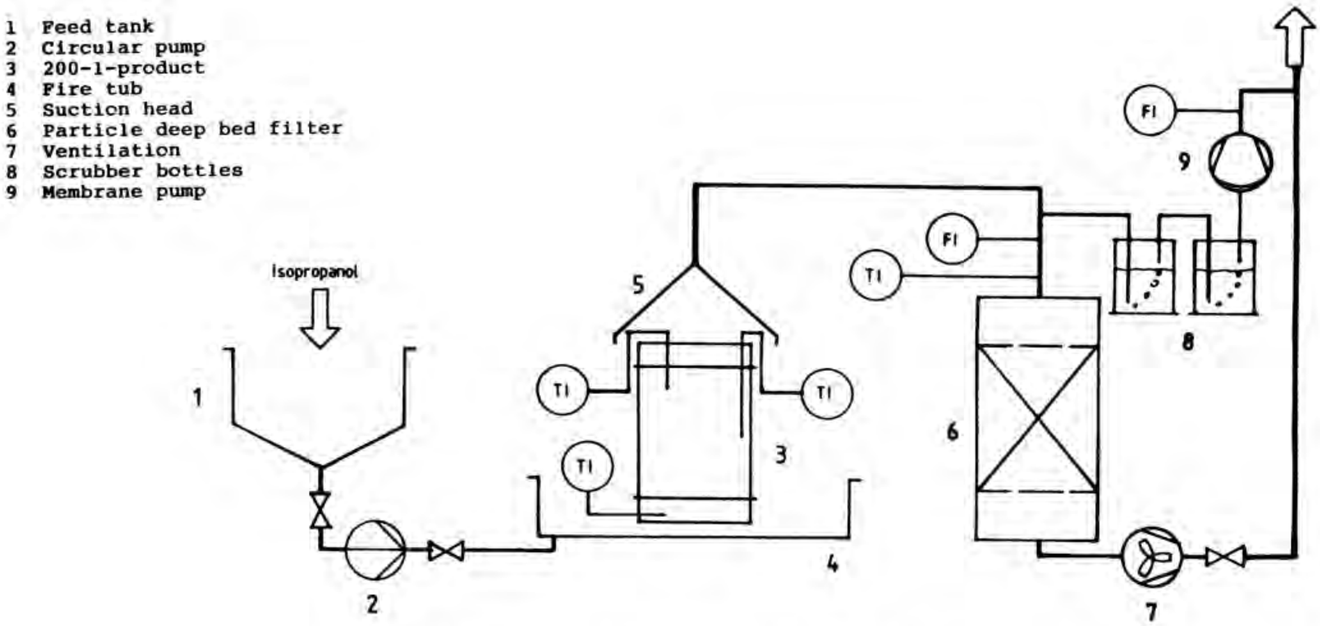

Fig. 1. Flow Sheet of the Full Scale Fire Test Facility.

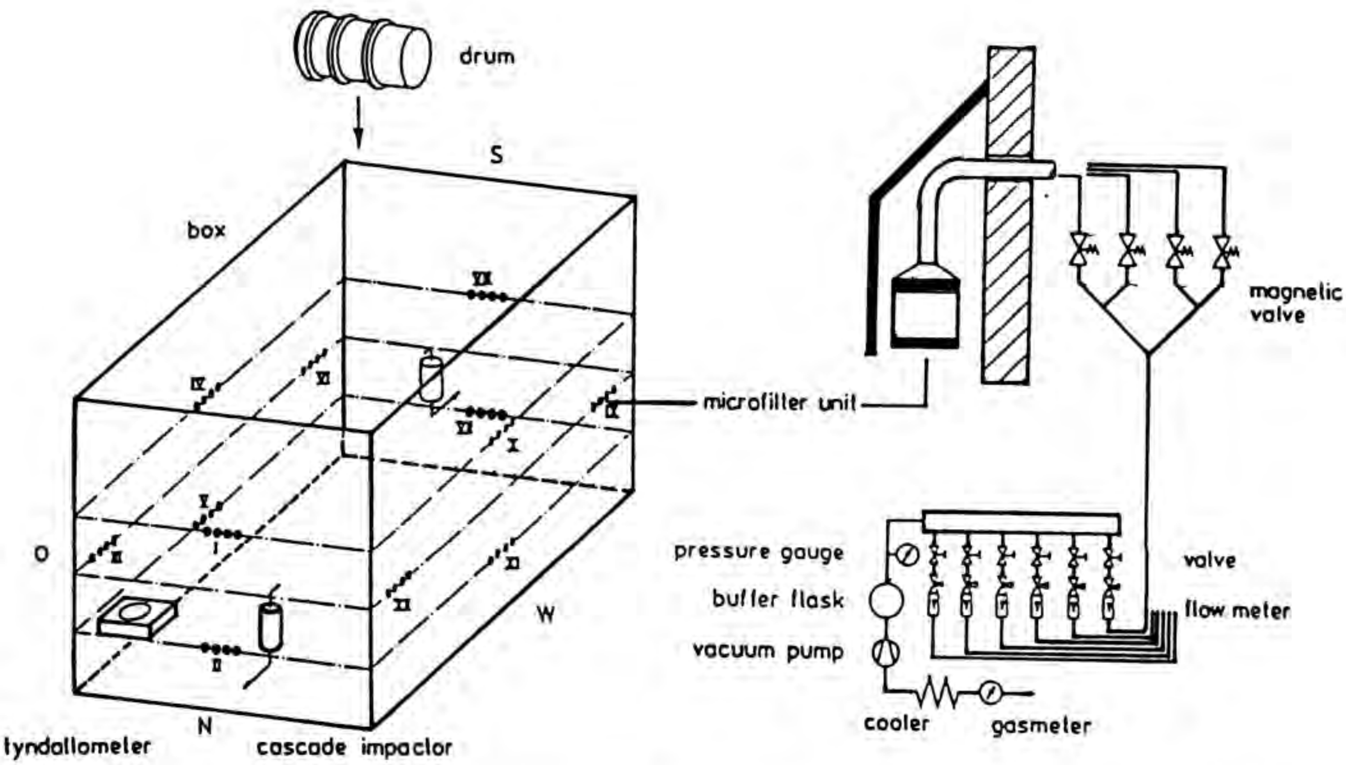

Fig. 2. Scheme of the Experimental Set Up for the Collection of Airborne Fines from the Waste Package After Drop Test.

Kernforschungszentrum Karlsruhe. From the amount of dust on the filters and taking into account the suck-off parameters, the dust concentration in the cage air volume and in consequence the source term can be calculated.

For the determination of the dust amount on the filter SEM-photographs of selceted filter sections were performed and evaluated using an automatic picture evaluation system (Zeiss Company). With this system it was possible to count the total number of particles and to classify them into fractions with different particle size. In addition, the time dependence of the average dust concentration in the cage was measured by using a tyndallometer equipment. To obtain further information on package behavior and dust spreading the impact on the waste package was observed by an installed video camera. In two experiments, the fraction with an aerodynamic diameter between 1 μm and 20 μm was determined using a cascade impactor.

RESULTS

Recipe Development

The development of a recipe for waste cementation is limited by the following items:

- workability of the mixture (min. liquid content)
- free standing water/liquid waste (max. liquid content)
- limit of compressive strength: ≥ 10 N/mm^2 (1450 psi) (12)

The use of additives results in a shifting of these limits. The workability of a cement mixtures can be lowered to w/c-ratios < 0.3 by adding liquefiers, the free standing water can be overcome by adding stabilizers. A significant upper limit for all products is the compressive strength necessary for the German disposal site KONRAD. The results for the range of possible mixture compositions for the experienced waste types is given by Fig. 3 and Table III.

The waste content (dry substance) in the cement products is normally given by the w/c-ratio in case of direct mixture. To raise this content without reaching the upper limits makes necessary to dry down the concentrates and to solidify it with a low w/c-ratio (0.25) (13). With this technique, dry substances (d.s.) contents up to 40 weight-% are possible without difficulties in hardening. The compressive strengths of these products are about 30 MPa.

The comparison of different cement types resulted in the fact, that blast furnace slag cements (BFSC) showed the best properties concerning leach rates and corrosion behavior. The BFSC-type HOZ 35 L-NW/HS was furthermore

TABLE III
Properties Of Cemented Waste Forms

Waste type	Cement	W/C-range	Range of leach rate in (brine 55°C) (E-3 g/cm^{2}d)
PWR concentrate	OPC	0.40 - 0.7	1.3 - 2.7
	BFSC		---
BWR concentrate	OPC	0.35 - 0.56	1.5 - 6.4
	BFSC	0.4 - 0.5	---
Reprocessing conc.	OPC	0.25 - 0.45	1.3 - 6.9
	BFSC	0.25 - 0.45	0.1 - 3.3
Decont. effluents	OPC	---	---
	BFSC	0.30 - 0.50	0.2 - 0.5
Filter sludge	OPC	0.40 - 0.70	0.6 - 3.0
	BFSC	0.40 - 0.50	0.4 - 1.0
Powered resins	OPC	0.43 - 0.70	---
	BFSC	0.30 - 0.70	2.6 - 3.7
Bead resins	OPC	0.25 - 0.35	---
	BFSC	0.25 - 0.35	0.2 - 1.2
Ashes	OPC	0.43 - 1.16	2.2 - 6.6
(Ash/cement = 1:2 - 2:1)	BFSC	0.35 - 0.45	1.1 - 3.1
Pyrolysis ash	OPC	---	---
(Ash/cement = 1:3 - 1.1)	BFSC	0.40 - 0.95	0.8 - 3.8

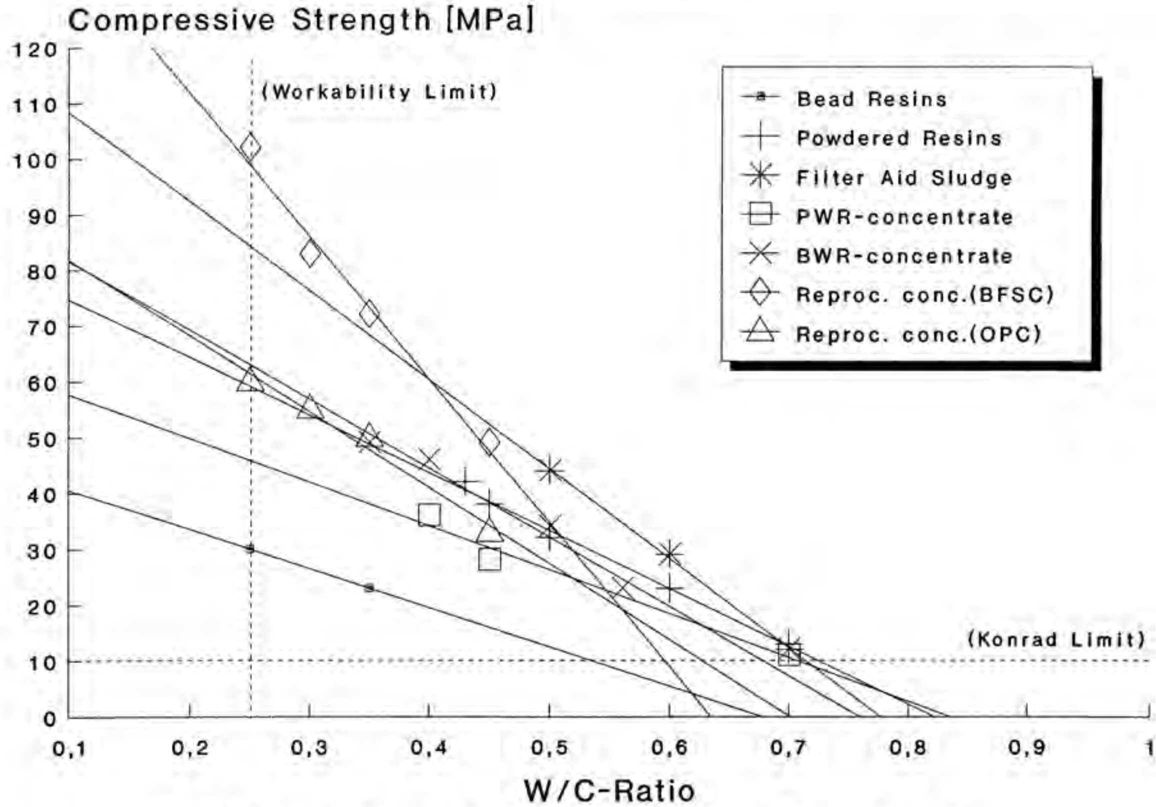

Fig. 3. Compressive Strength vs. W/C-Ratio for Different Cement Products.

TABLE IV
Element Specific Release Fractions After Full Scale Fire Tests

Cemented Waste Form	Release Fractions (-)			
	Cs	Sr	Eu	I
Evaporator conc.	8 E-5	2 E-5	4 E-6	----
Bead resins	8 E-5	----	5 E-6	2 E-4
Incinerator ash/srub water	3 E-4	9 E-5	9 E-6	----
Compacted Trash	2 E-3	1 E-4	----	----

TABLE V
Element Specific Release Fractions After Full Scale Drop Test

Waste	mech. impact	release fraction			
	(Nm)	< 10 μm	< 32 μm	< 63 μm	< 125 μm
powered resins	2,0 E+5	≤2 E-6	2 E-4	1 E-3	3 E-3
compacted solids	2,3 E+5	≤2 E-6	3 E-5	1 E-4	2 E-4
HEPA filter unit	2,2 E+5	≤2 E-6	4 E-5	2 E-4	5 E-4
HEPA filter unit	1,5 E+5	≤2 E-6	1 E-5	5 E-5	8 E-5
Evaporator conc.	3,0 E+5	≤2 E-6	---	2 E-4	1 E-3

(Experiment of the Nuclear Research Center Karlsruhe, KfK) used as standard binder. For better comparison nearly all experiments were performed also with ordinary portland cement (OPC) PZ 35 F.

Mixing Technique

The commercial available cement mixers showed principally sufficient functions from the viewpoint of product quality, but they had some disadvantages in process engineering, like e.g. difficult cleaning, insufficient feed accuracy or low power. This resulted in the development of two new cementation plants. The technical results have been published elsewhere (8 - 10). The technique, in particular the automatic control, was developed and experienced specially from the quality assurance viewpoint. With the control system equalized product properties are achievable and the product control can be minimized (6).

Leaching and Corrosion Properties

Leach experiments were performed in lab scale and full scale with all waste types listed in Table I. The results are summarized in Table III. More than 500 different products and more than 1000 samples have been leached in brines and water, and were analyzed for the release of Cs and Sr.

We can draw the following conclusions:

- For all waste types BFSC showed in the average lower leach rates than cement of the portland cement type. The reason is the much lower diffusion coefficients of ions in the gel pore system of the hydrated blast furnace slag (14).
- The leach rates were clearly determined by diffusion.
- The full scale samples showed slight higher leach rates (factor 1.5 - 2) than lab samples.
- Long term leach tests (> 10 years, without changing of leachant) showed after about 5 years a sharp decrease in leach rates and partially a precipitation of dissolved Cs.
- The presence of package corrosion products lowered the leach rate as well.
- A disintegration of the products could be only achieved with unrealistic conditions: 90°C, 5 years, 1 l-product, changing of leachant each month. Under these circumstances OPC products disintegrated totally to fines, BFCS products showed significant crack formation.

Fire Tests

The postulated fire accident (11) has a duration of 1 h at 800°C. This condition were adjusted for our field fire tests with several 200 - 400 l-products. The results were (see Table IV):

- At 1000°C the product surface showed maximal temperatures of 600°C, which decrease sharply to < 100°C after 5 cm,
- The average weight loss were 16 - 23 kg, which corresponds to 2 - 5 %. The release rates for Cs and Sr were about 10^{-4}, for Eu about 1 ppm.

Mechanical Properties

Cement products, produced by direct cementation of liquid wastes and therefore with dry substance contents up to about 15 weight-%, showed excellent mechanical properties. The compressive strengths at w/c-values between 0.25 - 0.7 (see Fig. 3) were between 10 - 100 N/mm². Lower values are not accepted for the disposal site KONRAD (11).

To experience the activity release in case of a mechanical accident, drop tests with several waste simulates were performed (4). For this, 200 l-products were dropped from a height of 60 m to a special measurement device. The result, listed in Table V, showed for aerosols (≤10 μm) release rates of only 2 ppm. A relation to the compressive strength was not obvious.

CONTRIBUTION TO THE SAFETY ANALYSIS FOR THE FINAL DISPOSAL

Like the results of many other R&D-institutions in Germany, the data of our work could be integrated in the safety analysis for the German disposal site KONRAD. Our results of the activity release in case of fire and crash accident served as one input to the preliminary requirements for waste products to be accepted in KONRAD.

The extensive results of our leach tests were used to calculate the influence of the source terms of the single nuclides to the long term safety of the final disposal in the geological formation surrounding the KONRAD mine (1).

It could be shown, that cement products are, also under very pessimistic conditions, a reliable barrier for hundreds of years. That is long enough for the disintegration of the most fission products, to ensure that the toxicity of a former waste disposal site is less than the toxicity of a coal mine.

Concerning the question of the title of this paper, we can say: Yes, cementation of radioactive waste is one solution for final disposal.

REFERENCES

1. B. Ganser; H. Brunner, R. Leicht, "Modellierung des Langzeitverhaltens von endzulagernden Abfällen mit vernachlässigbarer thermischer Beeinflussung des Wirtsgesteins"; Jahrestagung Kerntechnik, Aachen, 8. - 10.04.86

2. PTB - "Schachtanlage KONRAD - Vom Erzbergwerk zum Endlager für radioaktive Abfälle"; Fischer Druck + Verlag, Wolfenbüttel.

3. P. Johnson, R. Koester, P. Veymelka, H. Brunner, "Activity Release From Waste Packages Containing IL And LL Waste Forms Under Mechanical and Thermal Stresses", Waste Management '85, Tucson, Vol. 3, p. 321.

4. R. Koester, P. Vejmelka, H. Brunner, B. Ganser, "Characterization of Low and Intermediate Level Waste Forms"; Intern. Seminar of Radioactive Waste Forms - Suitability For Final Disposal, Jülich, 10. - 13.06.1985.

5. B. Ganser, A.W. Mehner, H.U. Brinkmann; "Entwicklung von Endlagergebinden für abgebrannte HTR-Brennelemente"; Jahrestagung Kerntechnik, Travemünde, 17. - 19.05.1988.

6. B. Ganser; "Study of the Industrial Operation of Plants for The Treatment of Radioactive Waste With Regard to Quality Control", Spectrum '88, Pasco, 11. - 15.09.88

7. W. Uhl, H. Brunner; "Qualitätssicherung von LAW/MAW-Produkten", NUKEM FuE 81074.

8. H. Brunner, B. Ganser, N. Iffland; "Qualitätssicherung von LAW/MAW-Produkten"; NUKEM FuE 85039.

9. H. Brunner, B. Ganser, J. Hofmann, G. Klein (+); "MOWA - the Mobile Waste Conditioning Plant"; Symposium on Radioactive Waste Management; London, November 1984.

10. H. Brunner, B. Christ; "Recent Experiences With Cement Solidification System"; Waste Management '85, Vol. 3, p. 321.

11. H.H. Homann, R.R. Kraemer; "Disposal of Low and Medium Level Wastes By Means of In-situ Solidification", Waste Management '85, Vol. 3, p. 441.

12. P. Brennecke, E. Warnecke (Hrsg.); "Vorläufige Endlagerbedingungen, Stand Mai 1989 - Schachtanlage KONRAD", Arbeitsbericht der Physikalisch-Technischen Bundesanstalt.

13. H. Brunner, W. Schlich, H. Huschka; "Trocknen und Zementieren, ein Verfahrenskonzept zu optimaler Volumenreduktion von Flüssigabfällen", Jahrestagung Kerntechnik 1983.

14. H. Brodersen, Dissertation RWTH Aachen, 1984; Betonforum 1984, Düsseldorf.