IAEA Coordinated Research Project:

Cementitious Materials for Radioactive Waste Management

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US DOE Cementitious Barriers Partnership Project

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International Atomic Energy Agency

Contents

I. IAEA Coordinated Research Projects

CRPs are tools to:

- Establish multilateral cooperation of interested Member States on the topical issues
- Encourage information exchange on research and development activities in Member States and facilitate access to results and application
- Promote multilateral and bilateral research agreements and contracts among its participants
- Disseminate information on the state of art to all Member States by publishing IAEA technical documents

I. IAEA Coordinated Research Projects

- CRPs are based on voluntary participation R&D technology development organizations and participants to present and discuss their results
- IAEA provides modest funding to support organizations from developing countries
- Typical CRPs have:
  - Participants from 10 to 15 countries
  - Duration of 3 to 5 years
  - Research co-ordination meetings (usually 3 RCMs) to facilitate discussions and exchange of information and progress on research activities, encourage bilateral / multilateral collaborations
- Results of CRPS are published as Agency Reports

II. CRP: Behaviour of Cementitious Materials in Multipurpose Packaging for Transportation, Long Term Storage and Disposal

Behaviour of Cementitious Materials in Long Term Storage and Disposal, 2007-2010

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II. CM CRP: Mission

- **Investigate behaviour and performance of cementitious materials used for waste packages:**
  - waste conditioning / waste forms
  - Backfilling
  - Containment / disposal structures
  - Transportation casks
- **Investigate interactions and interdependencies of these individual materials during long-term storage and disposal.**
- **Understand processes that can result in the degradation of their physical and chemical properties.**
- **Predict long-term behaviour and reduce long-term risk.**

II. CM CRP Participation

- 24 Research Organizations
- 21 Member Countries
- 3 RCM Meetings
- Publications

Lead IAEA Officer – Zoran Drace; IAEA

Chief Investigator – Michael Ojovan; IAEA

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II. CM CRP Participation

Member State, Org. Researchers	Research topics
Australia, ANSTO D. Perera, P. McGlinn, K. Hart	Emerging and alternative cementitious systems based on geopolymers for LL and IL radioactive waste immobilization. Water transport through cement-based repository materials and sorption processes. Preliminary studies using neutron imaging.
Belgium, SCK·CEN W. Bastiaens, J. Govaerts, P. Van Iseghem	Behaviour of cementitious materials in long term rad waste storage and disposal Behaviour of cementitious materials and interactions with host environment.
Brazil, IPEN-CNEN/SP R. Vicente	Assessment of the durability of cementitious materials in repository environment.
China, NUDT S. Bai, S. Yang	The immobilisation of radioactively contaminated soil in cementitious materials
China, INNET J. Li	Cementation of waste resins in calcium sulfoaluminate cement matrix

II. CM CRP Participation

Czech Republic, NRI Rez A. Vokal	Development of waste matrices for immobilisation of problematic wastes from Czech nuclear power plants
Egypt, AEAE A. El-Kamash	Evaluation of synthetic zeolite as a backfill material in radioactive waste disposal facility
Finland, Fortum, M. Ek	Cementitious materials for handling of radioactive waste - Overview of activities in Fortum/Finland
France, CEA/Valhro, C. Cau Dit Coumes	Behaviour of cementitious materials in long term storage and disposal. Potential of calcium sulfoaluminate cements to immobilise $ZnCl_2$-containing wastes
India, BARC, D.S. Deshingkar, R.G. Yeotikar	Characterization, improvement and long term evaluation of cementitious waste products – an Indian scenario.
Korea, KHNP/NETEC, J.H. Yoon, J. Wan Park	Long term behaviour of cementitious materials in the Korean repository environment
Romania, NIPNE, F. Dragolici	Long term behaviour evaluation of cement conditioning matrices used for management of radioactive wastes at IFIN-HH
Russia, SIA RADON, A. Varlakov.	Cementitious composite for immobilisation of radioactive waste into final waste form
Russia, VNIINM, L. Soukhanov	Methods and production of cementitious materials for immobilisation into waste form. Specific of cementation process of some kinds of liquid radioactive waste of radiochemical plants. Cementation of certain types of liquid radioactive waste of radiochemical plant

II. CM CRP Participation

Serbia, Vinca INS I. Plecac, D. Kićević	Behaviours of cementitious materials in long term storage and disposal
Slovakia, AllDeco M. Breza , P. Lichvar	Behaviour of aluminosilicate inorganic matrix, SIAL®,during and after solidification of radioactive sludge and spent resins and their mixtures
Slovenia, ARAO N. Zeleznik, A. Sajna	Assessment and measurements of degradation processes in LILW repository engineered barriers
South Africa, NECSA W. Meyer	Behaviour of cementitious materials in multipurpose packaging for transportation, long term storage and disposal
Sweden, SKB B. Torstenfeld, L. Almkvist	Cement waste matrix evaluation and modelling of the long-term stability of cementitious waste matrices. Thermodynamic modelling
Switzerland, PSI A. Wallisch	Long-term mechanical stability and leaching behaviour of a solidified radioactive sludge
Ukraine, IEG B. Zlobenko	Assessment of the biodegradability of containers for LL and IL rad waste
UK, Aberdeen University F. Glasser	Cements in radioactive waste disposal
UK, Sheffield University M. Ojovan	Acoustic emission monitoring of cementitious wasteforms
USA, SRNL (DOE-NRC CBP) C. Langton	Cementitious **B**arriers Partnership Project overview US DOE, US NRC, US NIST, Vanderbilt Uni., ECN (The Netherlands), SIMCO Tech., Canada

II. CM CRP Meetings

First CM Research Coordination Meeting was organised in Moscow, Oct. 10-14, 2007

- Hosted by the Moscow Scientific and Industrial Association “Radon”.

Purpose:

- Identify objectives of individual projects
- Justify R&D programs for the future work

II. CM CRP Meetings

Second RCM was held Nov 24 - 28, 2008 in Romania

- Cheile Gradistei, Nov. 24 - 27, 2008
- Bucharest, Nov. 28, 2008

2nd RCM led by IAEA Unit Leader Z. Drace

Prof F. Glasser overview lecture on cementitious systems.

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II. CRP Meetings

Third RCM was held Oct. 18 - 22 at the Bhabha Atomic Research Centre, Kalpakkam to Review Progress and Oct. 25 – 29, 2010 to Prepare Draft Technical Report

III. IAEA CM CRP Research Areas

Main research outcomes of IAEA CRP on Behaviour of Cementitious Materials in Multipurpose Packaging for Transportation, Long Term Storage and Disposal

1. **Conventional cementitious systems**
   - **Conditioning**
   - **Stabilization Fill Grouts**
   - **Containment Structures**
2. **Novel materials and technologies**
3. **Testing and waste acceptance criteria**
4. **Modelling long term behaviour**

III Topic A. Waste Conditioning Conventional Cements

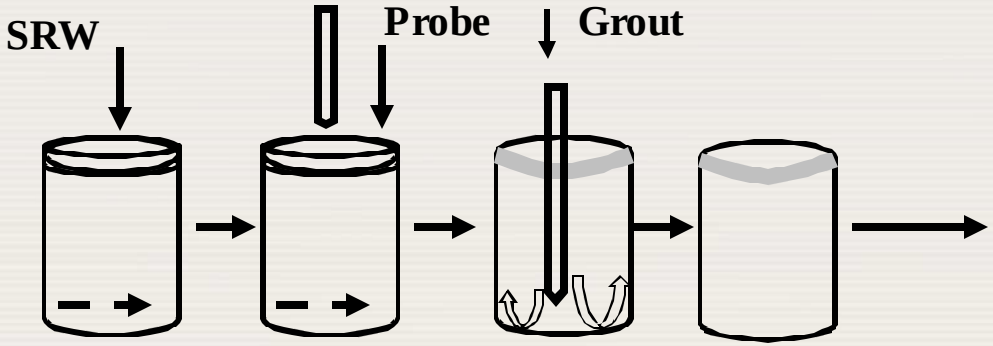
- Wastes differ from country to country, depending on the size and scope of the nuclear program.
  - Reprocessing tends to generate aqueous wastes containing tributyl phosphate and salt wastes.
  - Spent fuel storage generates mainly spent ion exchangers (organic and inorganic)
- Conventional cementitious systems are of interest in all countries and are used for immobilizing liquid and wet solid wastes – low waste loading.
- Higher waste loadings may be achieved by:
  - Chemical pre-treatment of wastes or by using blended cements (e.g., fly ash, slag or silica fume)
  - Addition of selected sorbents such as zeolites or bentonite clay

IIIA. Conventional Cement Waste Forms

Waste Stream	Cementitious Matrix*
Spent ion exchange resins	Slag – Portland blends
Sludge and concentrates generated from treatment of LLW, Incinerator ash	OPC, with or without additives
Mixture of sludge and ion exchange resin	OPC, Slag Portland cement
Intermediate level liquid waste	Slag -Portland blends, OPC with vermiculite
Secondary waste generated during treatment of spent solvent from reprocessing plant	OPC
Waste generated during reprocessing of thorium-based spent fuel	OPC
Evaporator concentrate containing boric acid	OPC

IIIA. In Drum / Container Cementation

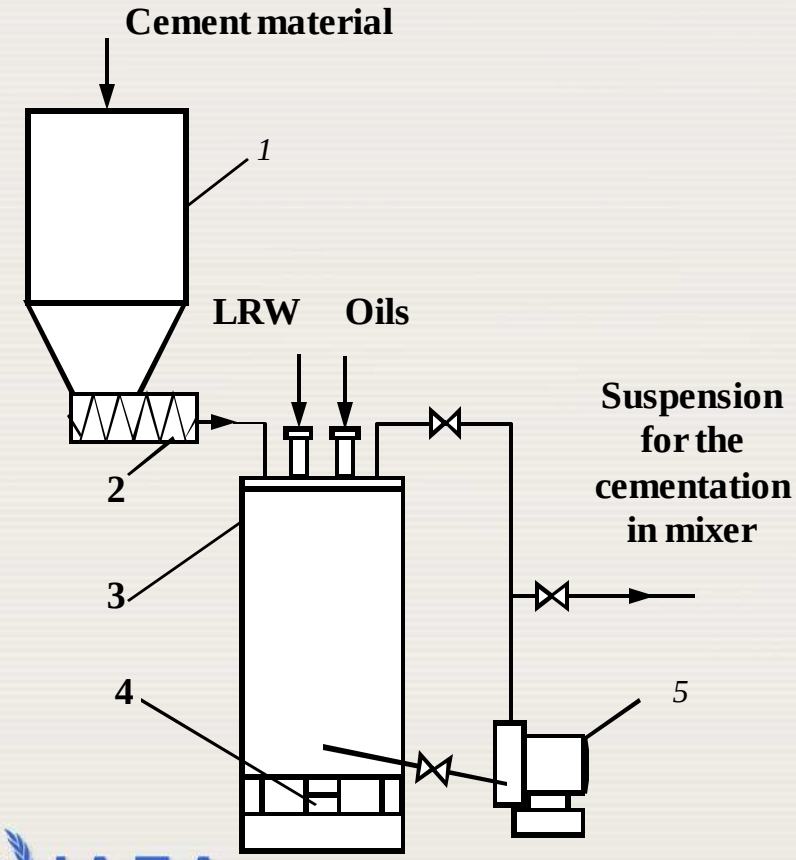
Components including waste are mixed in a standard 200 L drum with a disposable or removable stirring unit. After setting and hardening, the drum is closed by a lid and sent for disposal.



IIIA. In Drum / Container Cementation

IIIA. Mixer Unit Cementation Processing

Cement and waste are mixed and, when homogenized, poured into a standard 200 L drum or in a container. The drum / container is closed and, after strength gain and disposed.



IIIB. Novel Cements for Rad Waste Conditioning

The CRP reviewed progress on four types of alternative cementitious systems

- Geopolymer, SIAL matricies, alkali silicate (metakolin) + (sodium, potassium hydroxide)
- Magnesium Phosphate Cements (MKP formulations)
  - Moderate alkalinity, pH ~ 10.5, excellent bonding to metal, phosphate stabilization of divalent and multivalent cations
- Calcium aluminate Cements (CAC)
  - Less sensitive to set retardation that OPC systems (Zn salts, borate waste)
- Calcium Sulfoaluminate Cements
  - Moderate alkalinity, pH ~ 10
  - Reactive metals and acidic disposal environments

IIIC. Testing

- Process QC
- Disposal Site Acceptance
  - Strength
  - Hydraulic conductivity
  - Contaminant leachability
- Characterization for performance assessment model parameters
- Long term exposure testing (Test Beds)
  - Evolution of physical, hydraulic, and leaching properties
  - Evolution of macro and microstructure
- **Short term characterization results can only be used as a guideline for waste form development and durability predictions.**
- **Durability testing methodology is not standardized and long term durability research results on behaviour of cementitious materials under repository conditions are scarce.**

IIIC. Long Term Exposure Testing

Fig. 1. Mound-type experimental repository for cemented LILW set-up in 1965.

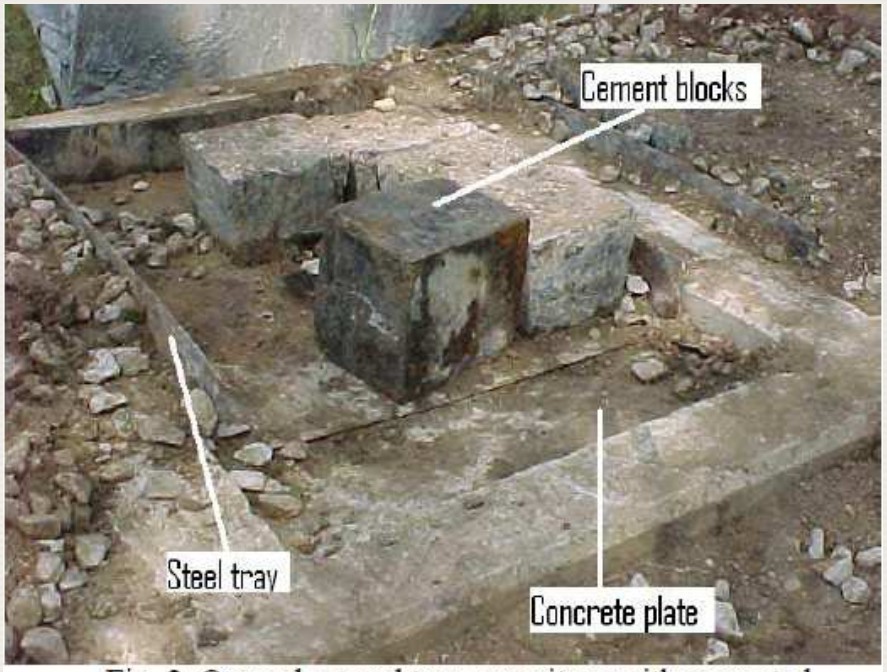
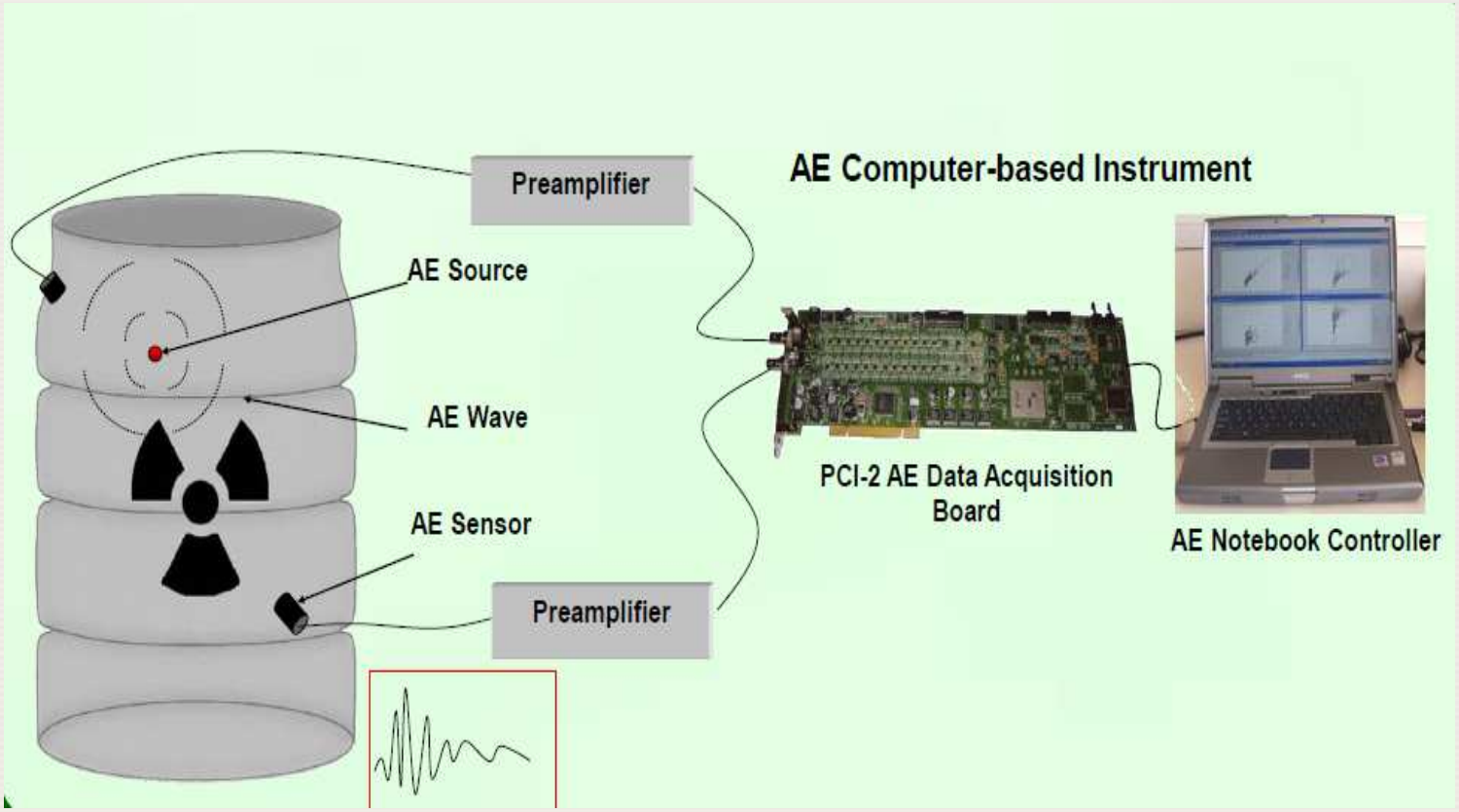


Fig. 2. Opened mound type repository with cemented radioactive waste after 39 years of storage.

ICEM'05:
The 10th International Conference on Environmental Remediation and Radioactive Waste Management
September 4-8, 2005, Scottish Exhibition & Conference Centre, Glasgow, Scotland

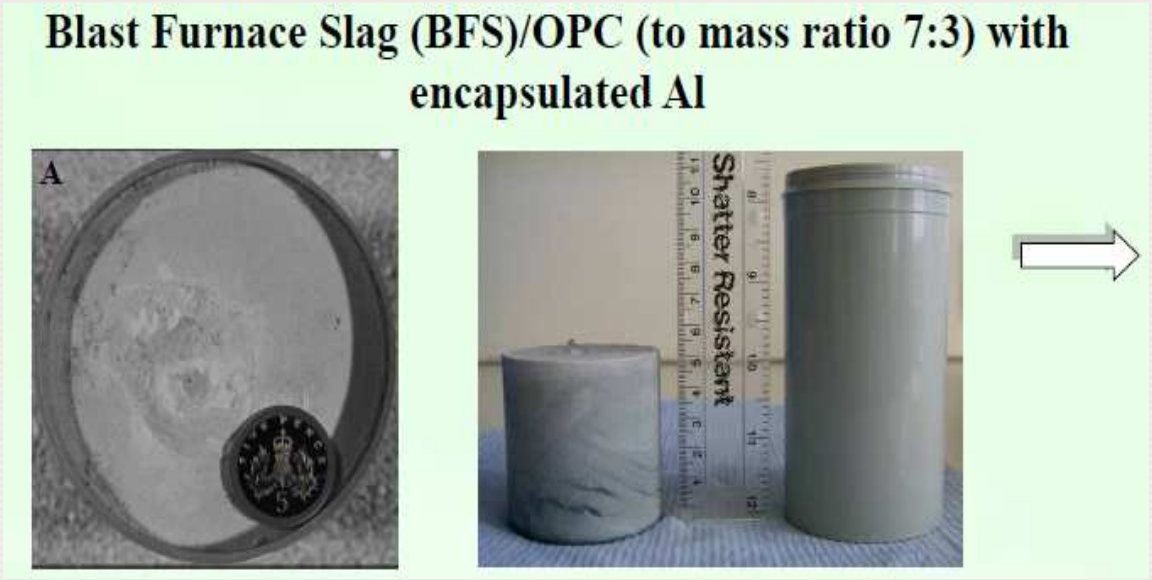
IIIC. Non Destructive Characterization

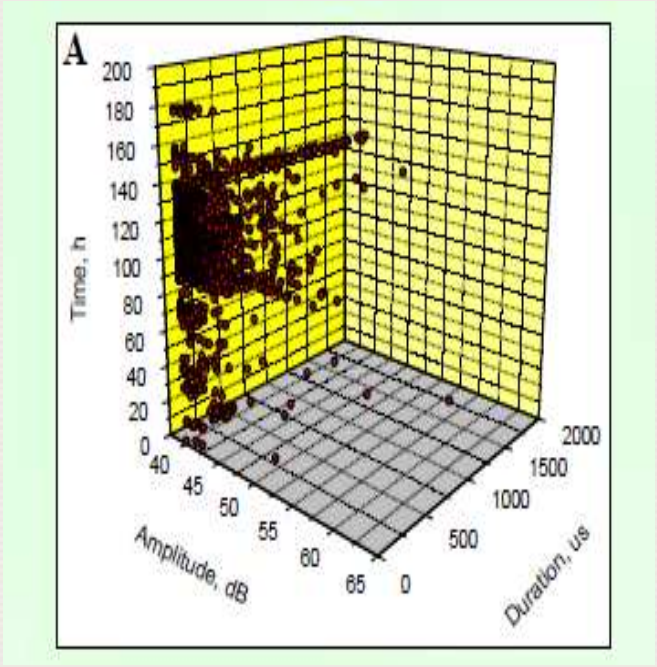
Acoustic emission technique was used for early detection, characterisation and time progress description of cracking phenomenon caused by the corrosion of Al encapsulated in cement matrix.



IIIC. Advanced Characterization

Neutron imaging used in South Africa for evaluating cracking in waste packages





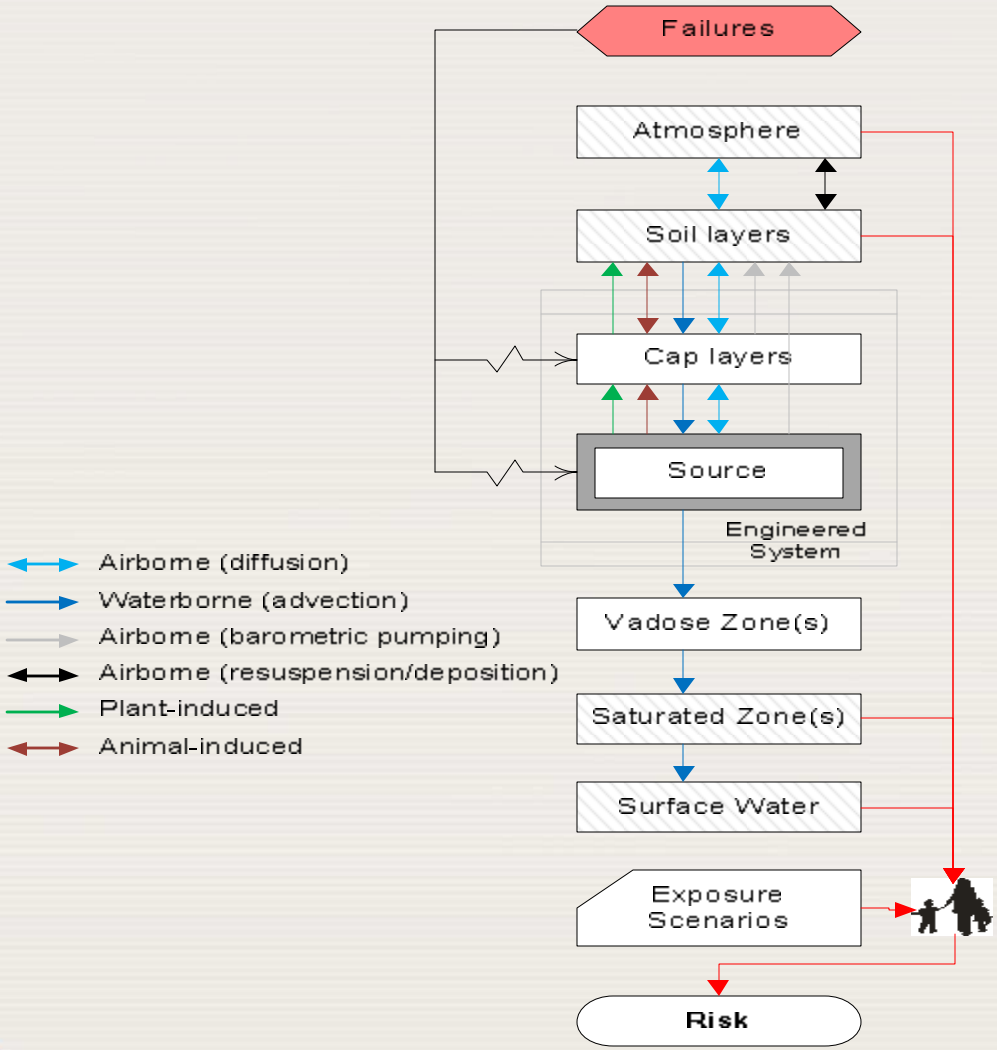
IIID. Performance Modeling

- Generally accepted that cementitious materials can be engineered to perform over long times (based on analogy with natural, archaeological analogues and old structures)
- Prediction of performance for 100s to 1000s of years is challenging
  - Methods for quantifying long-term performance are not standardized
  - Limited long term data and exposure testing
  - Flow and Transport Models
  - Thermodynamic databases

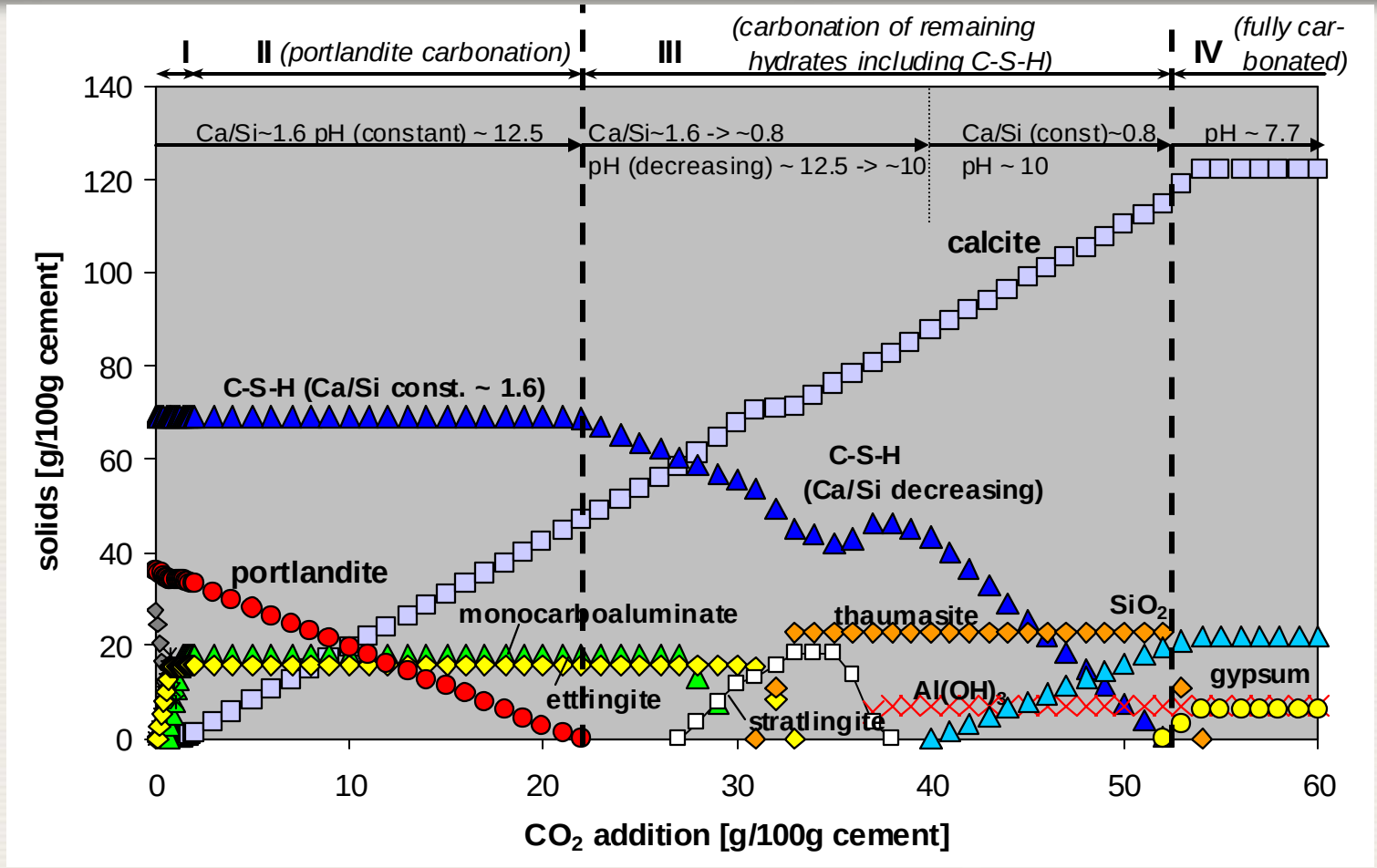
IIID. Modeling: Codes used in CRP

Process	Tool
Thermodynamic calculations	Commercial software CHESS software Commercial software PHREEQC-2 Commercial software GEMS2
Degradation modelling	Empirical relationship
Radionuclides leaching from waste matrices	Simple mechanistic models
Groundwater flow	Commercial software MODFLOW
Safety assessment of concrete degradation	Commercial software MOSAIC Commercial software GoldSim
Cement hydration	Commercial software GEMS-PSI /GEM-PSI 2009

IIID. Modeling: Codes used in CRP



IIID. Modeling: Phase Evolution (Aging)



Effect of carbonation on the mineralogy of hydrated ordinary Portland cement (Courtesy F. Glasser)

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IV. Conclusions

Cements are a suitable for immobilisation of a variety of waste constituents. Cementation technology is extensively applied in the international community.

IAEA facilitated creation of a USER GROUP and NETWORK of Organizations in 21 Member States with lasting cooperate and information exchange

Bilateral agreements between participating organizations were established during CRP. Cooperation among participants is occurring and will continue outside of the CRP framework.

IAEA supported and documented relevant topical research.

IV. CRP Publications

IAEA TECDOC to be published 2012

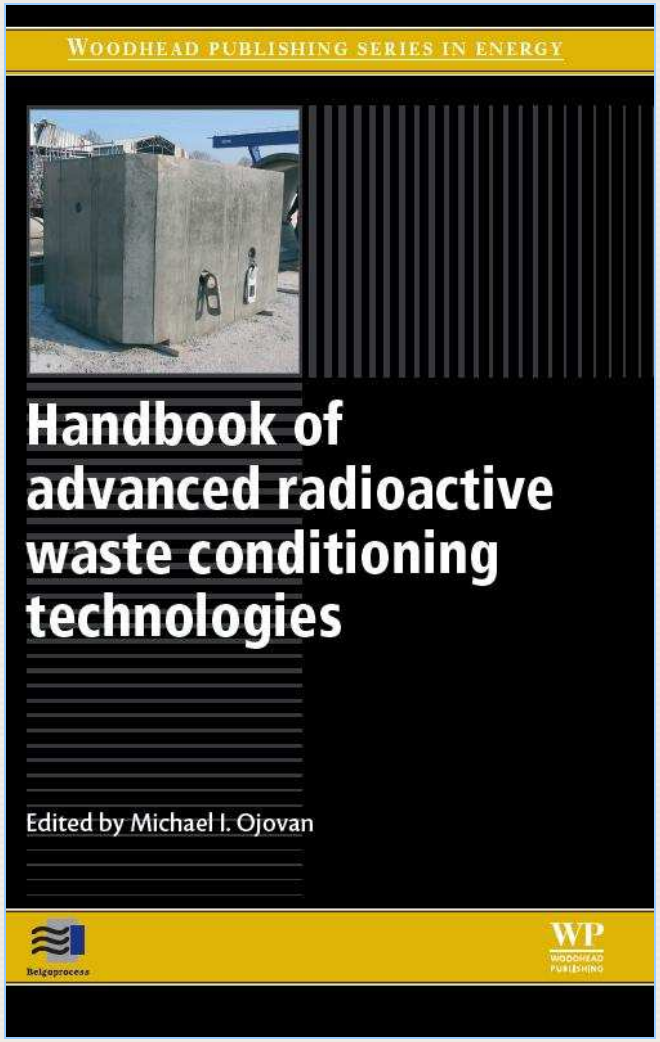
IAEA Website: CRP on Behaviors of Cementitious Materials in Long Term Storage and Disposal. http://www.iaea.org/OurWork/ST/NE/NEFW/wts_crp_cement.html (2010).

MRS09: Z. Drace, M.I. Ojovan. The behaviours of cementitious materials in long term storage and disposal: an overview of results of the IAEA coordinated research programme. *Mater. Res. Soc. Symp. Proc.* **1193**, 663-672 (2009).

MRS2011: Proceedings
ICEM2011: Proceedings to be published.
NUWCEM2011: Proceedings to be published

Other Publication

F.P. Glasser. Application of inorganic cements to the conditioning and immobilisation of radioactive wastes. In: Handbook of advanced radioactive waste conditioning technologies, Edited by M I Ojovan. pp. 67-135, Woodhead, Oxford (2011).



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