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**COVER SHEET  
FOR TRIP REPORTS SUBMITTED TO THE  
OFFICE OF ENERGY RESEARCH**

**Destination(s) and Dates for  
Which Trip Report Being Submitted:** Federal Republic of Germany and France  
November 7-26, 1986

**Name of Traveler:** L. R. Dole

**Joint Trip Report**  Yes  
 No

**If so, Name of Other Traveler(s):** \_\_\_\_\_  
\_\_\_\_\_

**MASTER** *ok*  
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FOREIGN TRIP REPORT

ORNL/FTR-2468

DATE: December 18, 1986

SUBJECT: Report of Foreign Travel of L. R. Dole, Program Manager  
in the Waste Management Technology Center (WMTC)

TO: Herman Postma

FROM: L. R. Dole

PURPOSE: To participate in the France/United States bilateral  
meetings, workshops, and site visits concerning the  
immobilization of radioactive wastes at Cadarache,  
Valduc, Saclay, and Fontenay-aux-Roses and to par-  
ticipate in FRG site visits and discussions of waste  
treatment, immobilization at Karlsruhe and Hanau, and  
the site remedial actions sponsored by the BMFT at  
Spredlingen.

SITES VISITED:	11/11-14/86	U.S./France Immobilization in Cement-based Waste Forms, Maison d'Hotels de Cadarache, Cadarache, France	M. Jorda
	11/17/86	Cadarache Nuclear Center	M. Josso
	11/19/86	Centre d'Etudes de Valduc Dijon, France	M. Mangin
	11/20/86	Saclay Nuclear Research Center, Saclay, France	M. Jorda
	11/22/86	Zublin, GmbH, Curtain Wall in the Spred- lingen Hazardous Waste Site, Spredlingen, FRG	Herr Glaeser
	11/23/86	Karlsruhe Kernfor- schungszentrum (KfK), Karlsruhe, FRG	Herr Hempelmann
	11/24/86	Nuclear Site Hannau (Nukem, Alkem, and Transnuklear), Hanau, FRG	Dr. Schneider

**ABSTRACT:**

The traveler participated as the cochairman of the France/U.S. Workshop in Cadarache, France, on the immobilization of radioactive wastes in cement-based materials. These meetings and site visits were conducted under the bilateral exchange agreement between the U.S.-DOE and the Commissariate a l'Energie Atomique (CEA-France). Visits in France included The Cadarache, Valduc, Saclay, and Fontenay-aux-Roses Nuclear Research Centers. As a result of these discussions, an exchange of scientists between Saclay and ORNL was proposed. Upon agreement, a scientist/engineer from ORNL would spend a month at Saclay, applying newly developed materials to radioactive waste streams of mutual interest to the United States and France. Then, a scientist from Saclay would spend a month at ORNL to apply their testing procedures to waste-form formulations with these waste streams and fixing materials. The CEA-France is also considering supplying two types of cement-based waste disposal containers to the Modular Disposal Unit (MDU) study at ORNL.

The traveler continued on to the FRG to visit a hazardous waste site remedial action project in Sprendlingen and the nuclear research and production facilities at the Karlsruhe Kernforschungszentrum (KfK) and the Alkem/Nukem/Transnuklear facilities at Hanau. Visits in the FRG were under the bilateral exchange agreement between the U.S.-DOE and the Bundes Ministerium für Forschung und Technologie (BMFT). The FRG supplied the traveler data on studies of super-compaction volume reduction efficiencies by KfK and Nukem. Also, Transnuklear is considering contributing two of their larger Konrad-certified packages to the MDU studies at ORNL.

REPORT ON TRAVEL TO FRANCE AND WEST GERMANY  
NOVEMBER 11-24, 1986

L. R. Dole

November 11-14, 1986 - Workshop on Cement Waste Forms at the  
Cadarache Nuclear Center for Nuclear Studies

The four concurrent workshops, (1) Tritium Waste Processing and Off-gas Systems, (2) Cement-Based Waste Forms, (3) Incineration Facilities and Off-gas Systems, and (4) Waste Management Strategies, were conducted November 12-14, 1986, in the Cadarache Guest House. The agenda is presented in Appendix C.

The traveler was a cochairman of the Cement-Based Waste Forms Workshop and gave two formal presentations, which are summarized in Appendix C. The following topics and issues were covered in the presentations and the ensuing discussions during an intense 2 days of workshop sessions:

Cement-based Waste Form Chemistry	Formulation Development
Process Selection Criteria	Regulatory Requirements
Leaching and Durability Tests	Models of Leaching
Radiolytic Gas Generation	Accelerated Testing
Scaling Laboratory Leach Tests	Remedial Actions

The U.S. delegation, composed of M. Christie and the traveler, was more oriented toward the process engineering and the implementation cement-based materials, and the French delegation was more interested in material science and basic mechanism studies. Nevertheless, the interests of the groups were very complementary. The recent materials studies of the French have looked at new materials that were not available during the U.S. screening studies. For example, Saclay has applied a W. R. Grace process, SynCrete, which uses a polymer monomer to stabilize organic resin beads. Also, studies at Saclay have used more alumina-based, Fondue cements than earlier U.S. studies. Table 1 summarizes wastes and binders.

Table 1. Wastes and binders used in France

Waste	Binder
Nitrates	Mortars with Portland I cement and liquifiers and Benotonite
Borates	Mortars with Portland I cement
Metal hydroxides	Portland I cement paste
Calcium phosphate	Depending on the type of phosphate: cement pastes with high alumina or Fondue (Alumina cement)
PbI <sub>2</sub>	Mortars with Pozzolanic cement
Ashes (oxides)	Fluid grouts for encapsulation with Portland I cement and liquifiers
Organic resins	SynCrete with Portland I cement and two component resin monomers

Accelerated aging tests at Saclay have confirmed that small increases in the temperature (20°C) alter the courses of the complex sequential and parallel chemistries in the curing of cement pastes. For example, the formation and stability of a chlorohydroxy aluminate changed abruptly between 40 and 60°C, and the microstructure of the product was shown to be greatly different. Therefore, simple acceleration of leaching by temperature elevation and Arrhenius plots of apparent diffusion coefficients are unreliable indicators of leaching mechanisms. All accelerated aging, leaching, and durability studies must be accompanied by detailed phase studies and alternative verification methods with analyses on the solids.

Also, studies of ancient Gallo-Roman grouts have given insights that parallel and augment the U.S. studies at ORNL and Penn State University (Roy and Langton). M. Petit reported on results of his studies at the University of Poitiers (Appendix D). He has examined and modeled the phases in a 1800-year-old Pozzolanic grout that lined a hot water pipe in a Roman bath that was in operation nearly 200 years. This Roman formula proved to be very durable in an extreme environment for a very long time.

At the conclusion of the Cement Workshop, the cochairmen, M. Jorda and the traveler, summarized the discussions before a joint session of all workshop participants and presented proposals for future exchanges under the U.S.-DOE/France-CEA Bilateral Agreement in the Field of Radioactive Waste. Two proposals for cooperative exchange programs between ORNL and Saclay were presented and approved by the constituents.

## PROPOSED BILATERAL PROJECTS

• Materials and Testing

A meeting would be held in Oak Ridge in January of 1987 to select two or more surrogate waste formulas of mutual interest to both the U.S. and French nuclear waste programs. After this meeting, the plans would be as follows: An ORNL engineer would spend 3 months in Saclay developing processable formulas with the French binders. This development stage would be followed by a 3-month visit by the French to ORNL laboratories to apply the waste form qualification tests developed by the Waste Immobilization Group in the Chemical Technology Division. A meeting would follow to document the results.

• Test Packages for ORO Demonstrations

The French would supply the ORNL demonstration program for Modular Disposal Units (MDUs) with three to five samples each of the two-package configurations (box and cylinder) that are currently used at their Centre de la Stockage de la Manche. ORNL would subject these packages to tests at SWSA 6 and share the results.

November 17, 1986 — Site Visit to the Cadarache Nuclear Research Center

On Monday, November 17, 1986, the U.S. delegation visited the Cadarache Nuclear Research Center. The facilities toured were (1) the Solid Waste Treatment Center, (2) the Alpha Waste Incinerator, and (3) the Organic Solvent Incinerator.

At the Solid Waste Treatment Center, 25 100-L drums are compacted in a 250-tonne press into one drum, measuring 3 ft in diameter and 4 ft high. The drums are assayed prior to compaction to assure that the plutonium content is <50 mg/drum.

The Alpha Waste Incinerator, shown in Appendix E, processes at the rate of ~20 kg/h at 700°C, and the ashes are drummed and stored. Currently, this incinerator is only used for beta wastes, but in the future it is expected to be used for alpha wastes. Appendix E also gives the data and the schematic drawing of the Organic Solvent Incinerator.

The Organic Solvent Incinerator for uranium-contaminated oils has been operating since 1981. The delegation also visited the Immobilization Laboratory, where experiments on the immobilization of ashes were being conducted with polymer-cement mixtures. Pilot-scale mixing studies are planned for CY 1987. A vertical-shaft, side-out mixer had been installed. Cadarache was experimenting with vacuum-mixed and poured batches to reduce gassing and bubble formation.

November 19, 1986 - Visit to the Centre d'Etudes de Valduc

On Wednesday, November 19, 1986, the U.S. delegation visited the CEA nuclear defense site at Valduc, near Dijon. The delegation toured (1) the Tritium Treatment Facility, (2) the Tritium Waste Storage Facilities, (3) the Low-Level Waste Evaporator, (4) the Dismantling Cell, and (5) the Metal Induction Melter. The agenda is shown in Appendix F.

The tritium was removed from the laboratory air by a zeolite filter system. This plant has developed a sophisticated distillation system to strip tritium from the liquid effluents. The processing of tritium-bearing metals is done by vacuum-stripping molten metal at 1500°C, in two 60-kg batches each week.

November 20, 1986 - Visit to the Saclay Nuclear Research Center

On Thursday, November 20, 1986, the traveler was given a tour of the Saclay laboratories where (1) the chemical mechanisms of durability, (2) the detailed interactions of wastes with cement phases, (3) scale effects on leach mechanisms, and (4) full-scale environmental exposures are studied and modeled.

At Saclay, M. Nomine showed the traveler the large-scale leaching pools and discussed a series of tests examining the effect of scale on leaching data for solids of the following sizes: 0.2, 2, 20, and 200 L. Nomine, with over 5 years of experiments behind him, contests the use of the surface-to-volume (S/V) ratio, which is the diffusion model scaling factor used widely by most waste form modelers. We agreed to continue the debate by correspondence.

The exchange of experts in grout formulation, characterization, and performance testing under the Bilateral Agreement will involve only personnel from Saclay and ORNL.

November 22, 1986 - Visit to the Sprendlingen Hazardous Waste Dump Remedial Curtain Wall Demonstration Site

On Saturday, November 22, 1986, the traveler was given a tour of the West German Bundes Ministerium für Forschung und Technology's (BMFT) hazardous waste site remedial action project between Mainz and Rudesheim near the Rhine River. This curtain wall project is to isolate a leaking chemical waste dump that was operated in an abandoned clay pit on the Rhine River meander. Zublin Company, AG, has developed a unique combination grout-and-plastic sheet curtain wall emplacement technique that has been demonstrated to be extremely effective in sealing water conducting sequences. Appendix G presents examples of in-situ remedial action technologies presently being demonstrated under the BMFT's hazardous waste program.

European countries are under ever-increasing pressure to manage the hazardous wastes — past and present. This trip coincided with the "Rhine Death Watch," which resulted from the fire and spill in Basel, Switzerland. Also, the environmental political party, the 'Green,' along with the 'Reds,' had unseated the pronuclear majority in the Hessian parliament and threatened to close the Alkem/Nukem/Transnuklear facility in Hanau. West Germany probably has the most advanced and aggressive hazardous waste program in the European community (EC).

November 24, 1986 — Visit to the Karlsruhe Kernforschungszentrum

On Monday, November 24, 1986, as guests of Herr Hempelmann, the Director of the Decontamination Operations Division, the U.S. delegation to the FRG (Bohrer, Christie, Dole, and Ziegler) visited the following facilities: (1) Super-Compaction, (2) Metal Decontamination and Recycle, (3) Middle-Level Waste Fixation, and (4) LLW and Alpha Incinerator. Previous trip reports by the traveler, ORNL-FTR-2263, ORNL/FTS-2172, and ORNL/FTR-512, give many of the details.

Karlsruhe and Nukem have completed a detailed study of the compaction factors for various materials and a study of the efficacy of pre-compaction with a normal "junkyard" press. Some data from a paper to be given at the SVA/ASPEA Tecknikum Winterthur on December 1-3, 1986, SVA, Postfach 2613, CH-3001, Bern, were shared with the traveler. Appendix H gives the summary figure from these studies.

November 25, 1986 — Visit to Hanau Facilities of Alkem, Nukem, and Transnuklear

On Tuesday, November 25, 1986, the U.S. delegation to the FRG visited the Hanau nuclear facilities for the (1) Alkem shred/grouting and plutonium recycle from the Mixed-Oxide (MOX) fuel cycle, (2) Nukem incineration pilot, and (3) Transnuklear transport and disposal cask development facilities. The agenda for these discussions and a summary of the Alkem operations are presented in Appendix I. Previous trip reports by the traveler, ORNL-FTR-2263, ORNL/FTS-2172, and ORNL/FTS-512, give additional details.

Several new topics were discussed in Hanau: (1) the safety question in the repository of critical masses of various transuranic nuclides, (2) use of the pebble-bed incinerator for organic resin beads in addition to organic solvents, and (3) the possibility of using the highly refined disposal packages developed and tested for the Konrad Repository for low-level wastes (LLW) and medium-level wastes (MLW).

The restrictions on fissile nuclides in waste packages in the Konrad and Gorleben Repositories resulted in very severe costs to the Alkem operation. The total cost of disposal in the Konrad Repository was estimated at 6,000 DM/m<sup>3</sup>. Because the safety analyses had made very

conservative assumptions, the disposal volumes to dilute the wastes were so expensive as to justify plutonium recovery operations on a limited scale. The traveler discussed U.S. studies and has supplied the FRG program with copies of the reports (Appendix J).

Second, Nukem discussed some recent promising results on the incineration of organic ion-exchange resin beads in their pebble-bed incinerator for organic solvents. The effective degradation of the resin beads without fouling the dry-candle filter off-gas system opens a new avenue to the disposal of organic resin beads. Current disposal schemes use either fixation or high-integrity containers (HICs) — neither of which have significant chemical or mechanical stability under shallow-land burial conditions. This treatment development offers both greater volume reduction and a route to a durable waste form and package.

Finally, Transnuklear agreed to consider supplying two of their larger, certified disposal packages to ORNL for testing in the tumulus and hill-cut demonstrations that use modular disposal units (MDUs). Time and cost estimates are being prepared by Dr. Christ, and he will pass this information through Dr. Schnider to the traveler.

## APPENDIX A

### ITINERARY

November 7-8, 1986	Travel to Marseilles, France
November 9, 1986	Travel to Aix en Provence
November 10, 1986	Aix en Provence meeting of U.S. delegation
November 11, 1986	Travel to Cadarache
November 12-14, 1986	US-DOE/France-CEA Workshop
November 14, 1986	Travel to St. Tropez
November 15, 1986	St. Tropez
November 16, 1986	Travel to Aix en Provence
November 17, 1986	Visit Cadarache Nuclear Research Center
November 17, 1986	Travel to Dole
November 18, 1986	Travel to Dijon
November 19, 1986	Visit Le Centre de Valduc
November 20, 1986	Travel to Saclay
November 20, 1986	Visit Saclay Nuclear Research Center
November 21, 1986	Travel to Karlsruhe, FRG
November 22, 1986	Visit Spredlingen Hazardous Disposal Site
November 23, 1986	Karlsruhe
November 24, 1986	Visit Karlsruhe Kernforschungszentrum
November 24, 1986	Travel to Hanau
November 25, 1986	Visit Hanau facilities of Alkem, Nukem, and Transnuklear
November 26, 1986	Return to Knoxville

## APPENDIX B

### PERSONS CONTACTED

Mr. Blauvelt, Mound	Mr. Faure, SPPC - Caderache
Mr. Giroux, Valduc	Mr. Lannaud, DAM - Valduc
Mr. Andrieux, SPR, Saclay	Mr. Lisonne, DRDD - Caderache
Ms. Bardolle, DAM/DQS, Siege	Mr. Madic, DGR - FAR
Mr. Malet, DIP, FAR	Mr. Martinez, DAM - Valduc
Mr. Malfondet, DAM, Valduc	Mr. Meyere, DGR - Marcoule
Mr. Ochem, DAM, Valduc	Mr. Otter, DRDD - FAR
Mr. Radeki, DAM, Valduc	Mr. Pourprix, DPT, Saclay (le 14 Novembre)
Mr. Saas, BECC/CIDN	Mr. de Seynes, Cogema - Marcoule
Mr. Jorda, DRDD - CEN.FAR	Mr. Soulier, Cogema - Marcoule
Mr. Christie, Hanford	Mr. de Tassigny, SPR - Grenoble
Ms. Atabek, DRDD-FAR	Mr. Dieckhoner, U.S. DOE/HQ
Mr. Bernard, DRDD-Saclay	Mr. Hagan, JIO/AL
Mr. Bernaudat, DRDD-FAR	Ms. Sugier, DED
Mr. Bouniol, DRDD-Saclay	Mr. Lefevre, DED
Mr. Chiappini, DAM - BIII	Mr. Jourde, DED
Mr. Josso, DRDD - Caderache	Mr. Cluchet, DAM
Mr. Mangin, DAM - Valduc	Mr. Baudin, DRDD
Mr. Oliver, DRDD - FAR	Mr. Launois, DAM
Mr. Nomine, Saclay	Ms. Kinsky, DED
Mr. Petit, DRDD - FAR	Mr. Gläser, Züblin AO
Ms. Revertegat, DRDD - Saclay	Mr. Hempelmann, KfK
Mr. Ziegler, RFP	Dr. Kroebel, KfK
Ms. Caramelle, DPT - GEN/Saclay	Mr. Kramer, KfK
Mr. Bohrer, Idaho Falls	Dr. Schneider, Alkem
Mr. Bartoli, DRDD - Caderache	Dr. Lederbrink, Alkem
Mr. Caillol, SCTC - Caderache	Dr. Demmich, Nukem
Mr. Calament, DAS - FAR	Dr. Christ, Transnuklear
Mr. Carpentier, SGN - St. Quentin	Mr. Kemmler, Nukem
Mr. Chevalier, DPT - FAR	Mr. Scherbaum, Nukem

APPENDIX C

CADARACHE WORKSHOPS

November 12-14, 1986



CEA/DOE AGREEMENT  
 CADARACHE WORKSHOP  
 12-14 November 1986

VENUE : Maison d'Hôtes de Cadarache

AGENDA :

11 nov. 7.30 PM	Dinner hosted by DAM/DQS
12 nov. 9.00 AM	Informal meeting with DED/fin <small>BIBLIOTHEQUE (Library)</small>
10.00 to 10.45 AM	Arrival of other participants, get together with coffee in Salle des Armures
10.45 AM	Till lunch and after lunch : Workshops in following rooms : H3 : Salon Vaibelle cement : Bergerie incineration : Salle des Programmes
lunch : at Maison d'Hôtes restaurant	
Dinner : please register the night before for dinner at Maison d'Hôtes restaurant	
13 nov. 8.30	Workshop as before lunch in Maison d'Hôtes restaurant
7.30 PM	Official dinner hosted by M. LEFEVRE and M. BAUDIN in Maison d'Hôtes restaurant for US participants and wives and french participants
14 nov. 10.00 AM	Plenary session : Salle de la Ferme
12.30	Lunch Break up

The "Bibliothèque" room will be available for discussions throughout the workshop

CEA/DOE  
CEMENT WORKSHOP  
12 - 14 November 1986

BLACKIE

Leaders : Leslie L. DOLE, Martin Marietta, ORNL  
Michel JORDA, DRDD - CEN.FAR

Members : Michael A. CHRISTIE, Rockwell, Hanford

Mme ATABEK	DRDD	- FAR
MM. BERNARD	DRDD	- SACLAY
BERNAUDAT	DRDD	- FAR
BOUNIOL	DRDD	- SACLAY
CHIAPPINI	DAM	- BIII
JORDA	DRDD	- FAR
JOSSO	DRDD	- CADARACHE
MANGIN	DAM	- VALDUC
OLIVER	DRDD	- FAR
PETIT	DRDD	- FAR
Mme REVERTEGAT	DRDD	- SACLAY
Annie SUGIER	DRD	- FAR

## COMMISSARIAT A L' ENERGIE ATOMIQUE

Nos réf. : SESD/86.191  
Le 10 juin 1986

EXPEDITEUR : DRDD/SESD - M. JORDA  
 DESTINATAIRE : DED/CD - A. SUGIER

COPIES : DRDD/DIR - G. BAUDIN  
 DRDD/ADU - G. COURTOIS  
 DRDD/SESD - R. ATABEK, A. BILLON, A. BERNARD,  
 J. OLIVER, J.C. PETIT, P. BOUNIOL,  
 F. BERNAUDAT, E. REVERTEGAT  
 DRDD/SEDFMA  
 /SEDFMA/SETED  
 CYA/SPR - M. CORTELLA, M. MANGIN

Please, find the following proposal for the next CEA/DOE workshop on "Cement-based material improvements and their applications to nuclear waste embedding and disposal".

1<sup>er</sup> Lecture (20 mn) and discussions (15 mn) on the following topics

- Choice of the cement in relation to chemical interaction with wastes  
( DRDD/SESD - R. ATABEK )
- Improvement of cement-based material properties : compactness and radionuclides confinement  
( DRDD/SESD - P. BOUNIOL )
- Cement-polymer mixtures : application to borate concentrates, incinerator ashes and long  
exchanger resins cementations  
( DRDD/SESD - A. BERNARD )
- Evaluation of radionuclide migration ( HTO, Cs ) in cement-based material  
( DRDD/SESD - J. OLIVER )
- radionuclide migration and microstructure  
( DAM/RCP - A. CHIAPPINI )
- Modeling of chemical equilibrium in cement pores water  
( DRDD/SESD - F. BERNAUDAT )
- Chemical durability of cements  
( DRDD/SESD - E. REVERTEGAT )
- Contribution of petrologic methods to microcracking and alteration studies of cements  
( DRDD/SESD - J.C. PETIT )
- An industrial example : the cementation of sludges and concentrates at VALDUC NUCLEAR CENTER  
( CYA/SPR - M. MANGIN ) \*\*

2<sup>nd</sup> Visits

- First day : VALDUC NUCLEAR CENTER - Cementation equipment \*\*
- Second day : SACLAY NUCLEAR CENTER - Concrete study Laboratory  
- Leaching equipment

\*\* sous réserve de l'accord de la DAM

OVERVIEW OF OAK RIDGE OPERATIONS  
AND THE WASTE MANAGEMENT ACTIVITIES

Leslie R. Dole, Ph.D.  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee

The Oak Ridge Operations Office (ORO) of the U.S. Department of Energy (DOE) encompasses seven facilities. Martin Marietta Energy Systems, Inc., manages the Paducah Gaseous Diffusion Plant in Paducah, Kentucky, and the three Oak Ridge facilities — Oak Ridge Gaseous Diffusion Plant (ORGDP), Y-12 Plant, and Oak Ridge National Laboratory (ORNL). The other three facilities located in Ohio include the Portsmouth Gaseous Centrifuge Separation Plant, the RMI extrusion facility, and the Fernald Feed Materials Preparation Center (FMPC) sites.

In order to coordinate the resolution of the many waste management issues at these facilities, DOE has organized the Oak Ridge Model for which the Waste Management Technology Research, Development, and Demonstration Center (WMTC) implements (1) treatment, (2) recycle, (3) storage, (4) disposal, (5) remedial actions, and (6) process improvements.

For example, projects underway and facilities under construction include (1) the Toxic Substance and Control Act (TSCA) incinerator at the ORGDP, (2) the Y-12 Plant Central Pollution and Control Facility, (3) in-situ biological digestion in the Y-12 S-3 ponds, (4) the scrap metal clean-up at ORGDP, and the supercompactor demonstration at ORNL and (5) the Low-Level Waste Disposal, Development, and Demonstration (LLWDDD).

The inventory of low-level waste (LLW) on the DOE-ORO sites totals 670,000 m<sup>3</sup> with an annual generation rate of 26,000 m<sup>3</sup>. In the three Oak Ridge plants, there is projected to be by 1988 37,000 m<sup>3</sup> of LLW and 512,000 m<sup>3</sup> of mixed waste with generation rates of 18,000 m<sup>3</sup> and 7,000 m<sup>3</sup> each year, respectively.

Within Oak Ridge National Laboratory, 140 sites have been targeted in the current remedial action plan that covers (1) burial ground closure, (2) pond closure, and (3) reactor decommissioning. The characterization and prioritizing of over 165 waste streams from the Oak Ridge three-plant complex is underway and the development of a treatment, storage, and disposal (T/S/D) demonstration has begun.

# WASTE MANAGEMENT TECHNOLOGY

Oak Ridge, Tennessee



United States Department of Energy

## THE WASTE MANAGEMENT TECHNOLOGY CENTER:

*The technical center for implementing the Oak Ridge Model,  
the new DOE/ORO approach for application of waste management technology*

Current needs, future concerns, and problems associated with past practices are being addressed by the Oak Ridge Model for Waste Management, a cooperative effort of the U.S. Department of Energy (DOE)/Oak Ridge Operations (ORO) and Martin Marietta Energy Systems. The Waste Management Technology Center (WMTC) has a leading technical role in the model. Here waste management needs will be identified and prioritized, applicable waste management technology will be selected for demonstration using actual wastes, and the results will be translated into engineering alternatives for solving the problems. A major goal of WMTC is to collectively involve the private sector, academia, and government groups in the solution of these national waste management problems.

### The Center

The Waste Management Technology Center is a systematic approach to using available technology, and resources for evaluating and implementing DOE/ORO waste management strategies developed by the Oak Ridge Model. The Center consists of a group of technical experts working with private industry and business, the academic sector, and government agencies to define solutions to waste management problems. The cornerstone of WMTC philosophy is that the proof of any waste management technology lies in demonstrated performance. Therefore, specific projects will be implemented by WMTC at appropriate sites in the Oak Ridge system.



WMTC will act as the catalyst that brings potential technology from a variety of sources to bear on the problem areas. This systematic matching of technology with specific waste needs will result in significant technology transfer between participants. The goal is to carefully match technologies to problems in order to save both time and money in solving them. Thus, WMTC represents a unique cooperative effort because the private sector, universities, and other laboratories provide the principal sources of the current and future waste management technologies. These resources will be used by WMTC in fulfilling its national mission.

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**WASTE MANAGEMENT TECHNOLOGY  
THE WASTE MANAGEMENT TECHNOLOGY CENTER**

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**WMTC Mission**

The primary mission of WMTC is to support the Research and Waste Management Division of DOE/ORO which has the responsibility for developing and implementing the Oak Ridge Model in all ORO facilities. The WMTC is responsible to the Oak Ridge National Laboratory Nuclear and Chemical Waste Program, which is the Martin Marietta Energy Systems contact point for the Oak Ridge Model. Technology demonstrations may also be carried out by the WMTC for other governmental agencies and for the private sector where they support the ~~philosophies~~ of the Oak Ridge Model.

**WMTC Philosophy**

WMTC is a consistent and organized approach to solving waste management problems. Waste management dollars can be saved by centralizing technology development and evaluation through WMTC, thereby avoiding duplication of costs for evaluation by several programs. WMTC provides a focal point for the exchange of waste management information among DOE, the regulatory agencies, and the private sector. Thus, WMTC is a primary mechanism for facilitating technology transfer.

**WMTC Approach**

Involvement of the private sector is the cornerstone of the WMTC demonstration program to provide answers to waste management problems. Through Request for Proposals (RFP), qualified vendors are contracted to develop answers to problems and to demonstrate available waste management technology on specific waste streams. The demonstrations provide important cost and performance information that will be made available through WMTC reports. The initial RFP issued by WMTC to the private sector was to carry out a demonstration of innovative technology for treatment and "delisting" of mixed waste sludges. The demonstration is scheduled to begin in FY 1987. It will provide experience in obtaining Research Development and Demonstration permits under the Resource Conservation and Recovery Act. Close cooperation will be maintained with regulatory agencies to determine that the technology being evaluated is approved for its intended use. Waste management systems analysis will be initiated through computer-based modeling of the waste management systems at the DOE/ORO facilities. This methodology will greatly aid prioritization or ranking of waste management problems and corresponding needs for technology demonstrations.

**WMTC Objectives**

The immediate WMTC objective is to implement the Oak Ridge Model to solve waste management problems in Oak Ridge. Long-term objectives include providing waste management tools to other waste managers; broadening the scope to include solving national problems; and transferring technology to other DOE organizations and to other Federal and State agencies, the private sector, and universities.

**INFORMATION ABOUT WMTC**

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OVERVIEW OF U.S. REGULATORY REQUIREMENTS,  
ENGINEERING SELECTION, AND PERFORMANCE REQUIREMENTS  
FOR WASTE PROCESSES AND HOSTS

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This paper summarizes the regulatory climate for the many U.S. Department of Energy (DOE) sites in the United States and reviews the criteria for prioritizing waste streams, selecting processes and selecting waste forms.

The regulatory scenario covers three decades: (1) the Atomic Energy Act (AEA) of 1954 that defined the categories of DOE wastes, (2) the Resource Conservation and Recovery Act (RCRA) of 1976 that established the criteria and remedies for newly generated hazardous wastes, (3) the U.S. District Federal Court ruling of 1984 that applied RCRA to DOE facilities, and (4) the DOE redefinition of "by-product" materials in 1985. The decisions since 1984 have altered the regulatory landscape and required a realignment of the DOE approach to permitting and licensing. Also, the Environmental Protection Agency and the affected states (for example, Tennessee, South Carolina, Washington, Idaho, Colorado, etc.) must also develop new infrastructures.

The result is that an additional set of regulatory waste definitions and treatment/storage/disposal (TSD) criteria have to be reconciled with the current DOE and Nuclear Regulatory Commission (NRC) statutes. Also, the affected state governments emerge as new permitting organizations, requiring them to address infrastructure,

staffing, education, and policy development. Finally, the national EPA has to oversee the states' performance and develop new policies for waste streams that have been outside their jurisdiction since the agency was established.

In a spirit of cooperation, the DOE has accepted the challenges of these rapid changes and has mounted a very large and comprehensive program to deal with their waste management problems. The "Oak Ridge Model," a component of that program, is designed to develop a coherent approach to the development of policies and the implementation of effective remedies.

From the hundreds of waste streams throughout the DOE complexes, a systematic selection of the most important problems must be done to ensure that limited resources are most effectively spent. Public confidence and peer acceptance will depend on successfully performing this complex task. The prioritizing of waste streams are based on several parameters: (1) compliance or legal status, (2) public perception, (3) regulatory classification by content and or hazard index, (4) generation status (old/new/continuing), (5) inventory status (stable solids to leaking ponds), (7) volume, and (8) solid/liquid/gas (type). A consistent and accurate risk management methodology needs to be developed and applied uniformly throughout the DOE facilities.

The selection of the treatment/storage/disposal processes will depend on: (1) costs, (2) product waste form and package compliance

with regulations for storage and land disposal, (3) minimization of the implementation interval, (4) volume reduction, (5) flexibility in feed variations and accepts a wide variety of wastes, (6) adequate reliability, (7) minimization of secondary streams, (8) minimization of personnel exposure, and (9) confidence level in vendor's ability to deliver. Since these waste treatment scenarios cut across so many functional divisions within the plants (such as, production, maintenance, research, etc.), a systematic decision process that integrates all of these needs must be used. If decision processes such as the "Delphi" or Kepner-Tregoe are successfully applied, the ultimate choice will be the collective wisdom of the group. At least, each of the functional divisions will share ownership of the problem and be more cooperative in accommodating any adjustments that may be necessary.

The selection of process equipment depends on (1) development status, (2) space required, (3) control of unit operation interface, (4) reliability and maintenance, (5) decontamination and recycle volumes, (6) tolerance to feed variations, (8) confinement of contamination, (9) cost, and (10) power consumption. The weighting factors for these parameters must be chosen to suit the particular case.

The criteria for the acceptability of the waste forms and packages are generally prescribed by four bodies of regulations from the Department of Energy (DOE), the Nuclear Regulatory Commission (NRC), the Department of Transportation (DOT), and the Environmental Protection Agency (EPA). The requirements of the first three are consistent

because their regulations evolved in cooperation with one another.

The requirements of the EPA were developed independently, however, and are irreconcilable in many cases because of divergent philosophies in the formulation of their regulations. The EPA regulations enforce a technical template for their remedies by prescribing strict adherence to a predetermined design and near-field performance thresholds. The other regulatory bodies set specific performance criteria for the waste disposal system's components (for example, waste form, package, trench cap, etc.) and overall system performance criteria at some critical interface with the public, such as an acceptable exposure to the nearest residents or risk to inhabitants after the loss of institutional control of the site.

The president's Office of Technical Assessment (OTA) has criticized the EPA for lack of innovative technology used in hazardous waste management. The current EPA regulations bind permits to limited and obsolete remedies. Under the current legislature, the reauthorization of the "Superfund Law," the Congress will require EPA to demonstrate new and innovative technologies. The Oak Ridge Waste Management Technology Center will assist in implementing those EPA demonstrations on DOE sites.

The DOE/NRC/EPA criteria for waste form performance address three major questions: leachability, durability, and compatibility. These questions must be answered in three very different arenas:

- (1) regulatory, permitting process, (2) technical peer-review, and
- (3) legal evidence, prescribed by statute for the permit or license.

The second requires data that demonstrate mechanisms and can be extrapolated to predict long-term performance. The last must be understandable, straightforward, and convincing to a nontechnical audience.

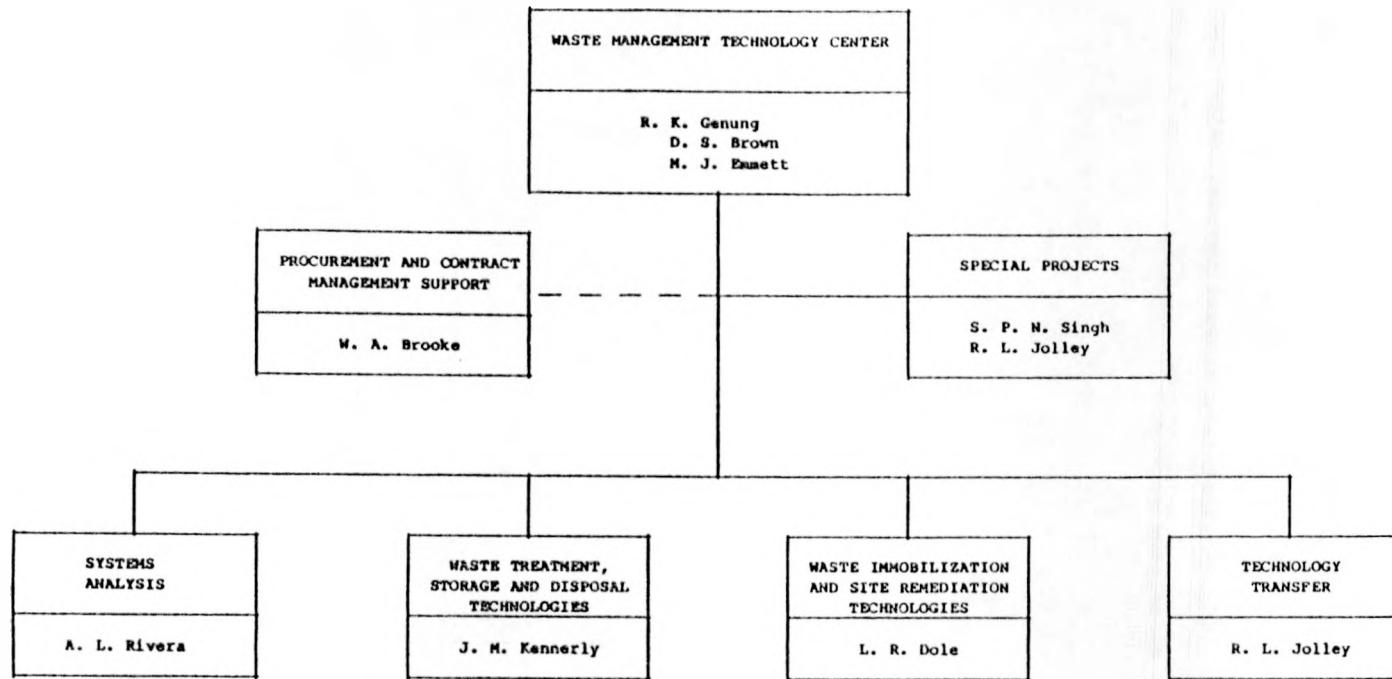
The current leaching tests required by regulatory statutes are (1) the EPA Toxicity Procedure and (2) the American Nuclear Society (ANS) 16.1 Leach Test, which is a version of the Modified IAEA multiple leachate replacement test. In order to develop source-term data for waste forms at specific disposal sites, we used the ANS 16.1 procedure with local groundwater. These data allow consequence analysis of a diffusion-controlled release from the waste forms in rapidly percolating groundwater.

To complete the data for source-term modeling, a third static leach test is added to assess the maximum concentrations that would be expected in a "low-flow," quasi-static hydrology. This test is a modification of the Materials Control Center's MCC-1 Static Leach Test. The modifications include using site groundwater and changes in the sample preparations to accommodate porous or soft waste forms.

Durability can be defined by a series of testing protocols, which include: (1) corrosion resistance, (2) chemical reactivity, (3) ignitability, (4) immersion resistance, (5) microbial and fungal resistance, (6) radiation resistance, (7) wet-dry cycling, and (8) thermal cycling.

Two aspects of waste-host/package compatibility are addressed in the current regulations. First, the potential corrosion of the

package material at the interface with the waste form, resulting in a premature loss of containment or structural stability. Second, the pressurizing of packages is addressed by requirements for venting the waste packages with waste forms that generate gases (such as cement-based, bitumen, polyester, cellulosics, nitrates, etc.). Also, the compositions of these radiolytic or biogenic gas mixtures are addressed, and limits are placed on components that can form ignitable or explosive gas mixtures (for example oxygen, chlorine, or NO<sub>2</sub> with hydrogen or methane).



- Interface with NCWP/R&D and WMCO
- Models & Analyses
- Waste Stream Data Base
- Prioritisation Methodology (to encompass all TSD facilities)
- Demo Project Summaries for WMES
- Definition of Demo Needs (Streams to be treated, technologies to be used, and questions to be answered)
- Interface with NCWP/OPRNS (LLWODD) and NCWP/HAZWRAP
- Coordinate the Development of Technical Statements of Work for RFPs
- Interfaces with ID, DEM, QA/QC, etc.
- Development of Permit Applications
- Interface with Procurement
- Vendor DB and Related Interactions
- Field Monitoring of Demo's
- Technical Summaries of Demo's/Technologies
- Interface with NCWP/ERFU and NCWP/HAZWRAP
- Development of Technical Statements of Work for RFPs
- Field Monitoring of Demo's
- Test and Evaluation Support
- Technical Review of Projects/Programs (e.g., for EPA Region IV)
- Technical Summaries of Demo's/Technologies
- Interface with WMCO
- Interface with Energy Systems' Technology Transfer Program
- Interface with ORNL Public Relations Office
- WMTC Publication Series
- Conference Liaison

APPENDIX D

PHASE STUDIES OF GROUTS INCLUDING AN ANCIENT GALLO-ROMAN POZZOLANIC



CONTRIBUTION OF PETROLOGICAL METHODS TO ALTERATION STUDIES  
OF CEMENT-BASED MATERIALS

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I. Introduction

The alteration of cement-based materials is a phenomenon of great importance for various radwaste disposal problems, such as the durability of low level waste matrices or engineered barriers. Although the basic processes of alteration of these materials have been already identified, it is still difficult to guaranty their long term durability over periods of time not directly accessible to laboratory experiments. Therefore, a careful study of the possible evolution of such materials is necessary.

Our approach of this question develops along three lines of research, namely:

- the detailed study of solid/solution interactions
- the investigation of archaeological analogues
- the modeling of alteration processes with geochemical codes such as EQ3/6

In our work, we are interested in both the kinetic aspects of alteration and the thermodynamic ones such as the identification of secondary mineral assemblings formed as a function of the degree of reaction (i.e. with time) between the solid and the solution. In addition, the role of microfissures in the kinetics of alteration is also investigated. This point could be of prime importance for alteration

rates if (as expected) a critical density of fissures induces a percolation threshold for the penetration of the altering fluid within the material. Finally, the behavior of radionuclides along the reaction path (in particular their distribution coefficients between the solution and secondary phases) is envisaged. In order to reach this goal, we apply a methodology which has been initially developed for studying the hydro-thermal alteration of crystalline rocks in natural systems (1, 2) and therefore combines various petrological techniques.

This program is still in progress. Hence we will only present here our methodology as well as some of our preliminary results in order to illustrate its interest for studying the alteration of cement-based materials used in the radwaste disposal technology.

### II. Experimental procedure

We are studying the experimental alteration of mortars made of two quite different types of cements, namely (in the french nomenclature) a CPA 55, which an ordinary portland cement and a CLC, which is a fly ash slag cement. ISO test samples (4X4X16 cm) were prepared with pure quartz of calibrated grain size (0.8-1.6 mm) and subjected in an isostatic press to increasing pressures up to 2000 bars. This treatment intended to induce increasing densities of quite isotropically distributed fissures. Alteration experiments are conducted at 40°C in both static and continuously renewed deionized water with an SA/V  $\sim 4 \text{ cm}^{-1}$ . The test samples are studied after 3, 6, 9, 12 and 18 months (plus the reference) in a first stage of this program. Prolonged leaching experiments will be performed if necessary. In addition a large sampling of archaeological cements have been collected in France in several gallo-roman baths. They are considered as possible analogue of present day materials when sufficient care is taken in interpreting and extrapolating data. These ancient materials could hopefully help us in identifying very slow processes which could dominate the alteration phenomenon on the long-term and to test the prediction of geochemical codes.

Our techniques of investigation, which combine the characterization of solids and the analysis of solutions, are the following:

1. Characterization of solids

After being weighted, the test samples are cut into two pieces: the first one is used for the measurement of classical mechanical properties whereas the second one is again cut into two more pieces. One part is used for making petrological thin sections, after coloring with a fluorescein solution which decorates the circulation paths of fluids; it is then carefully examined with an optical microscope for studying the fissures with a mean size  $\gtrsim 1\mu\text{m}$ . Another part is used for scanning electron microscope observations of submicrometer-sized fissures and minerals. Sites of interest, identified on thin sections, are quantitatively analyzed for elemental composition with an electron microprobe; very small quantities of matter ( $\sim 10^{-3}$  mg) are then picked *in situ* (by an original microdrilling technique), deposited on a silica lamellae and analyzed by means of step-scan X-ray diffractometry equipped with a linear localization detector. Such an approach allows a complete characterization of mineral assemblings on very small sites within the material. The writing of local mass balance and the description of alteration processes on a  $\mu\text{m}$ -scale is therefore possible. Both the mineralogical evolution of the paste and of fissures are investigated. Finally, the image analyzer is used to quantify the proportion of primary and secondary phases as well as the characteristics of the porous medium (density and orientation of fissures etc...).

2. Solution analyses

Major elements ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ) are analyzed by atomic absorption. Anions (such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) are measured by means of ionic liquid chromatography. Analyses of solutions are available up to 9 months. In future developments of this work, radionuclides will be measured by the appropriate  $\alpha$  or  $\gamma(\beta)$  spectrometries.

### III. Results and discussion

We present here data corresponding to the reference test samples as well as to 3 and 6 months of continuously renewed leaching; results for either longer periods of alteration or static leach tests are not yet available. Hence conclusion cannot be but preliminary.

#### III.1 Alteration of CPA 55

The data of electron microprobe analyses are reported on ternary diagrams Al-Si-Ca for the reference and the two leach times studied yet (figure 1):

1. reference (cured 28 days): one observes many remnants of unhydrated cement components, namely  $C_2S$ ,  $C_3S$  and  $C_4AF$ . Poorly crystallized hydrates of the CSH-type are formed in great quantities with a C/S ratio  $\sim 1.5$ - $1.7$ . In the paste, primary ettringite is noted as well as portlandite and very few monocrystalline calcite. At this stage, fissures are "dry" in showing no evidence for secondary minerals.

2. after 3 months (figures 2a and 3a): very few unhydrated minerals are still present. Primary ettringite is still noted in the paste whereas needles of secondary ettringite have formed inside fissures and bubbles. This last type of ettringite is always richer in  $SiO_2$  than the primary one. Big tablet-shaped monocrystals of portlandite are observable in fissures and bubbles. CSH, with a C/S ratio  $\sim 1.7$ , seem to have a better crystallinity (as observed with SEM), however not directly evidenced in XRD diagrams. Calcite is very abundant in the paste, particularly in fissures in the form of tiny crystals. Finally, carbonatation of the paste progresses inwards from the sample edges.

3. after 6 months (figures 2b and 3b): no unhydrated components are left in the paste (as expected). Similarly, primary ettringite have disappeared whereas few crystals of secondary one are still present in fissures and bubbles. Automorph crystals of portlandite now look heavily corroded, reflecting their dissolution. Large amounts of calcium monosulfo-aluminates have crystallized. CSH have now an increased C/S ratio  $\sim 1.8$ - $2$

and exhibit a much better crystallinity easily observable by XRD (figure 3b). Calcite is now very abundant in fissures and bubbles, and even in the paste in the form of well individualized rhombohedrons.

The analysis of solution show (figure 4a) a regular decrease of all cations as well as a drastic increase in the concentration of sulfates after 6 months probably related to the dissolution of ettringite.

One important observation made with the fluorescein solution is that this coloring additive does penetrate very deeply on both sides of fissures and hence invades the whole paste very easily (even for quite low densities of fissures). This behavior is completely different to that of CLC (see below). This reflects a high porosity of this matrix, likely favoring the migration of altering fluids, which must be understood. Hg-porosity measurements as well as high resolution texture observations with a TEM will be performed.

### III.2 Alteration of CLC

The data of electron microprobe analyses, also reported on ternary diagrams Al-Si-Ca, show distinctive features (figure 5):

1. reference (28 days cured): numerous spheres of fly ashes are visible, which mainly contain Si, Al, Fe, K and Mg. Also unhydrated minerals are still present in great amounts. Primary ettringite is noted in the paste, intricated with poorly crystallized hydrates of CSH-type with a low C/S ratio ~ 1.5-0.8. Less portlandite crystals than in the CPA 55 are observed, as expected. Moreover, calcite is very scarce. Finally, fissures are also "dry".

2. after 3 months: few unhydrated  $C_2S$  remnants are noted. CSH now have an increased C/S ratio ~ 1.5-1.7. Many  $C_2ASH$  crystals are formed in the paste. In addition, secondary ettringite as well as portlandite are present in fissures and bubbles; more calcite is now visible. Finally, paste carbonatation progresses inwards from the sample edges.

3. after 6 months : many voids have appeared in the paste. One notes a progressive disappearance of ettringite and the dissolution of the initial automorph portlandite crystals. Ca-monosulfo aluminates are present in great quantities. In addition, more calcite is now present, even in the paste in the form of individual rhombohedrons (figure 6a). Along fissures, calcite and CSH are dissolved (figure 6a). CSH have an even greater C/S ratio ~ 1.8 and an easily XRD-evidenced crystallinity (figure 6b).

Solution analyses show (figure 4b) an increase in Si and Al around 6 months whereas Ca and K continue to decrease. These variations are not clearly understood.

Contrarily to CPA 55 (see above), fluorescein colorings are now restricted to very narrow thicknesses around fissures where the fluid circulate, thus indicating a low porosity of the matrix which, a priori, would be favorable to the material durability.

### III.3 Alteration of gallo-roman cements

Many interesting features have been observed that demonstrate the feasibility of using these materials as analogues of current technological cements. However, we will restrict ourselves here to only one comment concerning samples collected in pipes for hot water conveyance in baths.

In fact, it appeared that the use of bricks for making these cements and the occurrence of some temperature in pipes led to actual pouzzolanic reactions. These reactions have induced the formation, among great quantities of calcite crystals, of hydrated Ca-aluminosilicates which we tentatively identify as very close to CSH formed in modern cements (figure 7).  $\text{CaAlSi}_2\text{H}_2\text{O}$  needle-shaped crystals are also noted. All these minerals will be soon studied by IR spectroscopy for further characterization.

One interesting conclusion of these observations is that such CSH-like minerals, which have been likely formed ~ 1800 years ago, have proved to be resistant on such a very long period of time.

#### IV. Conclusion

From these preliminary data, we conclude that our petrological approach is encouraging. Of course much more work is needed before a detailed description of cement alteration is possible. However, we have shown that identification of alteration phases on a submicron scale, and their sequence of occurrence with degree of solid/solution reaction, is possible. Hopefully, mass transfers along fissures and modeling will be attainable in the next future by using the thermodynamic data (such as solubilities) that, in parallel, we have estimated for hydrated phases of cement, for which very few data were reported. Also, results on archaeological samples lead us to be reasonably optimistic for the stability of CSH minerals, which are the major constituents of modern cement-based materials, over periods of a few 10 or 100 years.

Current developments of this work include characterization of secondary phases over at least 18 months, measurement of the rate of water penetration as a function of fissure density and modeling of alterations with EQ3/6.

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Figure captions

Figure 1: ternary Al-Si-Ca diagrams showing the evolution of the chemical composition (EPMA) of CPA 55 components with leach time in renewed conditions: 0 months or reference, 3 and 6 months (see text).

Figure 2: XRD diagrams of alteration products in fissures of CPA 55 for two leach times in renewed conditions (see text). a) 3 months: occurrence of ettringite (E), portlandite (P) and calcite (C); b) 6 months: smaller amounts of portlandite and much greater quantities of calcite are present.

Figure 3: XRD diagrams of alteration products in the paste of CPA 55 for two leach times in renewed conditions (see text). a) intense calcite peak and no CSH peak illustrating poor crystallinity; b) 6 months: noticeable CSH peaks.

Figure 4: Solution analyses (see text) for CPA 55 (a) and CLC (b) as a function of leach time in renewed conditions.

Figure 5: ternary Al-Si-Ca diagrams showing the evolution of the chemical composition (EPMA) of CLC components with leach time in renewed conditions: 0 months or reference, 3 and 6 months (see text).

Figure 6: XRD diagrams for altered CLC after 6 months of leaching in renewed conditions (see text). a) in the paste, much calcite (C) and partly crystallized CSH are noted; b) in fissures, calcite and CSH are dissolved.

Figure 7: ternary Al-Si-Ca diagrams showing the chemical compositions (EPMA) of various materials collected in gallo-roman baths (see text). Field 1: ground bricks; field 2: CSH-like minerals similar to hydrogarnets; field 3: mixture of hydrogarnets and calcite; field 4: pure calcite; field  $\text{Si}_2\text{AlCa.H}_2\text{O}$ .

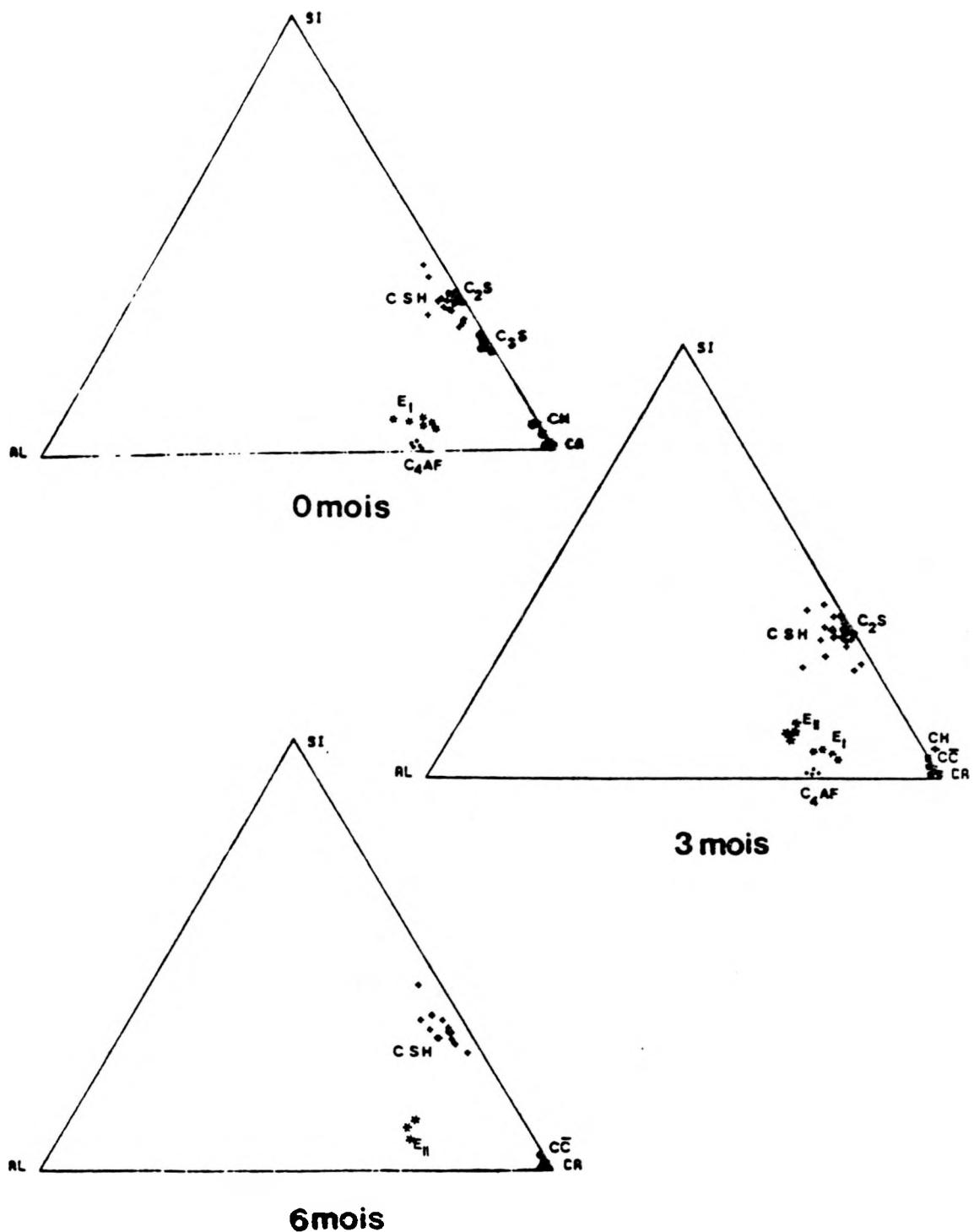


FIGURE 1

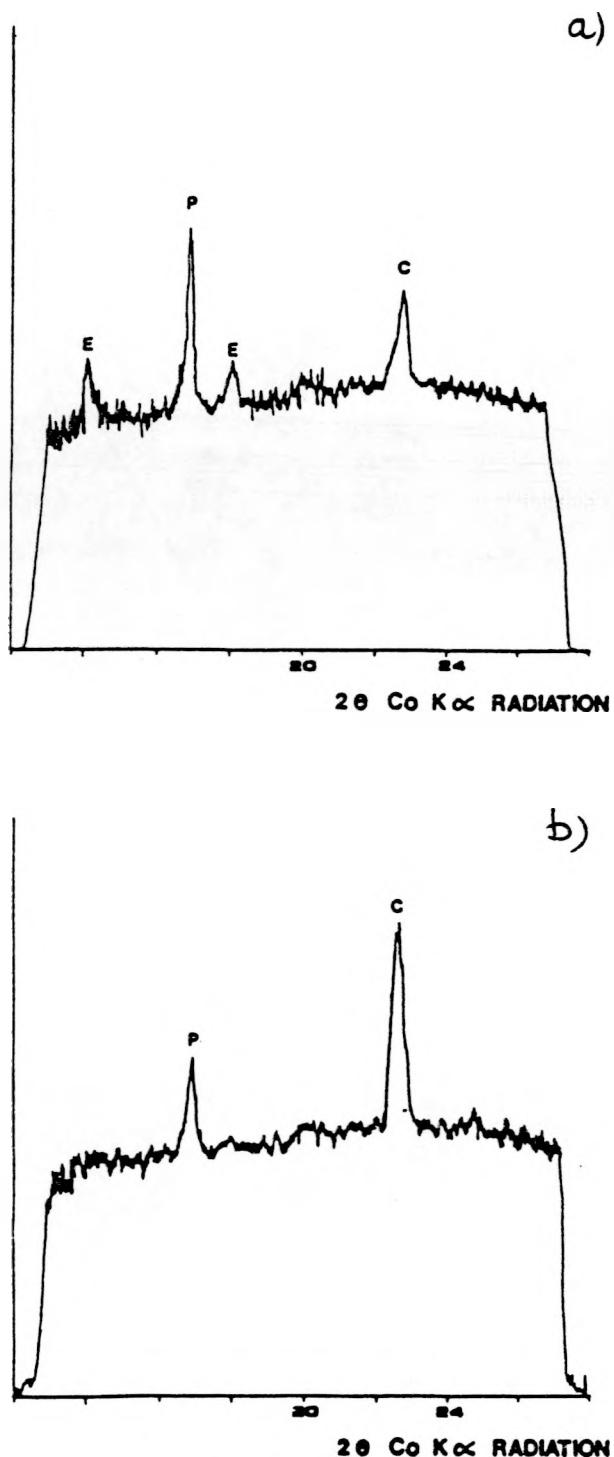


FIGURE 2

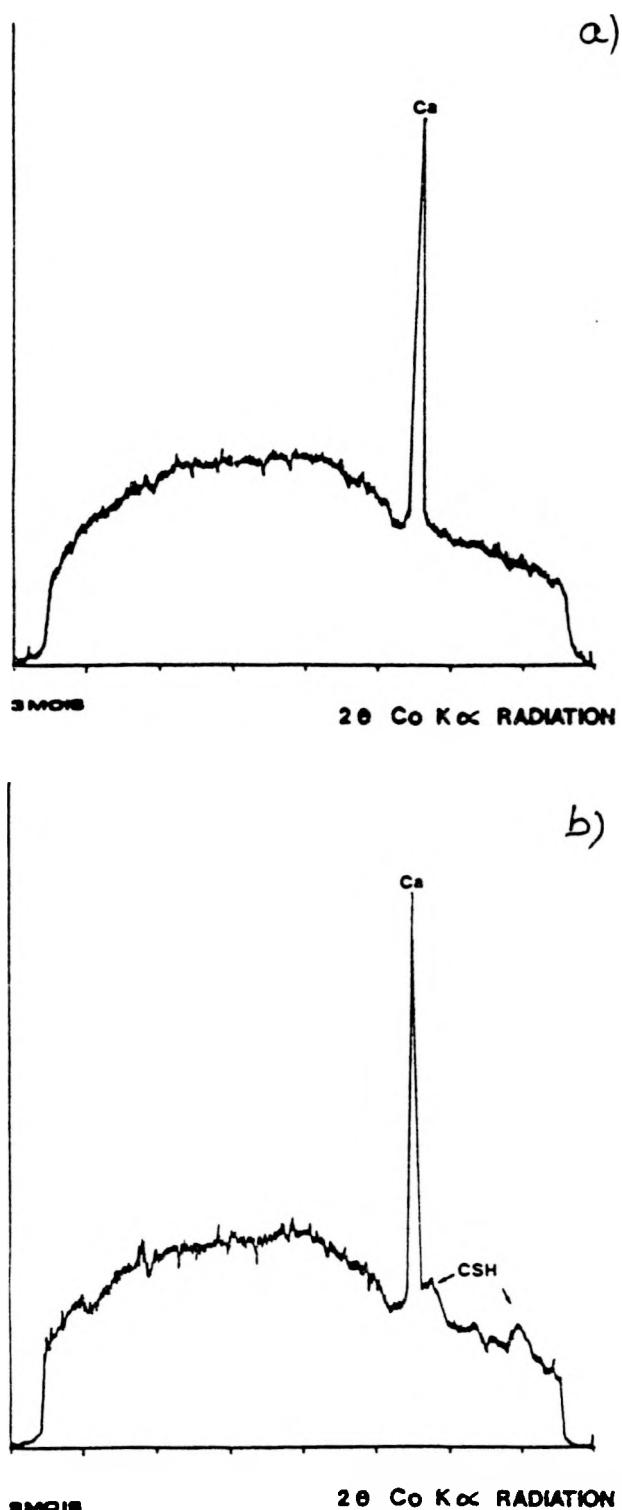
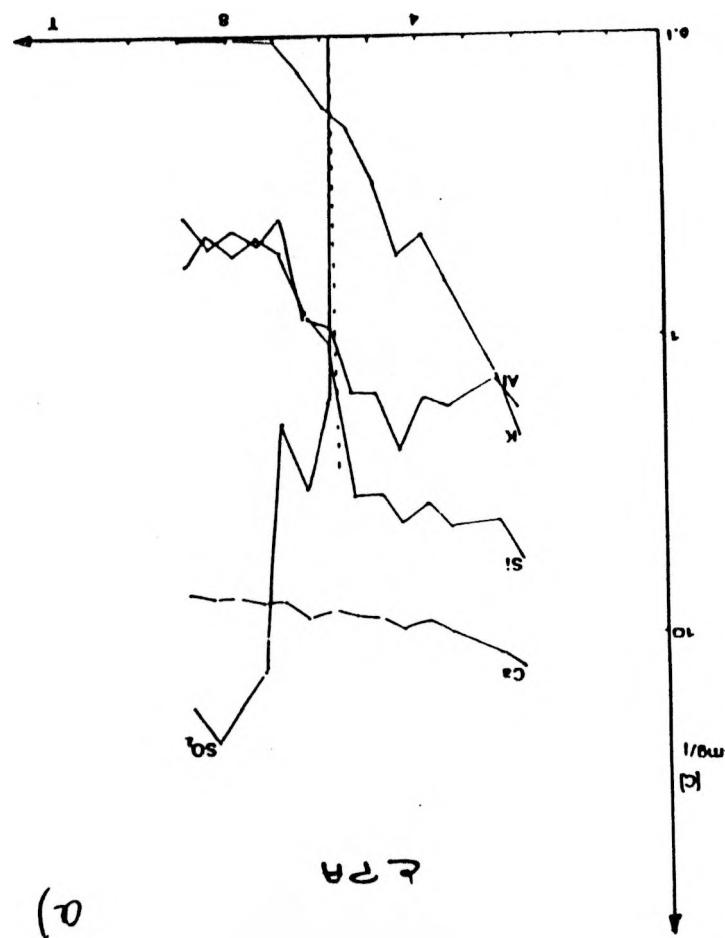
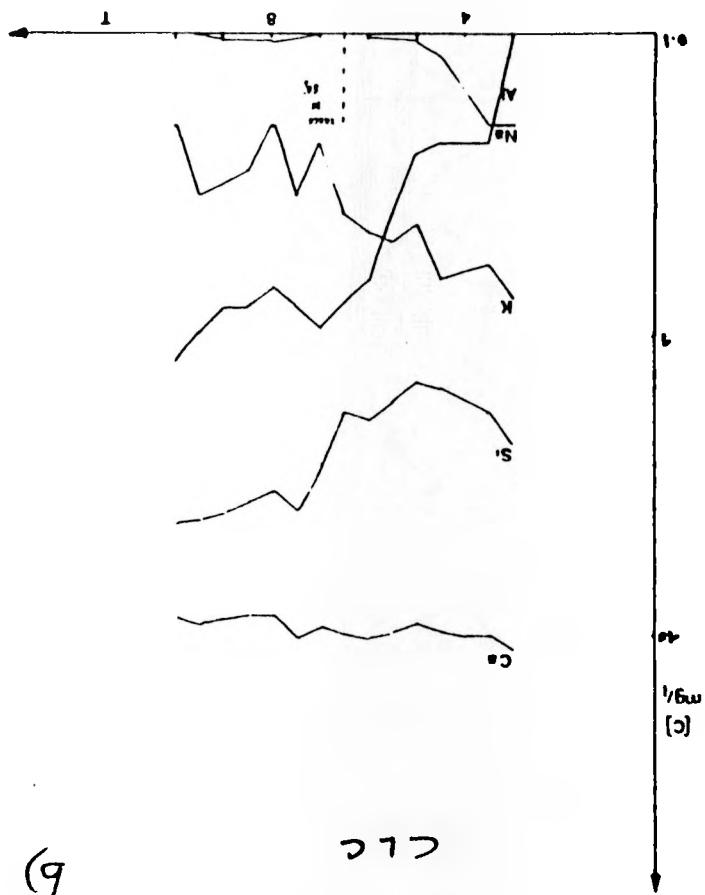


FIGURE 3

FIGURE 4

D-14



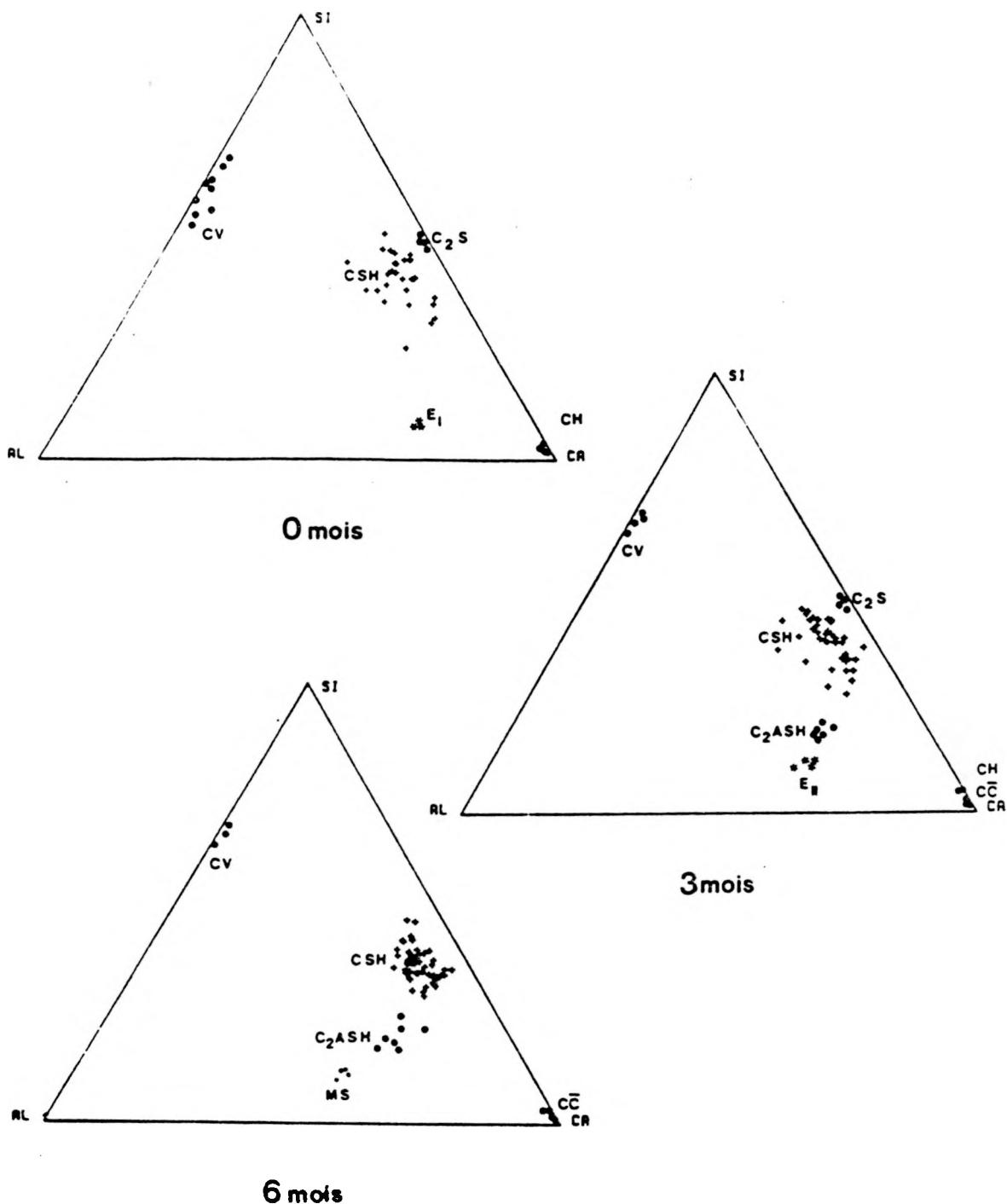


FIGURE 5

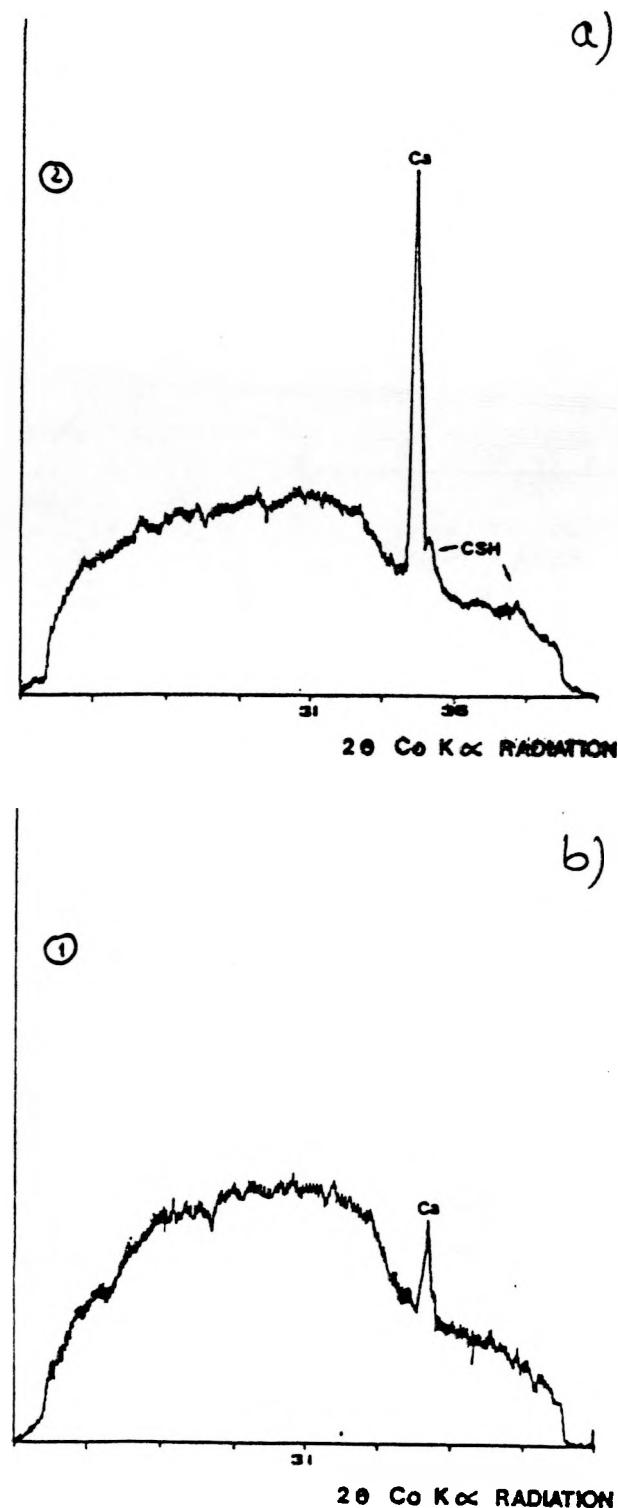


FIGURE 6

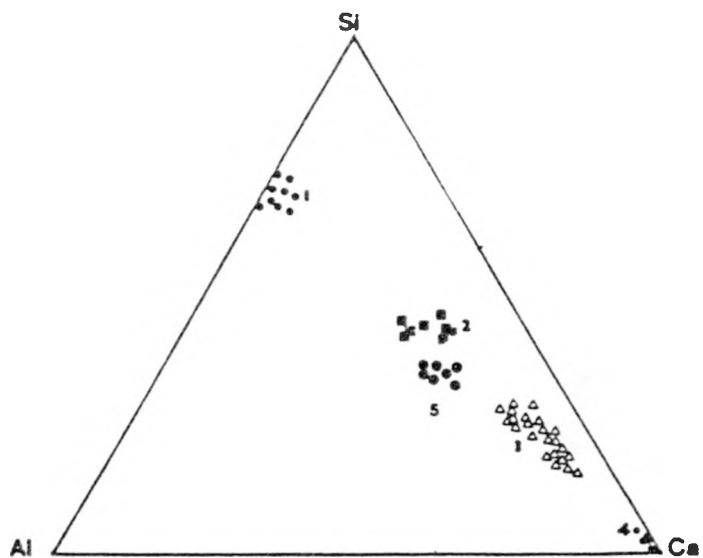


FIGURE 7

APPENDIX E

THE CADARACHE ALPHA AND ORGANIC INCINERATOR



C.E.A. - D.O.E.  
INCINERATION - WORK SHOP  
CADARACHE  
12 - 14 NOVEMBRE 1986

ORGANIC LIQUID WASTES INCINERATION  
B.BARTOLI - P.LISBONNE  
CENTRE D'ETUDES NUCLEAIRES DE CADARACHE  
D.R.D.D. - FRANCE

## 1. INTRODUCTION

In order to destroy organic liquids contaminated by radioelements we have selected incineration.

This treatment offers the advantage of reducing the volume of wastes considerably. Therefore an incineration plant has been built within the nuclear research center of Cadarache.

Starting operations, made with inactive organic liquids, were conducted from June 1980 to March 1981.

After this experimental work, the incineration plant was approved by safety authorities for the incineration of organic liquids contaminated by radioelements.

About 200 m<sup>3</sup> organic liquids, differing widely in their origins and nature, have been incinerated since the month of April 1981.

## 2. CHARACTERISTICS AND ORIGIN OF ORGANIC LIQUIDS

2.1 THE ORGANIC LIQUIDS, we are allowed to incinerate, have to meet the following specifications :

### 2.1.1 radiochemical standards

- . radioelements  $\alpha$  <  $37.10^6$  Becquerels/m<sup>3</sup>
- . radioelements  $\beta$   $\gamma$  <  $37.10^8$  Becquerels/m<sup>3</sup>  
(Co 60 <  $15.10^8$  Becquerels/m<sup>3</sup>)
- . tritium <  $37.10^8$  Becquerels/m<sup>3</sup>

### 2.1.2 Chemical and physical standards

- . chlorine < 20 % weight
- . phosphorus < 1 % weight
- . fluorine < 50 ppm
- . solid suspended matters < 5 % weight

Before incineration, we prepared a 5 m<sup>3</sup> batch of organic liquids that are homogenised and we check the specifications.

If chemical and physical standards are not reached, we can try to get them through additional treatments.

## 2.2 ORIGIN OF CONTAMINED ORGANIC LIQUIDS

Most of the organic liquids we usually incinerate come from four origins and are in nature very varied.

### 2.2.1 French nuclear research centres

Inside every centre there is a radioprotection department (SPR) that collects organic liquids used for the chemical treatment of nuclear materials or for cleaning contaminated materials.

These liquids are mainly :

- . solvents, such as tributyl phosphate or triaurylamine, used for refining uranium or plutonium
- . chlorinated hydrocarbons such as trichlorethylene

2.2.2 A specialized department (APSN), belonging to the Health Protection and Nuclear Safety Institute (IPSN) of the Atomic Energy Commission (CEA), must gather all contaminated organic liquids generated by small manufacturers in FRANCE such as hospitals, universities, industrial research centers.

These organic wastes are mainly scintillation liquids

### 2.2.3 Nuclear power reactors worked by the EDF

They mainly generate mechanical oils.

### 2.2.4 Industrial plants of COGEMA company

They generate also :

- . tributylphosphate
- . chlorinated solvents
- . various oils coming from mechanical equipments used for uranium or plutonium production.

## 3. DESCRIPTION OF THE INCINERATION PLANT

The standard characteristics of the incineration plant are the following :

- thermal power : 200.000 kcal per hour
- liquid flow : 20 to 50 liters per hour depending on heat of combustion
- combustion temperature : about 900°C

The main steps of incineration process are the following :

- reception and preparation of organic liquids to be burnt
- incineration
- filtration and purification of combustion gases
- removal and embedding of the incineration ashes

### 3.1 RECEPTION AND PREPARATION OF ORGANIC LIQUIDS

This unit has equipment designed to transfer liquid, from their various packing containers into a tank having a meshscreen of 1 mm in size.

The liquid then passes through a 300 microns cartridge filter and is poured into a 5 m<sup>3</sup> tank equipped with an impeller for continuous homogenisation.

In this way, we obtain a homogeneous batch ready for incineration. Beforehand, we take from this batch a sample in order to check radiochemical specifications.

### 3.2 INCINERATION

The incinerator plant is composed of burners, horizontal combustion chamber, followed by vertical chamber for cooling gases.

The pilot burner is fed with propane fuel gas and ignites the main burner. During starting time the main burner is first fed with fuel oil, until the kiln temperature reaches 900°C.

At this moment, contaminated organic liquids are injected through the burner in place of fuel oil.

Combustion is controlled by regulating the flows of organic liquids and combustion air.

The shape of the horizontal combustion chamber is cylindrical (900 mm diameter, 3000 mm length). It is made of special refractory bricks, a sheet of diatomite bricks, then insulating lining with mineral fibers and an external shell made of steel (6 mm in thickness). With this structure, external temperature of the shell stays lower than 50°C.

The vertical chamber for cooling gas is also cylindrical in shaped (600 mm in diameter, 4000 mm in height).

At the top of this chamber, demineralised water is injected counterflowing in order to lower the gas temperature to 650°C.

### 3.3 FILTRATION AND PURIFICATION OF COMBUSTION GAS

The combustion gases, successively flow through a prefiltration unit, a filtration unit and a water sprayed tower.

- . The prefiltration unit is equipped with filtering bags made of PTFE ; the maximum temperature allowed is 200°C. For this purpose, air at room temperature, is sprayed into the gaseous flux just before the prefiltration unit. Solid particles are caught on the external side of the filtering bags which are cleaned by counterflow blowing air. The solid particles then fall down to the bottom of the prefiltration unit.
- . Unit filtration has five absolute filters, made of fiber glass. Retention efficiency of each absolute filter is 99,9 % according to the standard AFNOR X 44.011. The working temperature must be lower than 200 °C. Coming out of the filtration unit the gases are cleansed of the dust particles, the average size being higher than 0.3 microns, but still contained acid compounds formed during the incineration. They are neutralised by sodium hydroxyde solution. The gas-liquid contact is obtained by spraying solution with a hydro-ejector. Two fans for extracting the gases are placed after the washing device and maintain the pressure inside the incinerator lower than 10 mm water column.

### 3.4 REMOVAL AND EMBEDDING OF THE INCINERATION ASHES

An initial device for the removal of the ashes is placed at the bottom of the vertical chamber.

Most of the ashes accumulate at the bottom of the prefiltration unit. An extraction device has been designed in order to transfer them into 100 liter containers where the ashes are kept before conditionning. The embedding of the ashes is processed into a well-fitted matrix based on thermosettle resins.

## 4. THE RESULTS OF EXPERIMENTS

4.1. The incineration plant works continuously five days a week. The resulting interruption, every week end, very often causes thermal stresses to the refractory materials of the kiln. In spite of this, the refractory bricks appear to be in satisfactory condition and do not present abnormal corrosion.

For maintenance, the front lining, surrounding the burner is changed every year. The incinerator has been in operation for 5000 hours. During this cumulated time about 170 m<sup>3</sup> of contaminated organic liquids have been burnt, and their distribution is represented as follows :

- .  $35 \text{ m}^3$  of solvents composed with 30 % TBP
- .  $45 \text{ m}^3$  of chlorinated solvents
- .  $90 \text{ m}^3$  of scintillation liquids
- .  $30 \text{ m}^3$  mechanical oils.

At the beginning, this experimental incinerator had been used as a research and development plant. We have therefore defined operating conditions to incinerate contaminated liquids of widely various compositions.

4.2 The incineration of solvents containing TBP was the most difficult problem to solve. The chemical compounds, resulting from combustion and derived from phosphorus acid, very quickly clog PTFE bog filters. To avoid this trouble, we have selected a calcium salt which is injected directly into the combustion chamber and neutralises phosphoric acid which is converted into calcium phosphate. The ashes formed this way are not sticky and are easily removed from the bog filters. Their apparent density varies from 0.3 to 0.4  $\text{g/cm}^3$ . About 70 kg ashes are formed for every  $1 \text{ m}^3$  TBP solvent incinerated.

4.3 The incineration of the other organic liquids does not present the same difficulties except if both chlorine and phosphorus are present.

For every  $1 \text{ m}^3$  of organic liquids incinerated about 7 kg of ashes are generated and this represents a very interesting concentration factor. Moreover ash density varies from 0.1 to 0.3  $\text{g/cm}^3$ .

4.4 More than 99 % of the radioactivity content, contained in the organic liquids, is concentrated into the ashes which will be embedded in thermoset resins.

Chemical and physical characterisations of the ashes have been determined relative to their origin and have been used to define the embedding process.

4.5 The other wastes resulting from the incineration are the alkaline solutions used for the neutralisation of acid vapors present in the combustion gas.

The alkaline solutions have practically no radioelements and the  $\alpha$  content is lower than  $37.10^3 \text{ Bq/m}^3$ . Therefore these liquid effluents are considered to be inactive chemical effluents.

The gases are released into the atmosphere but their contents of radioelements  $\alpha \beta \gamma$  are continuously monitored. The average  $\alpha$  activity remains lower than  $3700 \text{ Bq}$  per  $\text{m}^3$  of gases. On the gas flux there is an one line analyser with an alarm value set at  $10^5 \text{ Bq}$ . If we go beyond this limit the incineration is stopped and the origin of this irregularity must be found.

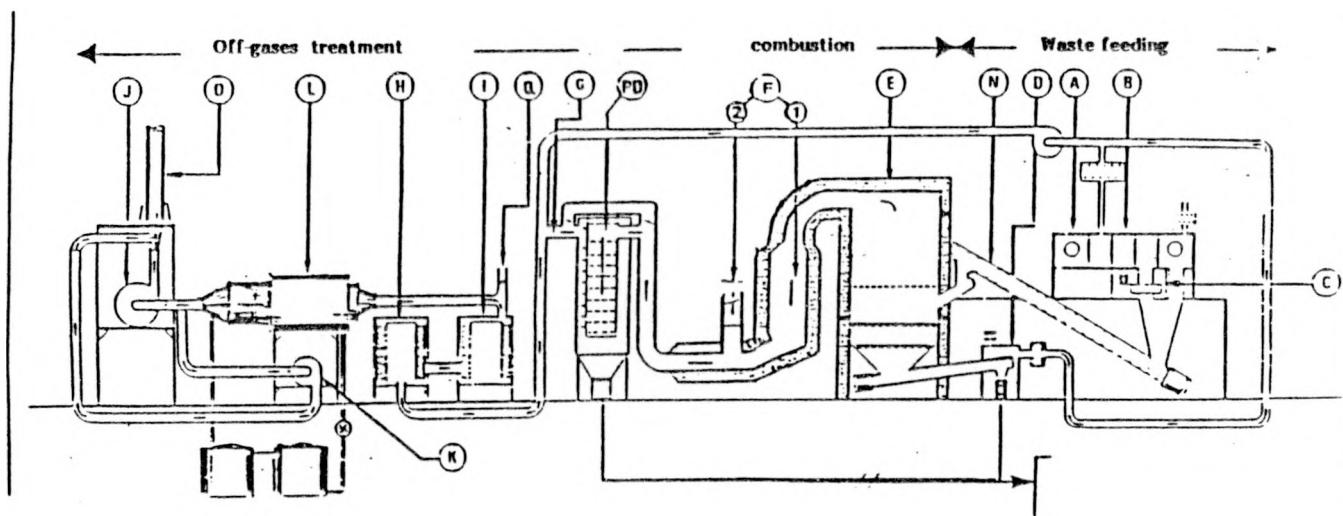
## 5. CONCLUSION

On the basis of five years of operation the incineration plant has shown reliable operating conditions in the destruction of various organic liquids contaminated with radioelements  $\alpha \beta \gamma$ .

The capacity of incineration ranges from 20 l/h to 50 l/h depending on the heat of combustion of organic liquids. Not only are we using this incineration to destroy organic liquids, but at the same time we are continuing research and development programs in order to improve unit operation of the process (for example gas filtration) or to obtain better knowledge concerning the lifetime of materials planned in the construction of future incinerator plants.

C. E. N. - CADARACHE

INCINERATOR SYNOPSIS



**A = WASTE INTRODUCTION**

**B = WASTE SORTING**

**C = SHREDDER**

**D = ASHES EXTRACTION**

**E = KILN**

**F = AIR COOLING n° 1**

**G = WATER SECURITY COOLING**

**H + I = HEPA FILTERS**

**J = MAIN BLOWER**

**K = SECURITY BLOWER**

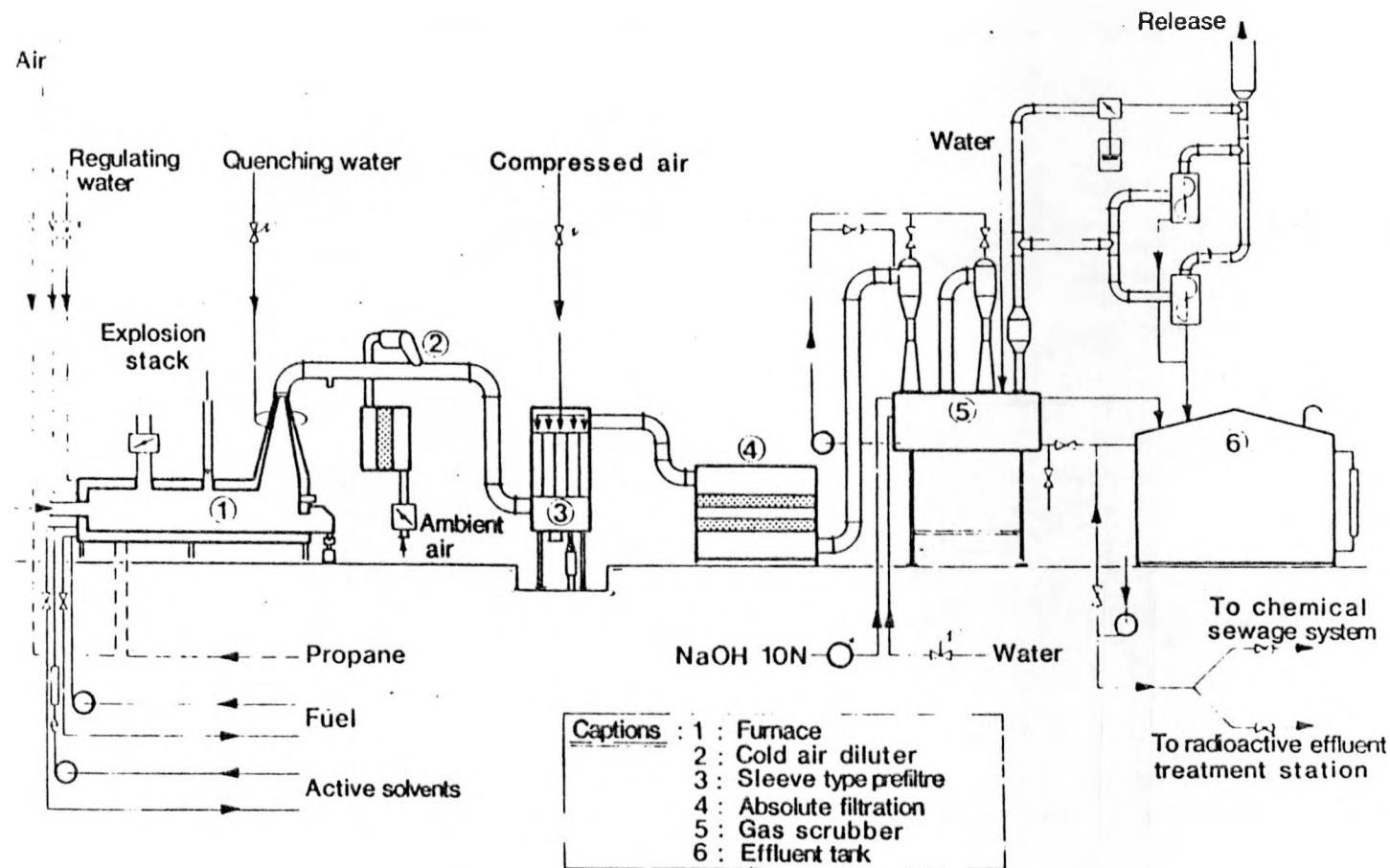
**L = OFF-GASES WASHING**

**O = STACK**

**Q = AIR COOLING n° 2**

**N = SHREDDED WASTE FEEDING  
(ENDLESS SCREW)**

**PD = CLEANING SYSTEM  
(COMPRESSED AIR REVERSE PULSE)**



## INCINERATION OF RADIOACTIVE ORGANIC LIQUIDS

**APPENDIX F**

**THE VALDUC AGENDA**



CEA/DOE AGREEMENT  
VALDUC VISIT  
19 NOVEMBER 1986

9 h 15 - ARRIVAL AT VALDUC

9 h 30 )

) TRITIATED WASTES REPROCESSING EQUIPMENTS

11 h 30 )

11 h 30 )

) TRITIATED WASTES STORAGE

12 h 10 )

12 h 15 )

) LUNCH

13 h 50 )

14 h )

) WASTES

15 h )

15 h 05 )

) DRINKS

15 h 25 )

15 h 30 DEPARTURE TO DIJON

(Arrival 16 h 30)

CEA/DOE AGREEMENT  
VISIT OF THE TRITIATED WASTES REPROCESSING EQUIPMENTS  
19 NOVEMBER 1986

9 h 30 - ARRIVAL IN THE TRITIUM BUILDING

- HEALTH PHYSICS CONTROL ROOM
- MASS SPECTROMETRY ANALYSIS
- DETRITIATION UNITS (Gazeous effluents)
- TRITIATED WATER REPROCESSING

BREAK - VIDEO FILM : "DISMANTELMENT OF A CAISSON"

11 h 30 - DEPARTURE TO THE STORAGE SITE

In addition to the U.S. workshop participants, those present during the tour of Valduc were:

Mr. Vergne, Director of Valduc  
Mr. Cluchet, CEA/DAM/Paris  
Mr. Cortella, Director of Health and Safety, Valduc  
Mr. Giroud, Manager of the Tritium Waste Treatment Facility  
Mr. Boucquey, Design Engineer  
Mr. Rabot, Design Engineer  
Mr. Radecki, Analyst for Tritium  
Mr. Ochem, Manufacturing and Processing  
Mr. Durand, Maintenance  
Mr. Morin, Analyst  
Mr. Rolland, Chief of Services for Plutonium  
Mr. Martinez, Plutonium Recovery/Incineration  
Mr. Malfondet  
Mr. Quinnez

**APPENDIX G**

**ZUBLIN HAZARDOUS WASTE ISOLATION TECHNOLOGIES**



HIGH SECURITY WASTE DISPOSAL SITES

Spatial Facilities  
Silo Facilities

### Introduction

High security waste disposal sites are long-term depositories for any pretreated hazardous waste. Pretreatment is physical, chemical or thermal.

Maximum environmental protection is obtained by the controlled encapsulation of hazardous waste as it leads to the long term withdrawal of hazardous waste from the environment.

Participation in the physical and chemical cycles that earth matter otherwise undergo is ruled out.

Züblin has developed two design concepts for future hazardous waste disposal sites:

- spatial facilities
- silo facilities.

The following safety requirements and fundamental rules were taken into consideration during design:

- together the composite bottom liner and final cover systems should prevent the uncontrolled entry of leachate and gas generated in the facility into the surrounding environs.
- precipitation should be hindered from entering the waste deposit both during operation and after closure so as to minimise the leachate quantity.
- an automatic inspection and damage detection system should be incorporated in the bottom liner and final cover systems.
- all damaged parts should be repairable.
- the load-bearing reinforced concrete structure should not have to incorporate a sealing function

- the composite bottom liner system should be situated above the ground water-level. Depending on the depth to the load-bearing subsoil either shallow or deep foundations should be constructed.
- the hazardous waste disposal facility should be located centrally with respect to the facility users (ie waste producers) as well als having an adequate infrastructure (roads etc.)
- the facility should be planned for future expansion.
- the natural surrounds should be restored after closure of the facility by replanting the final cover system.

#### High Security Waste Disposal Site

as a spatial facility

Hazardous waste is deposited on a reinforced concrete slab which in turn is supported by columns to produce an accessible area underneath the slab. Embankments form the edges of the facility.

The base of the embankment can be at a height of 10-15 m if a retaining wall is constructed along the perimeter of the facility.

The spatial facility can be of any size and can be extended at any time. The maximum possible height of fill is largely determined by the load-bearing capacity of the subsoil.

The design concept will now be described. The example illustrates a spatial facility with a deposit volume of 160.000 cbm.

Load-bearing reinforced concrete structure

The model has a plan area of 150 x 150 m and a 15 m height of fill. The reinforced concrete base slab with its composite bottom liner is designed as a monolithic slab which is supported on columns with a grid space of 3 x 3 m. The shallow foundation slab is designed similar to the base slab. The clearance between the base slab and the foundation slab is 1,80 m.

The base slab is divided by joints into subsections of 30 x 30 m to compensate for the possible deformations caused by differential settlement, temperature variations and shrinkage.

The whole slab is constructed with a gradient of 1,5 % to facilitate the drain-off of leachate.

Alternatively the base slab can be subdivided into even smaller sections which are connected together with expansion joints.

This design facilitates the replacement of a damaged bottom liner as only the slab in question must be dismantled.

Incorporated compensation slabs which are supported during the dismantling of the base slab stop the deposited waste from collapsing in on the area. The spatial facility also incorporates a final cover system. The surface run-off water flows into a specially constructed drain.

Ventilation shafts situated on two opposite sides of the facility ventilate the accessible base. The shafts are located every 30 m and have internal dimensions 1,5 x 3 m.

If necessary ventilating systems can be installed in the shafts. An access ramp leads to the base slab. By constructing a retaining wall, 10 m high for example, along the waste deposit bounda-

ry the deposit volume can be substantially increased.

The retaining wall should be constructed as a cavity wall to facilitate supervision. The cavity can also then be used to ventilate the accessible base. By increasing the height of fill from 15 m to 40 m the deposited volume on an area of 150 x 150 m increases from 160.000 cbm to 670.000 cbm.

The higher surcharge load requires an accordingly strengthened load-bearing reinforced concrete structure and a narrower column grid.

#### Composite bottom liner to prevent leachate migration

The bottom liner on the base slab is constructed as a composite system with incorporated drainage layers. The multi-layered liner consisting of low-permeability soil liners and flexible membrane liners enables the base liner system to be monitored at all times and can also be repaired if needed.

If the base of the sloped embankment is heightened (ie with the construction of a retaining wall) the wall is lined with a number of flexible membranes. The leachate collects in the drainage layer. The pipe network is monitored at the control sums.

A secondary leachate collection system situated between the two flexible membrane liners acts as a leak detection system and automatically detects liquids entering through a leaky flexible membrane. By subdivision of the flexible membrane liner into small areas the defect can be easily located. The damaged area can then be sealed by injecting grout inbetween the two flexible membrane liners.

An alternative design for the construction of the base slab can

be seen in Fig. 5. The bottom liner consisting of two flexible membrane liners directs the leachate into a gutter which is constructed in the expansion joint between the separate slabs.

#### Final cover system

The purpose of a final cover system is to provide long-term minimization of migration of liquids through the closed landfill as well as to control the venting of gas generated in the facility.

The barrier layer usually used are flexible membranes or low permeability soil liners or a combination of both.

The surface run-off water flows into a drain at the foot of the embankment and flows into the sewer system.

If a generation of gas in the facility is anticipated gas venting layers are placed. The collected gas can then be directed to a controlled discharge point where it can be used or disposed of by incineration.

#### Operation of the spatial facility

The hazardous waste is installed and compacted in layers. The section in operation is roofed over with a mobile covered portal frame structure whilst the rest of the facility is temporarily covered with a flexible membrane liner. The hazardous waste is always deposited under strict supervision and under cover away from the elements (see front page).

High Security Waste Disposal Sites

as a silo facility

The hazardous waste is deposited in separate, free-standing, circular, cylindrical, reinforced or prestressed concrete structures. An accessible base and a solid concrete roof are incorporated in the waste silo. If it is ever necessary to empty the silo the roof can be removed.

The height of such a waste-silo is restricted to between 20 and 30 m due to economic reasons and the load-bearing capacity of the subsoil.

The outer silo diameter should also not be in excess of 50 m. The facility can be covered with earth.

In comparison with the spatial facility this design concept has the following added advantages:

- different types of hazardous wastes can be stored separately.
- the liner system can be designed for a specific type of hazardous waste.
- the hazardous waste is covered and therefore protected from the elements (most importantly precipitation) at all times due to the solid concrete roofing after closure and the temporary roofing during operation.
- the state of each waste silo can be individually inspected and monitored.
- future waste recycling is greatly simplified due to the fact that the waste-silo can be easily emptied.

The design concept will now be described. The example illustrates a silo facility composed of 9 waste-silos with a total deposit volume of 160.000 cbm.

Load-bearing reinforced concrete structure

The nine free-standing waste-silos are erected in a double row with a minimum distance of 1,0 m between each silo. This enables the silos to be visually inspected from the outside. The earth covered alternative can also be visually inspected by constructing a retaining wall all along the periphery of the waste-silos. In this way an inspection passage is formed around each silo.

Each waste silo has a massive concrete roof. The intervening spaces between the waste-silos are also covered over.

This cover is then in turn covered with top soil and planted with vegetation.

The outer walls of the individual waste-silos in this example are cylindrical shells of 40 m diameter and 15 m height of infill. An access and inspection shaft is installed in the centre.

With the installation of another cylindrical shell of 15 m diameter one can store two different hazardous wastes in the one waste-silo.

The construction elements - outside silo wall, silo base and silo roof are structurally unconnected so that the statics of the structure are uncomplicated and clearly defined.

Just as with the spatial facility the base of the waste-silo can also be subdivided into smaller areas with expansion joints.

Composite bottom liner and final cover systems

The same liner systems can be used as in the spatial facility. The final cover system is graded down towards the centre of the waste-silo.

Operation of the silo facility

The facility in operation has a temporary roofing structure. Underneath this roofing structure is a portal crane with which the individual chambers can be filled. When the silo is full up the permanent final cover system and the roof covering is installed under the protection of the temporary roofing using the crane.

The crane and temporary roofing can then be dismantled.

Cost comparison of the two described concepts

Fig. 13 shows a cost comparison of the two concepts based on a deposit volume of 160.000 cbm.

The costs shown are investment costs only excluding land and development costs and VAT.

Fig. 1-13 TranslationFig. 1 Prinzipieller Aufbau einer Flächenanlage =  
General Layout of a Spatial Facility

From left to right

- Regenrinne = drain
- Lüftungs- und Kanalgang = Ventilator and supervision passage
- Oberflächenabdichtung = final cover system
- Müll = waste deposit
- Abdichtung und Drainage = composte bottom liner with drainage layer
- begehbarer Basis als Stahlbetonkonstruktion = accessible reinforced concrete base
- Gasentnahme = gas discharge point
- Flächendrainage = drainage layer
- Sickerwasserentnahme = leachate discharge point
- Lüftungsschacht = ventilation shaft

Fig. 2 Beispiel einer Flächenanlage =  
Spatial Facility

- 1,5 % Gefälle = 1.5 % gradient
- Fuge = joint
- Sickerwasserreinigung = leachate pipe network
- Einzelfeld 30/30 m = subsection 30/30 m
- Sickerwasserbehälter = leachate collection tank
- Kontrollschaft = inspection chamber (sump)
- Entlüftungsschacht = ventilation shaft
- Kontrollstation = inspection HQ

Fig. 3 Ausbildung des Deponierandes =  
Detail of the Edge of a Spatial Facility

- Müll = waste deposit
- Abdichtung und Drainage = composite bottomliner with drainage layer
- Deponieplattform = base slab
- begehbarer Basis = accessible area
- Gründungssohle = foundation slab
- Abdichtung und Drainage = final cover system and drainage layer
- Kontrollschacht = inspection chamber (sump)
- Lüftungsschacht = ventilation shaft

Schematischer Aufbau einer Basisabdichtung =  
Composite Bottom Liner

- Müll = waste deposit
- Drainage = drainage
- HDPE-Dichtungsbahn = HDPE flexible membrane liner (FML)
- Tondichtung = low permeability clay liner
- Sand = sand
- Lehmschlag = puddle clay
- Stahlbeton = reinforced concrete (coated) (beschichtet)

Schematischer Aufbau einer Oberflächenabdichtung =  
Final Cover System

- Wurzelboden = topsoil
- Filterkies = filter layer  
(for rest see composite bottom liner)

Fig. 4 Auswechslung eines Plattformteils =  
Replacement of a Base Slab Subsection

- Filterschicht = drainage layer
- Plattformteil = base slab
- Vlies = filter layer
- Müll = waste deposit
- Hilfsstützen = temporary supports
- Bodenplatte = foundation slab
- Ausgleichselement = compensation slab
- Raumfuge = expansion joint

Fig. 5 Raumfuge zwischen Plattformteilen =  
Expansion Joint Between Base Slab Subsections

- Kunststoff-Dichtungsbahnen = HDPE-FML
- Drainschicht = drainage layer
- Rinne aus Kunststoff = plastic gutter
- Raumfuge = expansion joint
- säurefester Formstein = acid resistant brick
- Gefälle = grade

Fig. 6 Modellaufnahme einer Flächenanlage =  
Picture of a Model of a Spatial FacilityFig. 7 Behälterkonstruktion, Querschnitt =  
Silo Construction, Section

- Elastomer-Lagerstreifen =
- Etb.-Stützen = reinforced cone (R.C.) columns
- Einstiegsschacht = access shaft
- Stb.-Ft.-Platten = reinforced precast construction slab
- Stb.-Ft.-Träger = reinforced precast construction beams
- Stahlbeton = R.C.
- Stb.-Plattform (Ortbeton oder Fertigteile) = RC base slab

(cast in-situ or precast)

- Stb.-Bodenplatte = R.C. foundation slab
- Spannbeton = prestressed concrete

Fig. 8 Prinzipieller Aufbau einer Behälteranlage =  
General Layout of a Silo Facility

- Abdichtung = liner
- begehbar Basis = accessible area
- Flächendrainage = base drainage layer
- Kontrollschacht = inspection shaft
- Gasentnahme = gas discharge point
- Müll = waste deposit
- Sickerwasserentnahme = leachate discharge point
- ohne - + - mit Erdüberdeckung = without/with earthcover
- Kontrollgang um die Behälter = inspection passage around the silos
- Abdichtung und Drainage = liner and drainage
- Wurzelboden und Begrünung = topsoil and vegetation
- Decke mit Abdichtung = roof with final cover system
- GW = groundwater-level GWL

Fig. 9 Behälterkonstruktion, Horizontalschnitt =  
Silo construction, horizontal section

- begehbar Basis = accessible base
- Müll = waste deposit

Fig. 10 Mülleinbau = Facility in operation

- umlaufender Halbportalkran = semi-portal crane
- Kammer = chamber
- Oberflächenabdichtung = final cover system
- Dachträger = roof truss

Fig. 11 Behälteranordnungen = Possible Silo Layout

- a) freistehende Anlage in der Ebene = free-standing facility on the flat
- b) freistehende Anlage im Einschnitt - free-standing facility in a depression
- c) geschlossene Anlage mit Bepflanzung in Hanglage = covered facility with vegetation near a slope
- d) geschlossene Anlage mit Bepflanzung in der Ebene = covered facility with vegetation on the flat

Fig. 12 Beispiel einer Behälteranlage = A Silo Facility

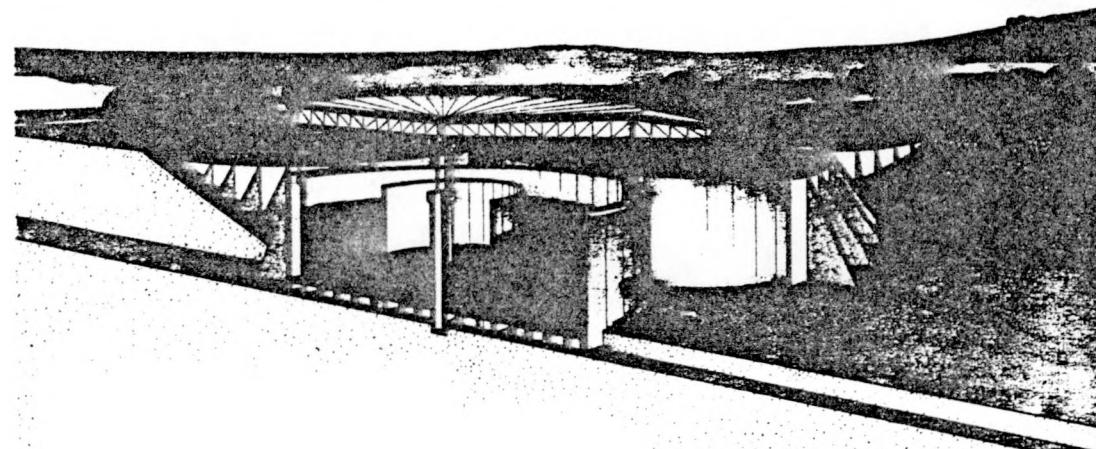
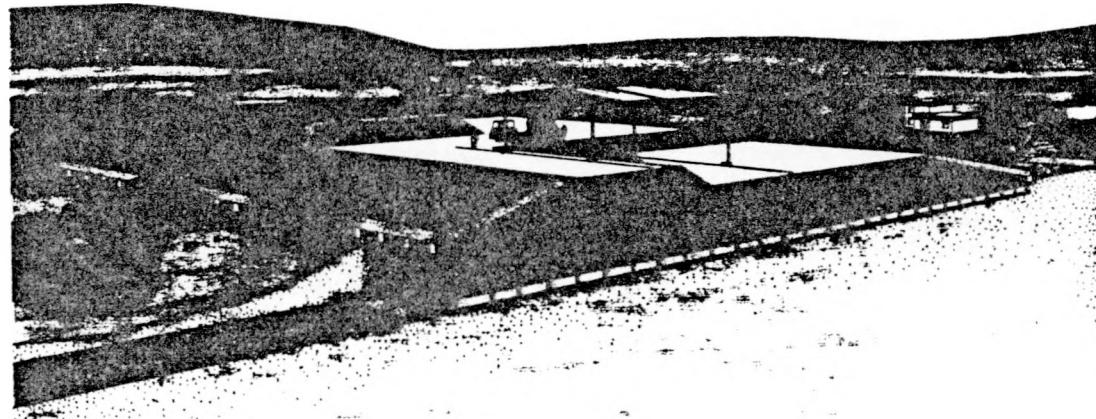
- 1 Hilfsbauten für den Betrieb = operation facilities
- 2 Winkelstützmauer = retaining wall
- 3 Behälterrohbau = concrete silo construction
- 4 umlaufender Halbportalkran = semi-portal crane
- 5 Dachbinder = roof truss
- 6 Behälterdeckel = roof slab
- 7 Endzustand = finished structure

Fig. 13 Kostenvergleich = Cost Comparison

- Kosten pro m<sup>3</sup> Müll = DM/m<sup>3</sup> waste
- Hochsicherheitsdeponie mit begehbarer Basis = spatial facility
- Hochsicherheitsabfalllager 9 Einzelbehälter = silo facility
- Kosten der Deponie = total facility cost

# Züblin-Hochsicherheitsdeponien

Flächenanlagen  
Behälteranlagen



## Allgemeines

Hochsicherheitsdeponien sind Langzeitabfallager, in denen physikalisch, chemisch und thermisch vorbehandelte Restabfallstoffe (Sondermüll) mit beliebiger Schadstoffbelastung gelagert werden. Ein Hochstmaß an Sicherheit für die Umwelt wird durch eine kontrollierte Einkapselung des Sondermülls, d. h. eine Herausnahme aus dem Stoffkreislauf, erreicht.

Züblin erarbeitete zwei Konzepte für Neuanlagen:

Hochsicherheitsdeponien als Flächenanlagen und

Hochsicherheitsdeponien als Behälteranlagen

Folgende Sicherheitsanforderungen und Grundsätze wurden hierbei verfolgt:

- Ein mehrfach wirkendes Abdichtungssystem schirmt das Sickerwasser und das Deponiegas von der Umwelt ab
- Feuchtigkeit aus Niederschlag wird sowohl im Betriebs- als auch im Endzustand vom Sondermüll ferngehalten, so daß hieraus kein zusätzliches kontaminiertes Sickerwasser entstehen kann
- Die Überwachung der Abdichtungen erfolgt durch ein automatisches Kontrollsystem
- Die vertikale und die horizontale Belastung aus dem Sondermüll wird über eine optisch kontrollierbare, von außen zugängliche Stahlbetonkonstruktion auf den tragfähigen Baugrund übertragen
- Sämtliche Anlagenteile sind reparierbar
- Die Stahlbetonkonstruktion hat nur Tragfunktion, keine Dichtfunktion
- Die Deponiesohle muß über dem Grundwasserspiegel liegen. Je nach Höhenlage des tragfähigen Baugrundes wird eine Flach- oder Tiefgründung vorgesehen
- Der Deponiestandort sollte sich zentral zu den Abfallverursachern befinden und verkehrsmäßig erschlossen sein
- Die Gesamtanlage muß erweiterungsfähig sein
- Der Landschaftsschutz ist zu beachten; er wird durch eine Bepflanzung der Deponiefläche erreicht

Titelseite:  
Graphik, Flächenanlage  
Desgl., Behälteranlage

# Hochsicherheitsdeponie...

## als Flächenanlage

Bei dieser Deponieanlage wird der Sondermüll über einer begehbarer Basis eingebracht und zu den Rändern hin abgeboscht. Die Böschungshöhe kann durch die hochgezogene Umfassungswand 10 m bis 15 m hoch sein. Die Deponie kann beliebig groß ausgebildet werden und ist erweiterbar. Die Füllhöhe wird im wesentlichen durch die Tragfähigkeit des Baugrundes begrenzt. Dieses Konzept wird an einem Beispiel mit einem Deponievolumen von  $V = 160\,000 \text{ cbm}$  erläutert.

### Stahlbetontragkonstruktion

Das Beispiel zeigt ein Modell mit einer Grundrissfläche von  $150 \times 150 \text{ m}$  und einer Ablagerungshöhe von 15 m. Die Deponieplattform mit darüber liegender Abdichtung wird als punktförmig gestützte Massivplatte ausgebildet, die auf Stützen im Raster von  $3 \times 3 \text{ m}$  gelagert ist. Die flach gegründete Bodenplatte wird statisch wie die Plattform ausgebildet. Zwischen Plattform und Bodenplatte ist für Kontrollzwecke ein Lichtraum von  $1.80 \text{ m}$  angeordnet. Zum Ausgleich von Verformungen infolge Temperatur, Schwinden und Setzungen wird die Konstruktion durch Fugen in Einzelfelder von  $30 \times 30 \text{ m}$  unterteilt. Um das Sickerwasser abzuleiten, erhält die gesamte An-

lage eine Neigung von 1,5 % in der Diagonale.

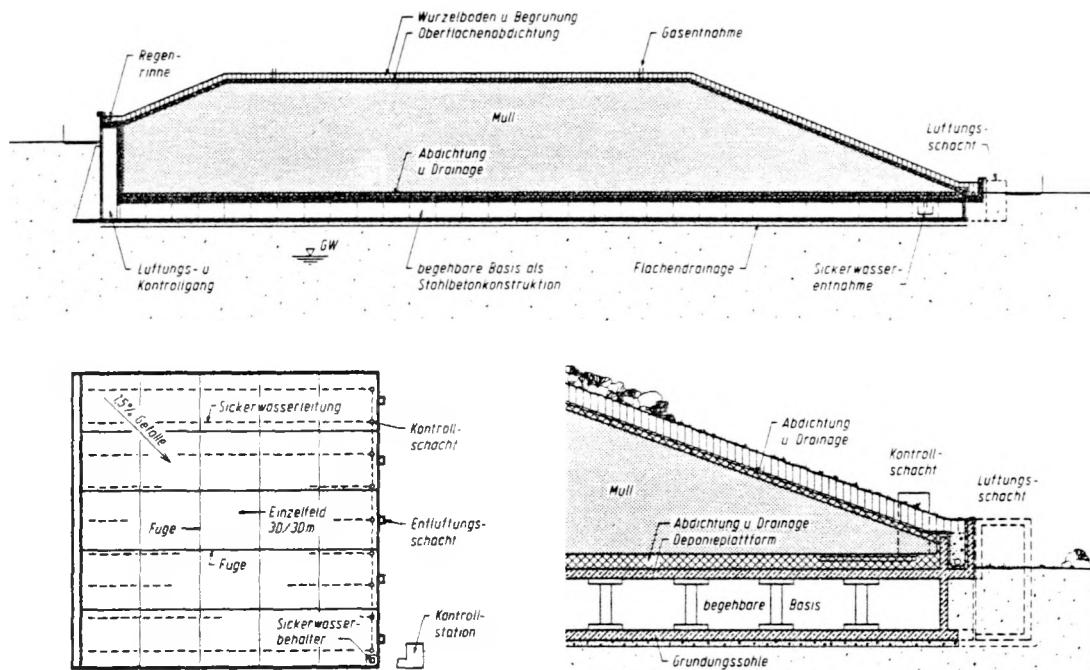
Alternativ kann die Deponieplattform in einzelne, kleine Plattformteile unter Bildung von Raumfugen unterteilt werden. Muß im Schadensfall die Plattformabdichtung ausgewechselt werden, so kann das betreffende Plattformteil leicht demontiert werden. Um ein Nachrutschen des Mülls ganz auszuschließen, werden über der Plattform Ausgleichselemente, welche vor der Demontage des Plattformteils unterstützt werden, angeordnet. Die Deponie ist an ihrer Oberfläche abgedeckt; das Niederschlagswasser wird in einer umlaufenden Regenrinne abgeleitet. Zur Entlüftung der begehbaren Basis sind auf zwei gegenüberliegenden Seiten der Deponie Lüftungsschächte angeordnet. Diese Schächte haben einen Abstand von  $30 \text{ m}$  und einen lichten Querschnitt von  $1.5 \times 3.0 \text{ m}$ . Bei Bedarf werden an den Schächten Ventilatoren installiert. Ferner ist eine Zufahrtsrampe zur Plattform vorhanden. Bei Anordnung einer Winkelstützmauer längs des Deponierandes von z. B.  $10 \text{ m}$  Höhe kann das Lagervolumen erheblich erhöht werden. Um eine Kontrolle an den Seiten zu ermöglichen, werden die Stützwände doppelschalig ausgeführt. Dieser Zwischenraum wird zusätzlich zur Entlüftung genutzt.

Bei Erhöhung der Füllhöhe von 15 m auf 40 m und durch eine  $10 \text{ m}$  hohe Winkelstützmauer kann bei einer Grundfläche von  $150 \times 150 \text{ m}$  das Fassungsvermögen von  $160\,000 \text{ cbm}$  auf  $670\,000 \text{ cbm}$  gesteigert werden. Die große Auflast erfordert in diesem Falle eine entsprechend ausgebildete Tragkonstruktion mit stärkeren Stahlbetonplatten und einem engeren Stützenraster.

### Abdichtung gegen Deponiesickerwasser

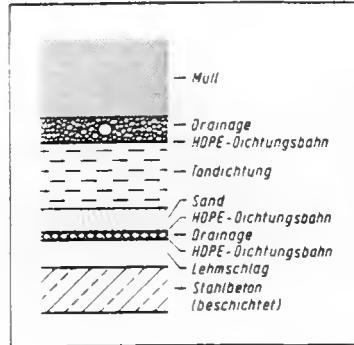
Die Basisabdichtung auf der Plattform wird als Kombinationsabdichtung mit Drainageschichten ausgebildet. Die mehrlagige Abdichtung aus mineralischen Schichten und Kunststoffbahnen ist kontrollierbar und reparierbar. Bei hochgezogenem Böschungstuß wird die Wand mit mehrlagigen Kunststoffbahnen abgedichtet. Das Deponiesickerwasser wird in die Drainageschicht abgeleitet. Die Drainagerohre sind über seitliche Schächte kontrollierbar. Das automatische

- 1 Prinzipieller Aufbau einer Flächenanlage
- 2 Beispiel einer Flächenanlage
- 3 Ausbildung des Deponierandes

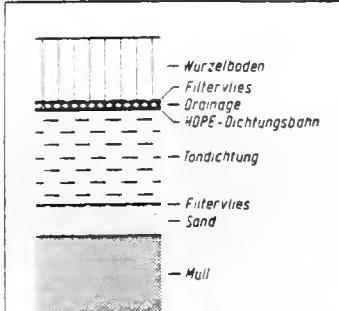


# Hochsicherheitsdeponie...

## als Flächenanlage



Schematischer Aufbau einer Basisabdichtung



Schematischer Aufbau einer Oberflächenabdichtung

wartungsfreie Kontrollsystem zeigt sofort an, wenn aufgrund unidichter Stellen zwischen den HDPE-Dichtungsbahnen Sickerwasser eintritt. Durch Einteilung der HDPE-Bahnen in getrennte Felder ist eine Lokalisierung der Schadstelle möglich. Die Schadstelle kann nachträglich durch Einpressen von Dichtungsmaterial zwischen die HDPE-Bahnen abgedichtet werden.

Bei der alternativen Plattformausbildung

gem. Bild 4 besteht die Basisabdichtung aus Kunststoffbahnen, welche anfallendes Sickerwasser in Rinnen ableiten, die unter den Raumfugen angeordnet sind.

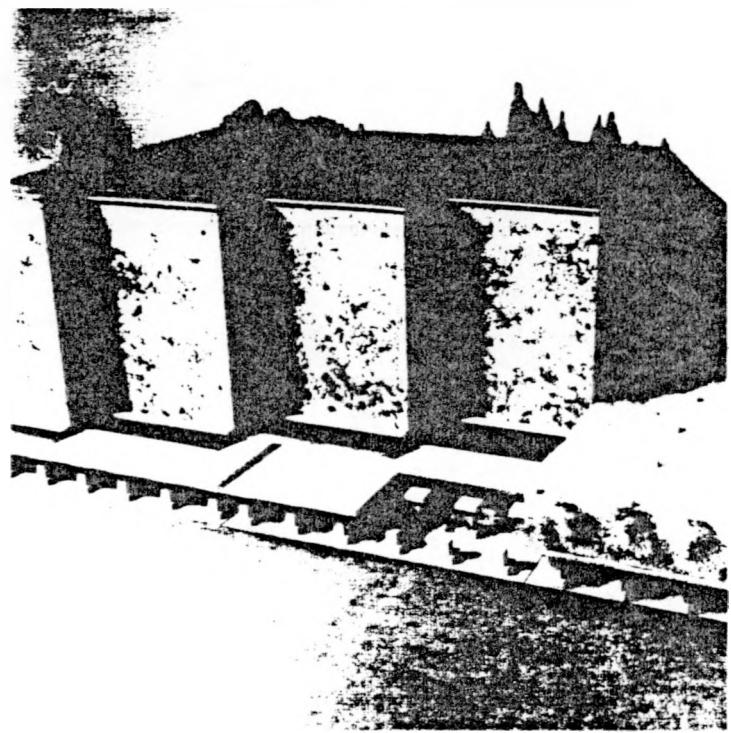
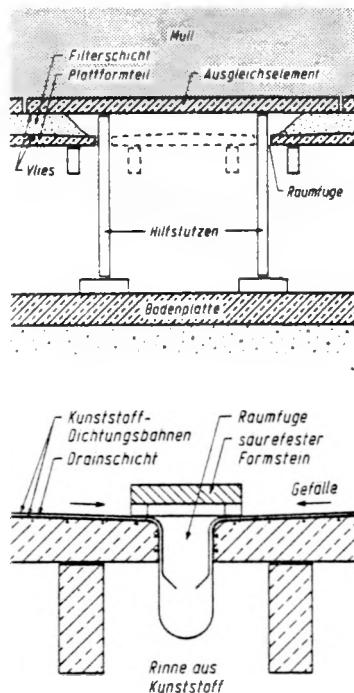
### Oberflächenabdichtung

Eine Oberflächenabdichtung über dem Müllberg hält den Niederschlag vom Müll fern und verhindert einen unkontrollierten Gasaustritt

aus der Deponie. Zur Anwendung kommen künstliche oder mineralische Abdichtungen bzw. beide in Kombination. Das Oberflächenwasser wird zur Regennenne am Böschungsfuß und von dort in eine Kanalisation abgeleitet. Bei erwartetem Gasanfall werden in der Drainageschicht Gasfilterrohre verlegt. Von dort wird das Gas in Sammelleitungen der weiteren Verwendung zugeführt.

### Betrieb der Flächendeponie

Der gesamte Sondermüll wird schichtweise eingebracht und verdichtet. Der jeweilige Betriebsabschnitt wird mit einer mobilen Hallenkonstruktion überdeckt, während die übrige Deponiefläche provisorisch mit Abdichtungsbahnen versehen ist. Es wird dafür gesorgt, daß der Sondermüll nur kontrolliert unter einer umsetzbaren Dachkonstruktion deponiert wird (s. Titelseite).



# Hochsicherheitsdeponie...

## als Behälteranlage

Bei diesem Abfallager wird der Sondermüll in voneinander unabhängigen, freistehenden, kreiszylindrischen Einzelbauwerken aus Stahlbeton oder Spannbeton deponiert. Die Behälter erhalten eine begehbar Basis sowie eine massive Behälterdecke. Diese wird so ausgebildet, daß sie bei einer Auslagerung des Sondermülls entfernt ist. Aus wirtschaftlichen Gründen und wegen der Tragfähigkeit des Baugrundes ist die Behälterhöhe auf etwa 20 bis 30 m begrenzt. Auch der äußere Behälterdurchmesser sollte 50 m nicht überschreiten. Die Deponieanlage mit freistehenden Behältern kann auch mit Erde überdeckt werden.

Im Vergleich zur Flachendeponie bietet diese Lösung zusätzliche Vorteile:

- Unterschiedliches Deponiegut kann getrennt in Einzelbehältern gelagert werden
- Die Abdichtung kann gezielt auf eine bestimmte Sondermüllzusammensetzung abgestimmt werden
- Der Sondermüll kann durch eine Überdeckung der Einzelbehälter im Betriebszustand sowie durch die massive Überdeckung im Endzustand absolut sicher vor Niederschlag geschützt werden
- Die Sicherheit jedes Behälters kann individuell kontrolliert werden

Die Weiterverwertung des Sondermülls und die damit erforderliche Auslagerung wird wesentlich erleichtert.

Dieses Konzept wird an einer Behälterdeponie mit 9 Behältern und einem Deponievolumen von  $V = 160.000 \text{ cbm}$  näher erläutert.

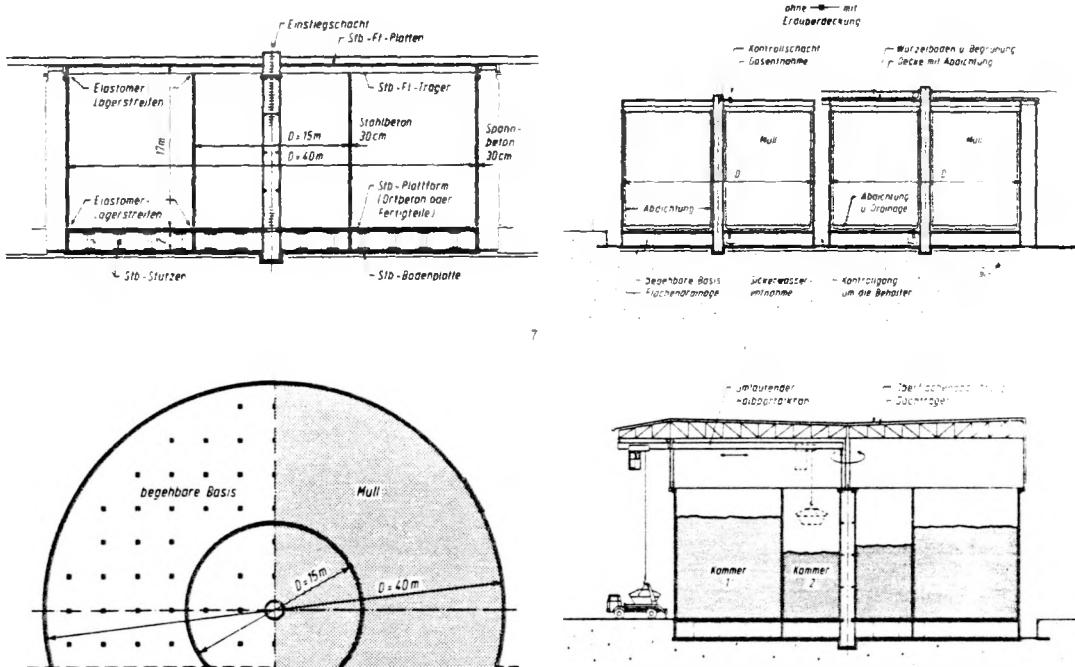
### Stahlbetontragkonstruktion

Die 9 freistehenden Behälter der Anlage werden in einer Doppelreihe und einem Mindestabstand von 1,0 m angeordnet, damit können die Behälteraußenflächen optisch kontrolliert werden. Auch bei der erdüberdeckten Lösung ist diese Kontrolle gewährleistet. Hierzu wird an der äußeren Peripherie eine umlaufende Winkelstützmauer vorgesehen, um einen Inspektionsgang um jeden Behälter freizuhalten.

Jeder Behälter wird mit einer massiven Decke versehen. Die Zwischenräume der einzelnen Behälter sind ebenfalls abgedeckt. Die Abdeckung wird bei der »erdüberdeckten« Lösung mit Erde überschüttet und begründet. Die Außenwandungen der Einzelbehälter bestehen bei diesem Beispiel aus Zylinderschalen von 40,0 m Durchmesser mit 15 m Füllhöhe. Im Zentrum befindet sich ein Einstieg- und Kontrollschaft.

Durch die Anordnung einer inneren Zylinder-

7 Behälterkonstruktion, Querschnitt  
 8 Prinzipieller Aufbau einer Behälteranlage  
 9 Behälterkonstruktion, Horizontalschnitt  
 10 Molenbau



# Hochsicherheitsdeponie... als Behälteranlage

## Kosten

schale mit 15 m Durchmesser ist es möglich, unterschiedliche Ablagerungsgüter getrennt in einem Behälter unterzubringen. Die Konstruktionsglieder – außenliegende Behälterwand, Behältersohle und Behälterdecke – sind konstruktiv voneinander getrennt, um möglichst klare statische Verhältnisse zu schaffen.

Wie bei der Flächendeponie kann auch bei der Behälterdeponie die Deponieplattform unter Bildung von Raumfugen aufgeteilt werden.

### Abdichtungen

Es können grundsätzlich die gleichen Abdichtungen verwendet werden wie bei der

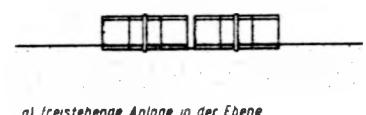
Flächendeponie beschrieben. Die Oberflächenabdichtung über der Behälterdecke hat ein Gefälle zur Benaltermitte.

### Betrieb der Behälterdeponie

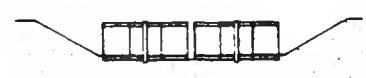
Das in Betrieb befindliche Abfallager erhält vorübergehend eine Dachkonstruktion. Unterhalb der Dachkonstruktion befindet sich ein Portalkrane, mit dem die Kammern nach Wunsch beschickt werden können. Ist das Füllvolumen erreicht, wird im Schutze der Dachkonstruktion mit dem vorhandenen Portalkrane die endgültige Behälterabdeckung verlegt und die Oberflächenabdichtung aufgebracht. Danach werden Dach- und Krankonstruktion abgebaut.

### Kostenvergleich der Deponievarianten

Basierend auf einem Deponievolumen von  $V = 160.000 \text{ cbm}$  zeigt Bild 13 einen Kostenvergleich. Dargestellt sind die Investitionskosten ohne Grundstücks- und Erschließungskosten sowie ohne Mennwertsteuer.



a) freistehende Anlage in der Ebene



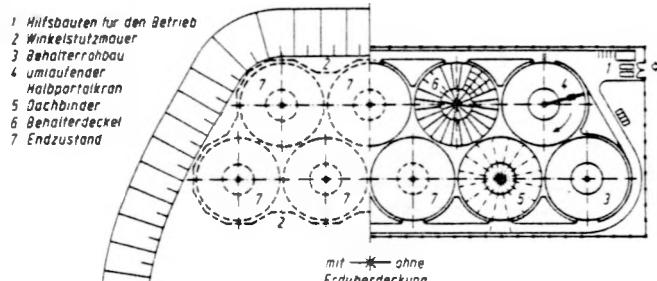
b) freistehende Anlage im Einschnitt



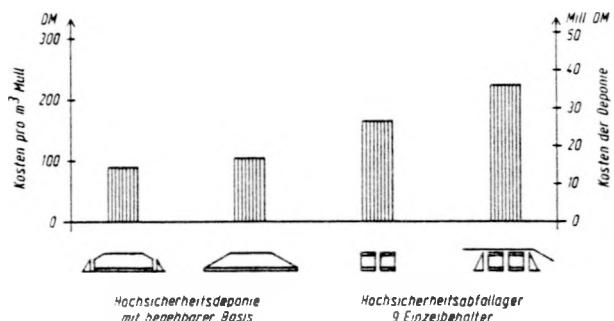
c) geschlossene Anlage mit Beplantung in Hanglage



d) geschlossene Anlage mit Beplantung in der Ebene



- 11 Behälteranordnungen
- 12 Beispiel einer Behälteranlage
- 13 Kostenvergleich



APPENDIX H

FRG COMPACTION DATA SUMMARY

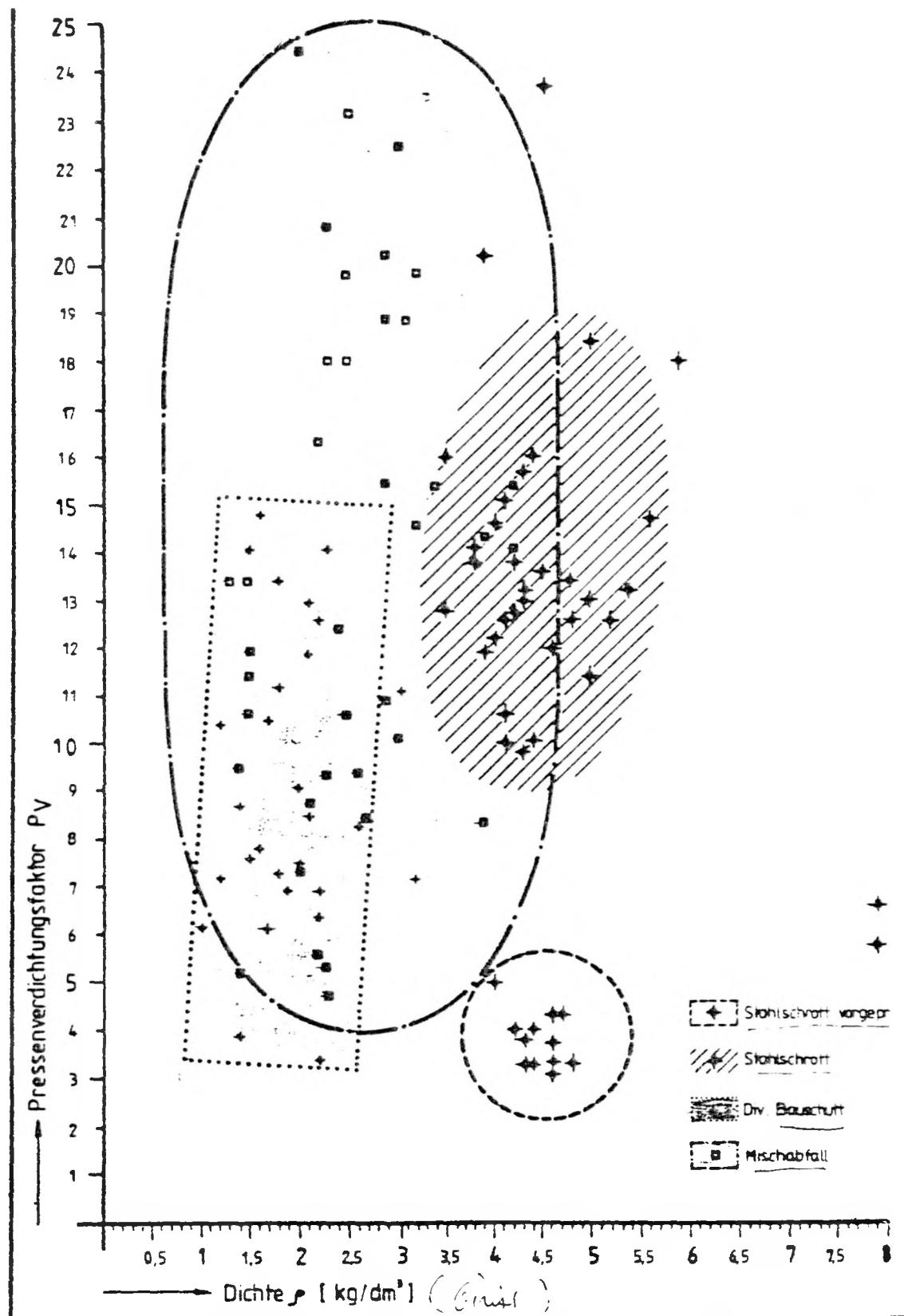


Fig. H.1. Compaction in Volume Reduction Efficiencies Studied by Karlsruhe Kernforschungszentrum.

APPENDIX I

HANAU VISIT AGENDA AND SUMMARY OF ALKEM OPERATIONS

ALKEM GMBH

## AGENDA

FOR VISIT OF US REPRESENTATIVES

NUCLEAR SITE HANAU November 25, 1986  
KHU Waste Reduction Plant, Karlstein November 26, 1986

within the scope of the US-DOE/BMFT Cooperative Radioactive Waste  
Management Agreement

- TRU - WASTE -

### Members of the

### German Representatives

ALKEM : F.W. Ledeburk, V.W. Schneider  
NUKEM : J. Demmich, G. Kemmler, L. Scherbaum  
KWU : Dr. W. Steinkilberg, W. Feiler

Tuesday, November 25, 1986

Visit at ALKEM and NUKEM

8.30 a.m.	Pick up at Hotel Brüder Grimm, travel to Nukleargelände Hanau	
9.00	Welcoming address to Nukleargelände Hanau	V. Schneider
	Survey of activities	
9.15	US Introduction	D. Ziegler
9.30	Tentative acceptance criteria	V. Schneider
	Konrad	
9.45	Management of TRU-Waste by ALKEM	F.W. Ledeburk
	. Analysis of the waste	
	. Treatment	
10.15	Coffee Break	
10.30	US presentations about processes chosen at several sites and present status of planning	
11.30	Tour of ALKEM's waste facility	F.W. Ledeburk
12.45 p.m.	Lunch	
2.15	Incineration of LLW	L. Scherbaum
2.45	Pyrolysis	G. Kemmler
3.00	Tour of Incineration facilities	
3.30	Wrap up discussion	
6.00	Pick up at the hotel	
8.00	Dinner at castle Heusenstamm	

Tuesday, November 25, 1986

Visit at KWU Waste Reduction Plant, Karlstein

8.30 a.m.	Pick up at Hotel Brüder Grimm	
9.00	Welcoming address and introduction	W. Feiler
9.15	Tour of KWU incineration facility	
10.30	US-presentation	D. Ziegler
10.45	Wrap up discussion	
12.00	Lunch	

## Cementation of TRU waste by a new process: Properties of the products

VOLKER W. SCHNEIDER AND FRIEDRICH W. LEDEBRINK

ALKEM GmbH  
Hanau, West Germany

The background for selection of a process to solidify the waste arising from the fabrication of MOX fuel is provided. Cement has many advantages as a matrix for TRU waste. Improvements of the cementation process make it possible to include all types of waste in only one product. A process description is followed by a detailed presentation of the product and its properties. Finally, properties are outlined which may be subject to quality control.

During plutonium mixed oxide (MOX) fuel fabrication a small, but unavoidable, amount of  $\alpha$ -bearing [transuranic (TRU)] waste is formed. The second line of Fig. 1 categorizes 4 main classes of waste according to source and nature. There are wastes arising in the glove boxes which are caused by operation steps (solid box waste) or replacement of equipment (retired equipment); others are generated by the processes themselves as filtrates from conversion or liquids from analytical procedures (liquid box waste). Waste from outside the glove box but inside the working area ("room waste") is suspected of being contaminated and therefore handled as active waste, although it is usually free from plutonium. It is worthwhile keeping this waste separate from the box waste.

Before these wastes can be disposed of, they have to be treated to meet legal requirements set up by licensed authorities and the operators of the disposal site.

When selecting an appropriate process which had to fulfill those requirements as well as to meet the needs of a mixed oxide fuel fabrication plant (MOFFP), we had to bear in mind a number of conditions. The process chosen should be easy to operate, with a few process steps and high reliability. The process should be capable of handling all of the different waste streams shown in the second line of Fig. 1. According to German regulations, all the wastes should be solidified. Currently, all TRU waste is buried in deep geological repositories in the Federal Republic of Germany. No shallow land burial is planned. Therefore, there is no incentive to separate primary wastes into categories according to  $\alpha$  activity.

### Process selection

Many different methods for immobilization of wastes have been suggested to date. Ross et al.<sup>1</sup> have recently summarized the major advantages and disadvantages of a number of immobilization systems. They concluded that "each system has its own inherent considerations. An evaluation of these considerations suggests the implementation of a cement or glass system."

The various processing techniques to immobilize wastes by cement are simple to use, less costly compared to other processes, and based on a large amount of

Am. Ceramic Soc. Columbus (1987)

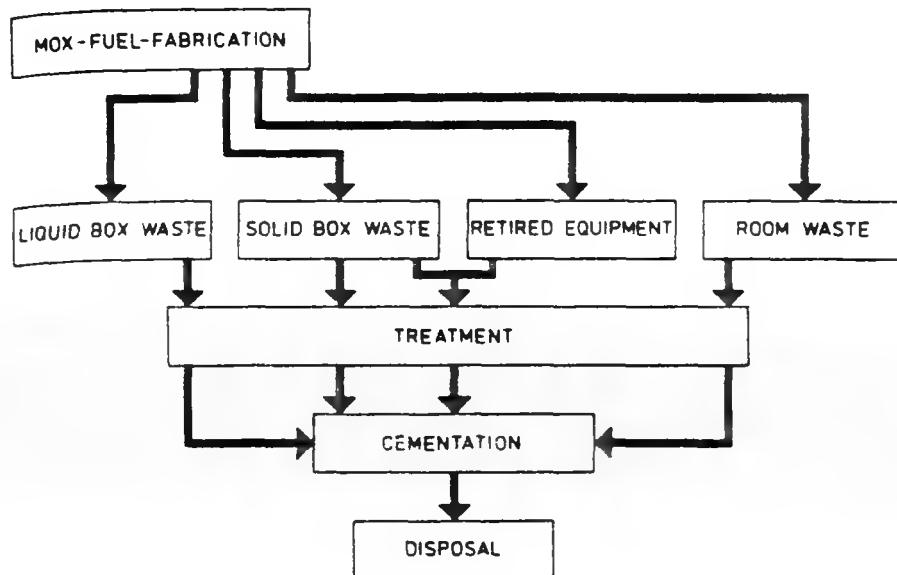


Fig. 1. Scheme for treatment of TRU waste arising from the fabrication of MOX fuel.

conventional experience. Operations are generally carried out at low temperature and thus avoid the risks of fire.

During its solidification and during its contacts with water, cement provides an alkaline environment. This offers an additional advantage, because plutonium which is not present as insoluble  $\text{PuO}_2$  forms the very insoluble  $\text{Pu(OH)}_n$ . It is therefore understandable that the leach rates for plutonium immobilized in cement are reported to be very low.<sup>1,2</sup> We have therefore considered ways that the four waste streams shown in Fig. 1 could be combined and solidified by a simple cementation process.

As about 50% of the solid glove-box waste is combustible, incineration is often suggested for volume reduction. However, with the high percentage of PVC and neoprene in this waste, a large volume of contaminated secondary wastes (NaCl from off-gas scrubbing) is produced along with the ash. If these secondary wastes cannot be disposed of in a more simplified way, the process loses much of its interest.

On the other hand, we knew that while others had found materials such as gloves and plastic foils unstable and heterogeneous when solidified in cement, we overcame this difficulty by shredding all the soft material to particles <5 mm in diameter.

#### Process description

The wastes are segregated according to nature and composition upon entering the waste facility. Wastes worthwhile of Pu recovery (about 20%) first undergo washing processes<sup>3</sup> and are then fed into the main streams of solid box waste and retired equipment. The soft materials of these streams are sent to a shredder (conventional type adapted for glove-box use) which cuts about 80 kg/h of waste

into particles <5-mm diameter. The shredded material is pneumatically transferred to a cyclone above the cement blender, where the waste can be homogenized.

In the cementation unit (a conventional, continuously working screw feeder type), the shredded soft waste is blended with cement and the liquid waste stream which has been treated for Pu recovery before. The flow of all three materials can be regulated separately, thus meeting the process parameters. This process control is part of the quality assurance of the product.

This blend of cement liquid and solid (soft) waste is poured directly into a 0.21-m<sup>3</sup> (55-gal) drum over the pieces of hard solid waste.

#### Product

The product resulting from the above process is a package consisting of a 0.21-m<sup>3</sup> drum filled with a homogeneous cement block which is reinforced by stainless steel (most of the hard solid waste is stainless steel). The drum is filled to about 95% (0.2 m<sup>3</sup>). Table I gives an example of a typical composition. In practice the plutonium amount will be about 15 g/0.21-m<sup>3</sup> drum.

We used blast furnace cement because it showed the best resistance against corrosion in saturated brines. A cement liquefier and stabilizer are added to keep the water/cement ratio down (0.4 or even lower) without affecting flowability.

Table I. Typical composition of the immobilized TRU waste in a 0.21-m<sup>3</sup> drum

Item	Quantity (kg)	Volume (dm <sup>3</sup> )
Cement	200	65
Liquid waste containing sodium nitrate	80	87
	20	
Soft solid waste	40	32
Hard solid waste	60	10
Porosity, 3%		6
Final cement product	400	200

#### Properties of the package and cement product

The properties needed for safe disposal of the waste are different, depending on whether the repository is open and being operated or whether the repository is closed. In the case of a closed deep geologic repository the geology will provide the final and most important barrier so that additional engineered barriers around the TRU waste will not reduce any leak of activity very much. Such barriers therefore have their importance mainly for the operations before closing the repository.

Some of the properties are expected to show a dependence on the composition of the conditioned waste. We therefore carefully investigated the dependence of the properties of our product on the type of cement and the proportions of the different components. This allowed us to optimize the product and also have a broad understanding about the reliability of the process. It turns out that the properties of the package and cement product as reported below are not limited to the figures in Table I but represent a wide range of composition. This provides sufficient room for process deviations and normal waste composition variations.

#### Surface dose rate and surface contamination

The surface dose rate ( $<10^{-4}$  Sv/h [ $<10$  mrem/h]) will be far below the required threshold value ( $2 \times 10^{-1}$  Sv/h). Also, the limit of the surface contamination required can be met. The mild steel drums are protected against corrosion by an epoxy resin coating of 150- $\mu$ m thickness and are therefore expected to survive undamaged for an intermediate storage time of several decades. The epoxy resin coating also allows the drums to be easily decontaminated.

#### Compressive strength

The compressive strength was studied as a function of the portion of soft waste in the product and the water/cement ratio. As a result it can be stated that the compressive strength of the product as given in Table I is about 20 N/mm<sup>2</sup> which is much higher than the present minimum need. The stocking of the filled drums also has to be considered in this connection.

#### Radiolysis gas generation

This phenomenon was investigated with a number of 1-dm<sup>3</sup> samples, each corresponding to the standard product with the exception of salt content (Pu content, content of soft solid waste, water/cement ratio, but not sodium nitrate); in half of the samples the Pu was added as PuO<sub>2</sub> and in the second half as Pu solution. It was found that about 1.6 L of H<sub>2</sub>/Ci<sub>n</sub>·year in the case of PuO<sub>2</sub> and 2.2 L of H<sub>2</sub>/Ci<sub>n</sub>·year in the case of the solute plutonium are generated. Oxygen was not generated; on the contrary, the oxygen in the gas phase (air) above the samples was removed, resulting in an underpressure corresponding to the portion of oxygen in air. The results are in good agreement with values reported by Kosiewicz.<sup>4</sup> The investigations will be continued in two directions: leakage rate for H<sub>2</sub> of the drums to avoid overpressure in the package and addition of nitrate or nitrite which will reduce H<sub>2</sub> generation up to a factor of 50, according to Bibler.<sup>5</sup>

#### Behavior in case of incidents

*Drop tests:* Three types of experiments were conducted in which four packages were stacked up and the top drum made to fall onto the steel-covered concrete floor. The first experiment used drums filled to not more than 95%, with the mushroom-shaped lid kept empty. The packages remained tight after the drop, still having the underpressure caused by the setting. Even the cement product was nearly undamaged. The second used a package as before, but this was dropped onto another full package lying on the floor instead of the steel plate. The result was the same as above for both packages. The third used drums completely filled, with no voids. Here the drum broke open a few centimeters up near the flange, but only about 10 g of the product leaked out.

These results show that the container when exposed to mechanical power as might occur by maloperation during transportation or storage will remain tight, or if failing, the amount of activity released will be very limited.

*Fire tests:* A filled drum was placed into an isopropyl alcohol fire for one-half hour. The temperature measured in the gap between the drum and the product was 800°C; 50 mm inside the block the temperature was 90°C, and 100 mm inside the block it was 40°C. The gasket of the lid was destroyed and white steam escaped the drum. The loss of weight was 15 kg (about 3.8%) compared to 10–12 kg in the case of cement product without the organic waste component. The organic waste was affected up to 5 mm depth. We intend to repeat these experiments with europium-doped cement waste product in order to investigate the activity release more quantitatively.

Table II. Corrosion tests with blast furnace cement product at 90°C (2×2×8-cm<sup>3</sup> samples containing 10% soft waste with a water-cement ratio of 0.40)

Media	Bending strength (N/mm <sup>2</sup> )	Compressive strength (N/mm <sup>2</sup> )
Damp room	3.8	17.6
Brine	4.2	15.0
Sodium chloride	3.8	13.0
Water	2.0	11.8

Table III. Corrosion test with blast furnace cement product at 55°C for 365 days (2×2×8-cm<sup>3</sup> samples containing 10% soft waste, 0.3% liquefier, 0.5% stabilizer, with a cement-water ratio of 0.43)

Time (days)	Damp room		Water		Brine (Q type)	
	Bend. strength (N/mm <sup>2</sup> )	Compr. strength (N/mm <sup>2</sup> )	Bend. strength (N/mm <sup>2</sup> )	Compr. strength (N/mm <sup>2</sup> )	Bend. strength (N/mm <sup>2</sup> )	Compr. strength (N/mm <sup>2</sup> )
56	7	28.7	4.3	17.4	7.1	23.2
112	6.8	35.4	3.7	22.3	4.8	24.2

#### Corrosion resistance

Corrosion tests have been performed in order to find the most adequate type of cement. Water and brine (Q type) have been used as leachants. The corrosion attack was determined on the basis of changes at 90°C in the bending and compressive strength. Table II shows the results for blast furnace cement, which was better than the other 5 candidates under the conditions of this "quick" test. Tables II and III show a very good resistance against corrosion. One should not compare the figures of both tables with each other. The samples in Table III have been prepared with a high-speed lab blender which produced a higher porosity and therefore lower strength. Therefore, the data in the two tables should not be compared.

#### Leachability

Investigations of the leachability of the product are still going on. Three types of prisms (about 2×2×8 cm) are being leached in stagnant brine following the ISO norm: (1) cement product containing 10% soft waste contaminated with PuO<sub>2</sub>, (2) same as (1) but without the soft waste, and (3) same as (1) but with Pu(OH)<sub>4</sub> instead of PuO<sub>2</sub> as contaminant.

Our conclusion from Fig. 2, which shows results obtained up to now, is that at the very beginning some activity is leached from the surface of the bodies which later disappears from the solution either by precipitation or by resorption on the surface of the cement body. We expect that the cement surface gets coated by a layer of magnesium hydroxide when exposed to the brine.

The experiments will be continued. Additionally, the behavior of crushed cement products are being investigated to simulate the case where the monolithic block was disintegrated after being in brine for centuries. For this purpose prisms as described above are crushed in a mortar. Preliminary results show that this procedure will change the values in Fig. 2 only by a factor of 10.

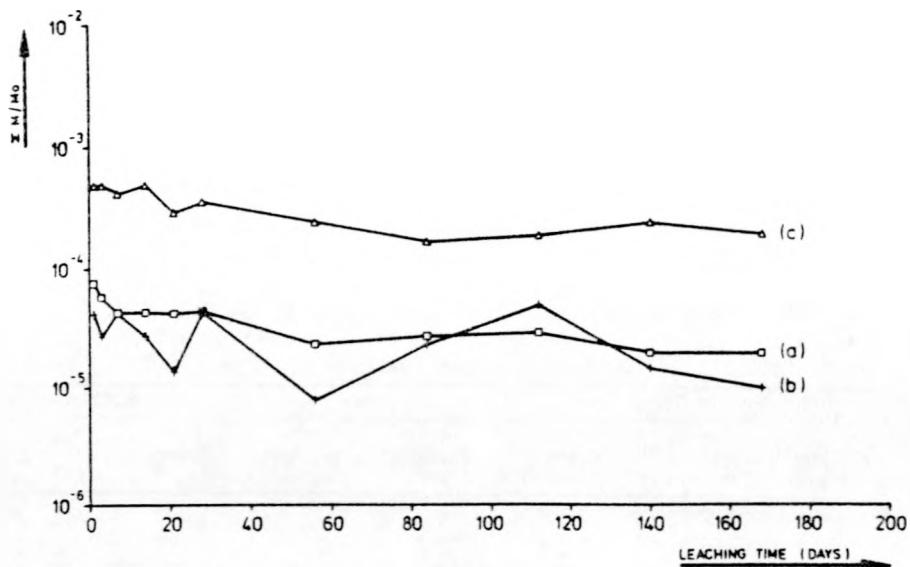


Fig. 2. Cumulative leached plutonium fractions.

#### Quality control

The quality control to which parameters and properties of radioactive waste conditioned for disposal have to be subjected has not been finalized. There is a broad common understanding that destructive controls on the final products should be avoided. The quality control therefore will concentrate on process control procedures and nondestructive product controls. Table IV shows the properties which are currently envisioned as being controlled. There is no difficulty in adapting this system of quality control to the process or product as described in this paper.

#### Conclusion

The process meets all the desired standards for a solidification process for TRU waste. It is easy to operate and, because conventionally proven, highly

Table IV. Properties subject to quality control

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Inventory of activities
Dose rate
Surface contamination
Chemical composition of primary waste
Quality of the cement
Quality of the container
Ratio waste/cement/water
Degree of homogeneity
Weight
No free liquid

---

reliable. The properties of the conditioned waste as assured by process control meet the requirements.

It is often argued that adding cement would mean an undesirable increase of the waste volume. Here we can state a very unexpected result. Table V illustrates that a volume reduction of 40% can be achieved when wastes originally tightly packed but not compressed from the plant are processed as discussed in this paper.

Table V. Comparison of waste loadings for a 0.21-m<sup>3</sup> drum

Material	Primary waste (kg)	Immobilized waste (kg)
Soft solid waste	24	40
Hard solid waste	36	60
Total	60	100

#### Acknowledgment

The authors thank H. Brunner (NUKEM GmbH, Hanau) for his excellent collaboration when investigating the product properties and assistance in preparing this paper.

#### References

- <sup>1</sup>W. A. Ross et al., A Comparative Assessment of TRU Waste Forms and Processes, Vol. I and II, PNL-4428, Pacific Northwest Laboratory, Richland, WA, 1982.
- <sup>2</sup>R. Neilson and P. Colombo, "Plutonium Leachability from Alternative TRU-Incinerator Ash Waste Forms," IAEA-SN-246/45, International Atomic Energy Agency, Vienna, Austria.
- <sup>3</sup>V. W. Schneider and F. W. Ledebrik, "Treatment of TRU-Wastes Recent Results of Developments Underway in Germany", p. 362 in Proceedings of ANS Topical Meeting on Treatment and Handling of Radioactive Wastes, Richland, WA, 1982.
- <sup>4</sup>St. T. Kosiewicz, "Gas Generation from Organic TRU-Wastes," *Nucl. Technol.*, **54**, 92 (1981).
- <sup>5</sup>N. E. Bibler, "Radiolytic Gas Generation in Concrete Made with Incinerator Ash Containing Transuranic Nuclides," DP-MS-79-25, presented at the Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, 1979.

APPENDIX J

REPORTS TRANSFERRED TO THE FRG

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OAK RIDGE NATIONAL LABORATORY  
OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS INC

POST OFFICE BOX P  
OAK RIDGE, TENNESSEE 37831  
December 15, 1986

Herr Dr. Volker Schneider  
ALKEN GMBH  
Postfach 110069  
Rodenbacher Chaussee 6  
D-6450 Hanau 11 (Wolfgang)  
Federal Republic of Germany

Dear Volker:

Enclosed for your information are the two reports that we discussed in our meeting at Hanau on November 25, 1986. They are titled "Geochemical Constraints on Accumulation of Actinide Critical Masses from Stored Nuclear Waste in Natural Rock Repositories" and "Criticality Analysis of Aggregations of Actinides from Commercial Nuclear Waste in Geological Storage."

Thank you very much for the warm and gracious hospitality that you and the staffs at Alkem, Nukem, and Transnuklear showed to the American delegation during our visits. We found these meetings very informative and hope that we have returned your cooperation in kind.

If you have further questions, please call me (615/576-7421) or telex (854492 WITG ORNL).

Sincerely,



Leslie R. Dole, Ph.D.  
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LRD:dsb

Enclosures

cc w/o enc: W. R. Bibb, DOE/ORO  
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