EUROPEAN COMMISSION
European Research Area

EC CAST Project Overview

Dr Simon Norris, Radioactive Waste Management, UK
EC CAST Project Coordinator

Radioactive Waste Management

CAST

European Commission
European Research Area

CAST Acknowledgement

The project has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

For more information, please visit the CAST website at:

http://www.projectcast.eu

C14AST

EURATOM

Radioactive Waste Management

EUROPEAN COMMISSION
European Research Area

CAST Drivers / Motivations

- Carbon-14 (radiocarbon, ^{14}C) is present in important amounts in the radioactive waste inventories of many national waste management programs.
- The knowledge regarding the chemical form and the release mechanism of carbon-14 from these wastes in disposal is limited.
- Precedent safety assessments: conservative treatments of carbon-14 release, possibly giving rise to over-estimated radiological impacts.

Radioactive Waste Management

CAST

EUROPEAN COMMISSION

European Research Area

CAST Objectives

- The EC CAST project (CArbon-14 Source Term) aimed to improve understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities.
- The project focused on the release of carbon-14 as dissolved and gaseous species from irradiated metals (**WP2** steels, **WP3** Zircaloys), from ion-exchange materials (**WP4**) and from irradiated graphite (**WP5**).
- Results from CAST evaluated in the context of national safety assessments (**WP6**) and disseminated to interested stakeholders (**WP7**).

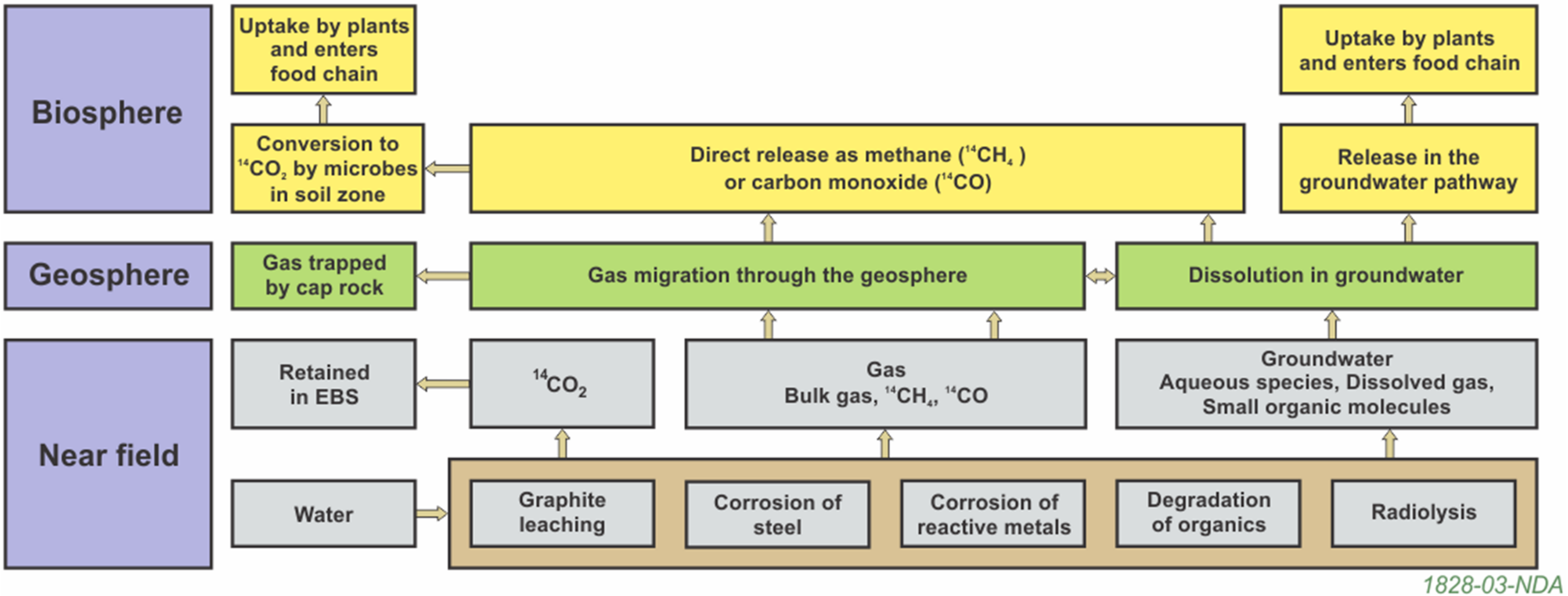
Radioactive Waste Management

CAST

CAST Participants

- The CAST consortium has brought together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation.
- The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

Key generation and migration processes affecting the fate of C-14 in the disposal system

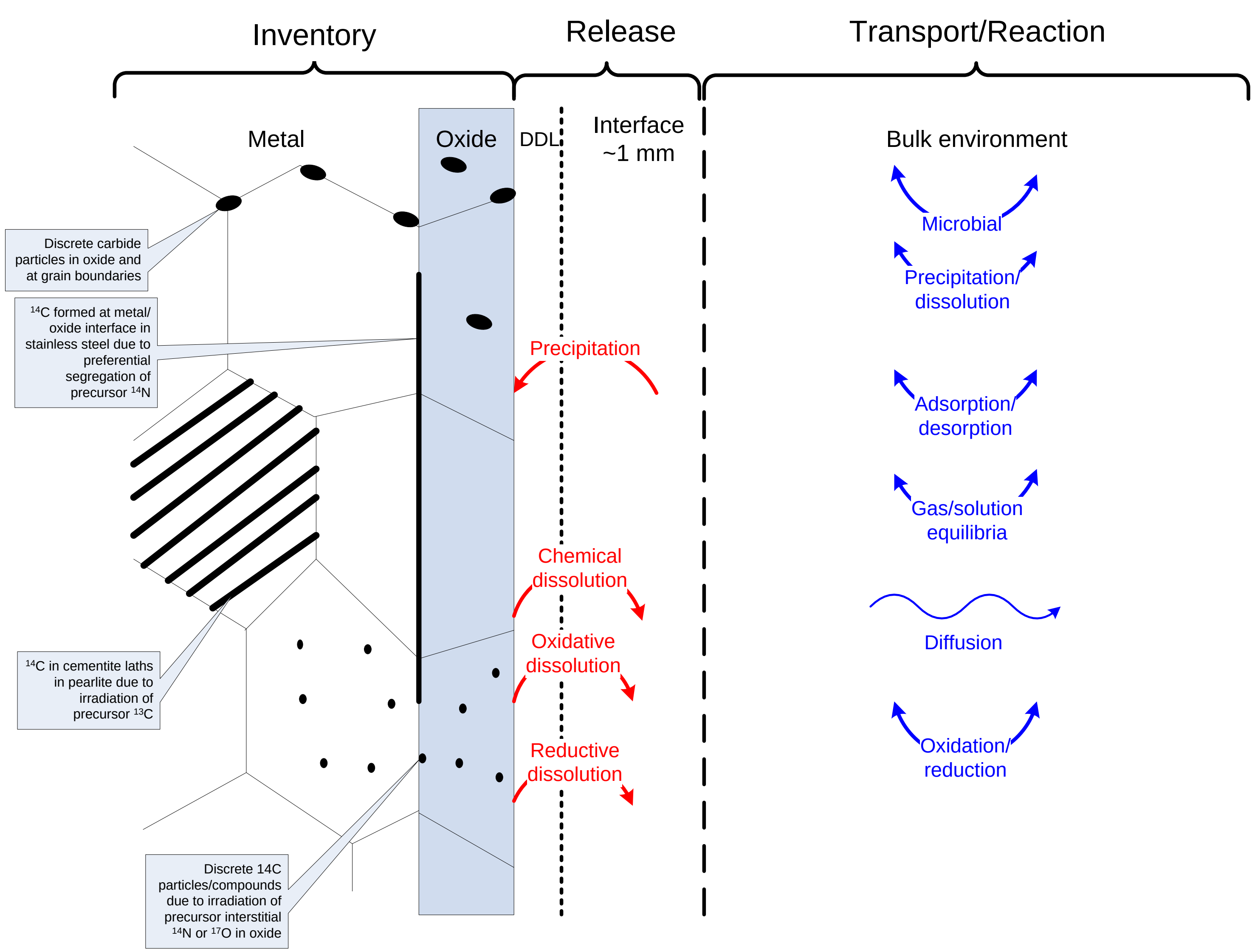


European Commission
European Research Area

Radioactive Waste Management

C14AST

CAST Experimental Work Packages



- Inventory
  - How much?
  - In what (chemical) form?
  - How is it distributed?
- Release
  - Rate
  - Mechanism
  - Speciation
- Transport/reaction
  - After release
  - Possibility of change of speciation

Radioactive Waste Management

EUROPEAN COMMISSION
European Research Area

Work Package 2 Steels

- Aims
  - State-of-the-art review
  - Advance understanding of C-14 speciation
  - Develop analytical techniques
  - Measure release rates
  - Confirm/measure inventory
- Challenges
  - Obtaining and working with irradiated samples
  - Extremely low C-14 release rates in test environments
  - Measuring corrosion rates of irradiated materials under alkaline conditions
  - Demonstrating congruent release of C-14
  - Distinguishing surface contamination from IRF from long-term release
  - Uncertainty in inventory, in part because of lack of archive material (actual N content)
  - Effect of dose rate on release and speciation of C-14
  - Duration of experiments
  - Characterisation of inventory – how much, in what form, and distribution within samples

Radioactive Waste Management

CAST

EUROPEAN COMMISSION
European Research Area

Summary release of ^{12}C and ^{14}C

Organisation	Conditions	Material	Liquid phase		Gas phase	
			Species	%	Species	%
PSI inactive	alkaline anoxic	SS	**AA, FA, OA**	**95**	**Methane, Ethane**	**5**
PSI active	alkaline anoxic	SS	**FA, AA, LA**	**n.d.**	**n.d.**	**n.d.**
NRG / Wood	alkaline anoxic	SS	**CO_3**	**90**	**Methane, (CO)**	**10**
KIT	acidic digestion	SS	**organic**	**70**	**organic**	**30**
SCK-CEN	alkaline anoxic	CS	**AA, FA**	**n.d.**	**Methane**	**n.d.**
Ciemat	alkaline oxic	SS	**n.d.**	**n.d.**	**CO**	**n.d.**
	acidic oxic	SS	**OA**	**n.d.**	**CO**	**n.d.**

SS – Stainless steel; CS – Carbon steel; OA - Oxalic acid;
FA - Formic acid; AA - Acetic acid; n.d. - Not Detected

Radioactive Waste Management

CAST

European Research Area
EUROPEAN COMMISSION

WP2 Steels

- Achievements/highlights
  - Obtaining samples and making C-14 measurements on activated materials
  - Improved understanding of release of C-14
  - Microstructural characterisation of irradiated material
    - Where is C-14 located and in what form?
  - Improved understanding of inventory
  - Good understanding of rate of corrosion under disposal conditions (inactive samples)
  - Issue of congruent release
  - D 2.18 Final synthesis report on results from WP2

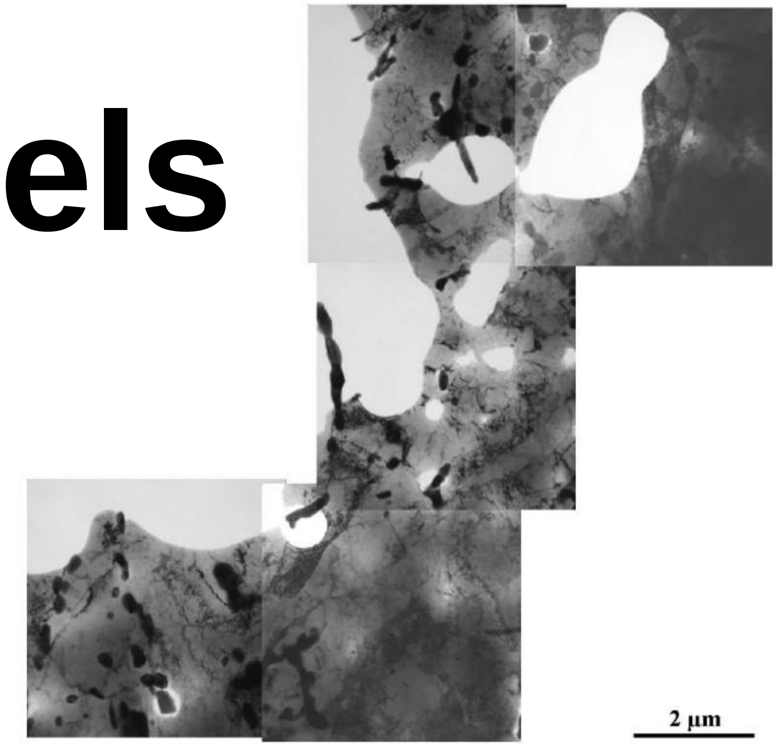


Figure 25. Collage of bright field micrographs showing the grain structure and carbide distribution.

Microstructure irradiated JRQ carbon steel (Druyts et al., CAST Report D2.7)

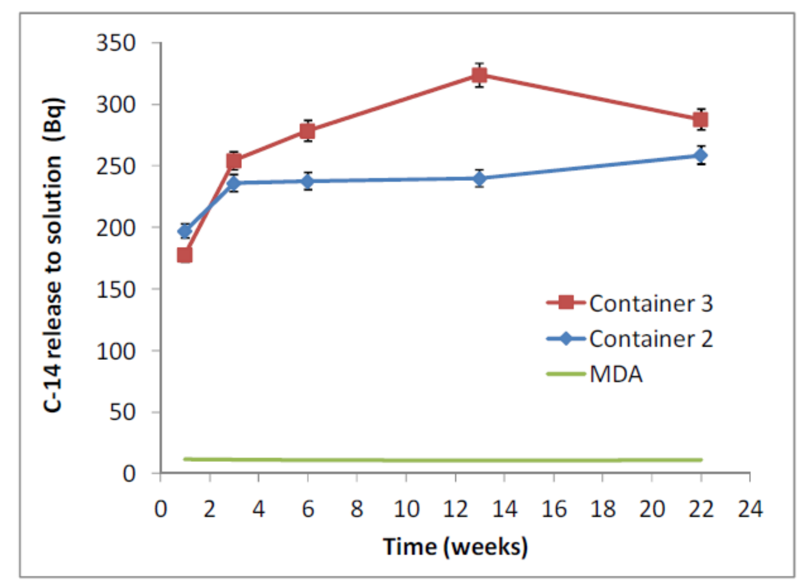


Figure 3 Cumulative carbon-14 activity released to solution over time during leaching of irradiated stainless steel samples in 0.1 mol dm^{-3} NaOH solution; no carbon-14 has been detectable in the leachate samples from Container 1, i.e. it is below the minimum detectable activity (MDA)

Release of C-14 from two irradiated SS samples in alkaline anoxic solution and one blank (Visser-Týnová et al., CAST Report D2.8)

Radioactive Waste Management

CAST

European Commission
European Research Area

WP3 Zircaloys

- Aims
  - State-of-the-art review
  - Advance understanding of C-14 speciation
  - Develop analytical techniques
  - Measure release rates
  - Confirm/measure inventory
- Challenges
  - Obtaining and working with irradiated samples
  - Extremely low C-14 release rates in test environments
  - Measuring corrosion rates of irradiated materials under alkaline conditions
  - Demonstrating congruent release of C-14
  - Uncertainty in inventory, in part because of lack of archive material (actual N content)
  - Effect of dose rate on release and speciation of C-14
  - Duration of experiments
  - Characterisation of inventory – how much, in what form, and distribution within samples
  - *Influence of hydride layer*
  - *Possibility of change in corrosion/release rate as oxide thickens*

Radioactive Waste Management

CAST

European Commission
European Research Area

Zircaloys - C-14 analyses

Organisations	Speciation				Method
	Solutions	Organics	Inorganics	Gas	
CEA	NaOH	Glycolate Acetate Formate Oxalate	Carbonate		Anionic Chromatography
	Blank	Acetate Formate	Carbonate		Anionic Chromatography
SCK.CEN	$Ca(OH)_2$	Acetate Formate		Methane Ethene CO_2	Ion Chromatography Gas Chromatography
SUBATECH	NaOH	Formate Acetate Propionate Oxalate			Ion Chromatography

- Zr type does not influence C-14 speciation (Zr-4 + M5^{TM})
- Some differences for CEA + SUBATECH => Difficulty of the analyses
- Liquid phase=> Carboxylic acids + Carbonates
- Gas phase => Hydrocarbons + CO_2

Radioactive Waste Management

CAST

EUROPEAN COMMISSION
European Research Area

Zircaloys - Corrosion rate measurements

Organisations	Materials / Methods	Corrosion rate (nm/yr)					
		Duration	Unirradiated		Duration	Irradiated	
			H_2 measured	Electro-chemistry		C-14 leaching fraction	Electro-chemistry
RATEN ICN	Zr-4 (CANDU) Oxidised As-received Cut at one end	12mths		0.3 110 60	6 mths 18 mths		110 50
RWMC	Zr-2	2 yrs	~5		6.5 yrs	~ 1	
SCK.CEN	Zr-4				6 mths	84	

- Decrease of the corrosion rates with time
- Influence of irradiation on the corrosion rates
- Significant uncertainties on the measurements (various techniques,…)

Radioactive Waste Management

CAST

WP3 Zircaloys

- Achievements/highlights
  - Obtaining samples and making C-14 measurements on activated materials
  - Good agreement between measured and calculated inventories
  - Good database of long-term corrosion rates
  - Unclear whether C-14 released congruently
  - Less C-14 in oxide (7.5%) than currently assumed as IRF in PA
  - [D 3.20 Final report on C14 behavior in Zr fuel clad wastes under disposal conditions]

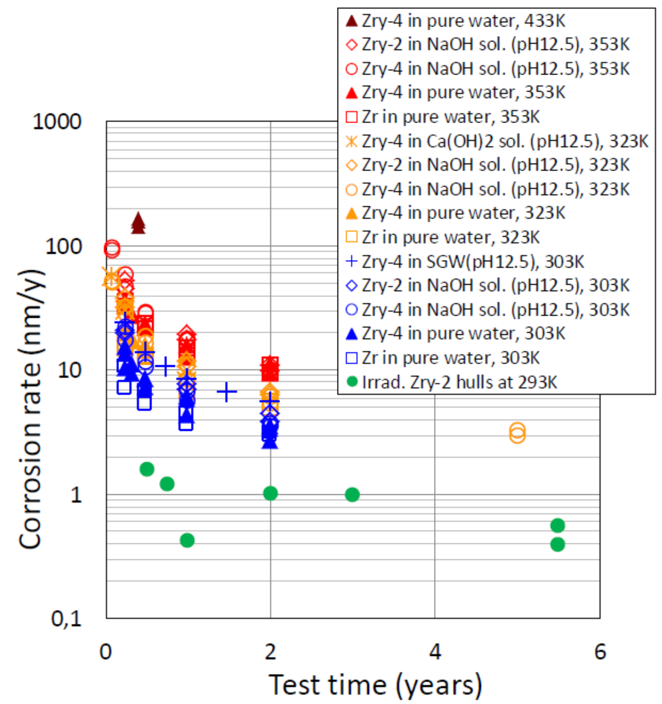


Figure 3: Corrosion rate for unirradiated Zircaloys obtained by hydrogen measurement under different conditions and for irradiated Zircaloy-2 hull (BWR cladding without oxide) obtained from leached ^{14}C in a NaOH solution (pH 12.5) at 293K.

Comparison of irradiated (assuming congruent C-14 release) and inactive corrosion rates of Zircaloy (Herm et al., CAST Report D3.15)

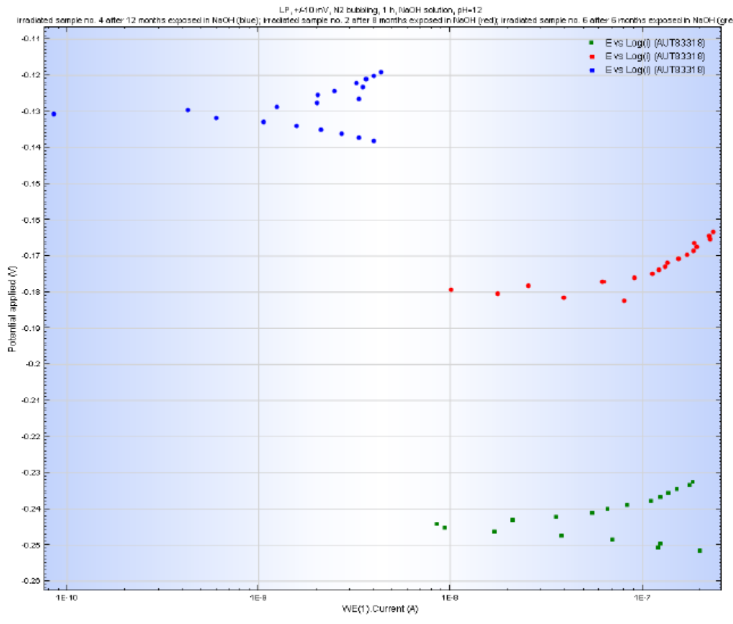


Figure 27 (E vs log(i)) polarization curves for: irradiated sample after 12 months immersion in NaOH (blue); irradiated sample after 8 months immersion in NaOH (red) and irradiated sample after 6 months immersion in NaOH (green)

Electrochemical behaviour of Zy-4 after 6, 8, 12 months (Bucur et al., CAST Report D3.16)

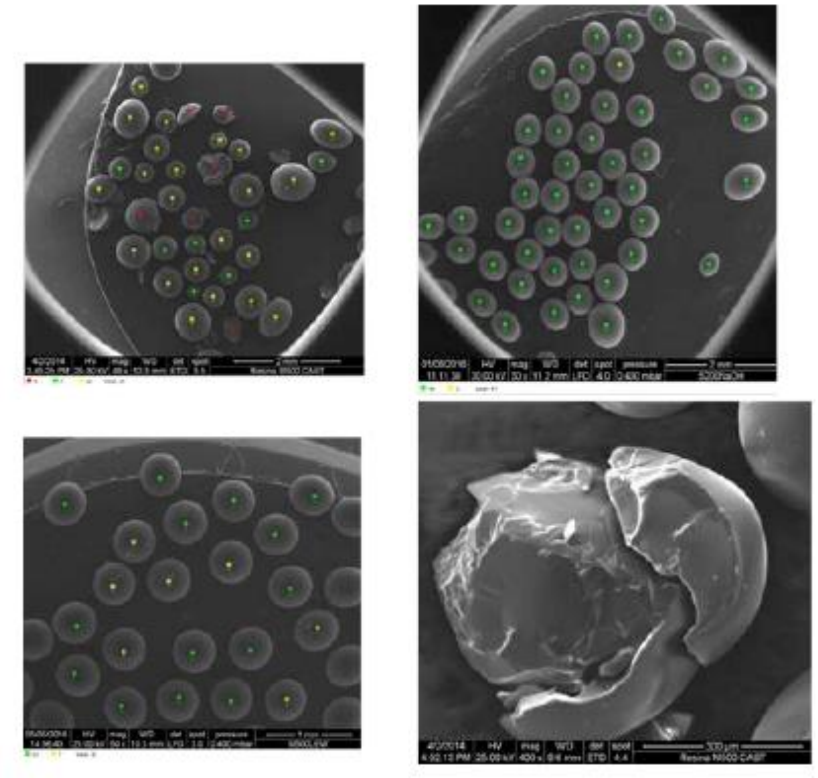
European Commission
European Research Area

Radioactive Waste Management

CAST

WP4 Spent Ion Exchange Resins

- Aims
  - State-of-the-art review
  - Understanding inventory and speciation
  - Determining release rate and mechanism
- Challenges
  - Wide range of SIER characteristics due to different types of operating plants and different IX locations within a given plant
  - Relating release to geological disposal conditions for cemented and immobilised SIERs
    - Effects of porosity, groundwater flow, etc.
  - Uncertainty over long-term (radiation) stability of resins



Rizzo et al., CAST Report D4.5, Appendix V

European Commission
European Research Area

WP4 Spent Ion Exchange Resins

- Achievements/highlights
  - Because of the wide variability of SIERs, country-specific inventories and speciation are required
  - Good understanding of speciation
    - In general, majority present as inorganic C-14 but fraction depends on reactor type
      - PWR: 1-70% organic
      - BWR: 1-5% organic
      - CANDU: 7% organic (single sample)
  - Gas-phase inorganic C-14 is released when SIERs are contacted with alkaline pH **solutions** (precipitation of $CaCO_3$ under storage and long-term disposal conditions (cement)
  - Effect of immobilization in cement, epoxy, bitumen matrix
    - At least for cement, significantly reduces release of C-14
- D 4.9 Final synthesis report

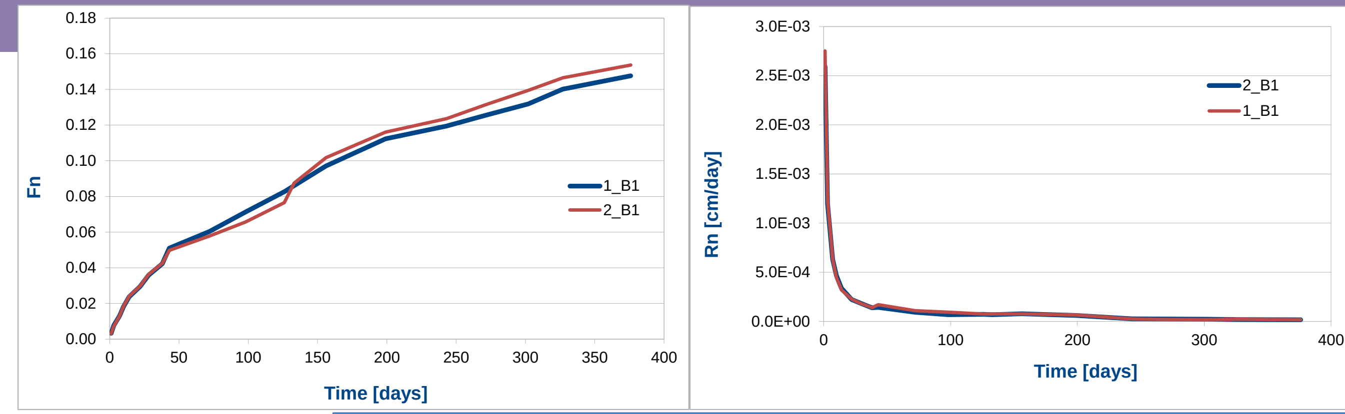
Radioactive Waste Management

CAST

WP5 Irradiated Graphite

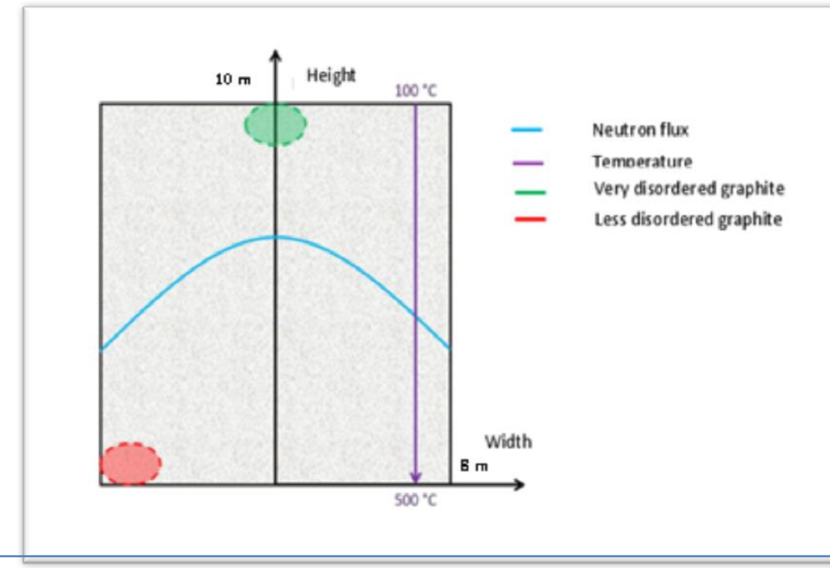
- Aims
  - Built on earlier EC CARBOWASTE project and took input from other relevant international projects
  - Determine inventory and distribution of C-14 and factors that may control these
  - Measure rate and speciation of gaseous and dissolved C-14 released
  - Assess impacts of selected waste treatment options
- Challenges
  - Diversity of national interests
    - Amount of irradiated graphite waste
    - Surface vs. deep geological disposal

WP5 Irradiated Graphite

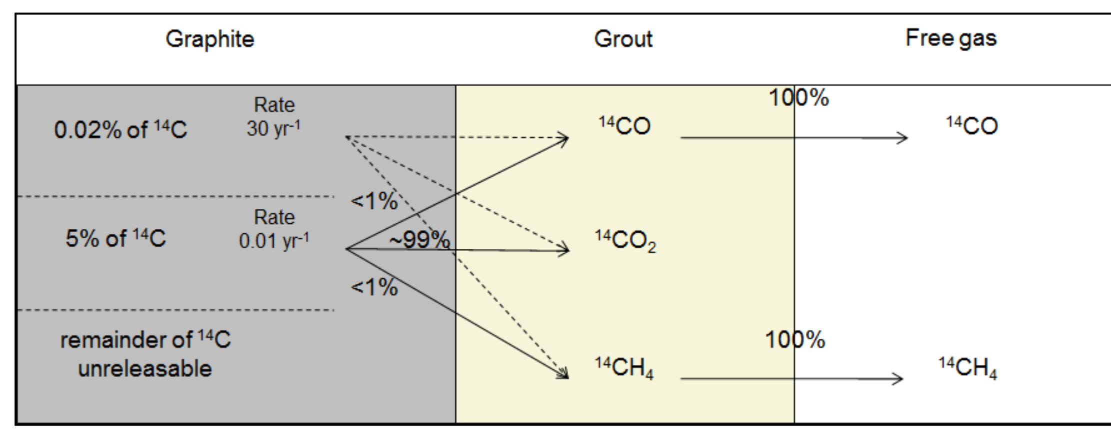


Graphite leaching tests at RATEN ICN, Toulhaut et al., CAST Report D5.19

- Achievements/highlights
  - Detailed understanding of distribution of C-14 within the waste
  - Improved mechanistic understanding
    - Small releasable fraction
    - Initial fast release, slow long-term
    - Speciation
    - Inventory and especially distribution
    - Consequences of in-reactor behaviour
- D 5.19 Final report on results from WP5



Impact of in-reactor irradiation and temperature, Toulhaut et al., CAST Report D5.19



C-14 release mechanism proposed by RWM, Toulhaut et al., CAST Report D5.19

WP6 Relevance to the Safety Case

- Aims
  - Improve treatment of C-14 in safety analysis/ assessment
    - Speciation, IRF, release rate, etc.
  - Improve treatment of C-14 in safety case
    - Scientific understanding
- Challenges
  - Working with experimental groups to ensure the study of processes that are safety-relevant
  - Diversity of national disposal programmes
  - Abstraction of data (and uncertainties) from experimental programmes

WP6 Relevance to the Safety Case

- Achievements/highlights
  - Understanding of relative importance of C-14 for different host rock types
    - Clay vs. crystalline vs. salt
  - Understanding of relative importance of C-14 for different waste types
    - e.g., for spent fuel, C-14 will likely decay in long-lived canister
  - Understanding of relative importance of C-14 depending on repository location
    - Surface vs. deep disposal
  - CAST has produced a lot of useful information for the safety case as well as for underlying safety analyses
  - D 6.4 Final WP6 report

WP7 Dissemination

- The objectives of WP7 Dissemination were to disseminate information about CAST activities and results (provided they are suitable for public circulation) as widely as possible to various target groups having an interest in the project and its results.

EUROPEAN COMMISSION
European Research Area

WP7 Dissemination

- For public dissemination, workshops were held for waste management organisations, regulators and waste generators.
- Continuous update of developed information has been provided in reports, presentations at scientific fora, scientific publications and newsletters through the public website.
- There were also training courses to actively train early-career participants in CAST activities.
- www.projectcast.eu/programme/wp7-dissemination

Radioactive Waste Management

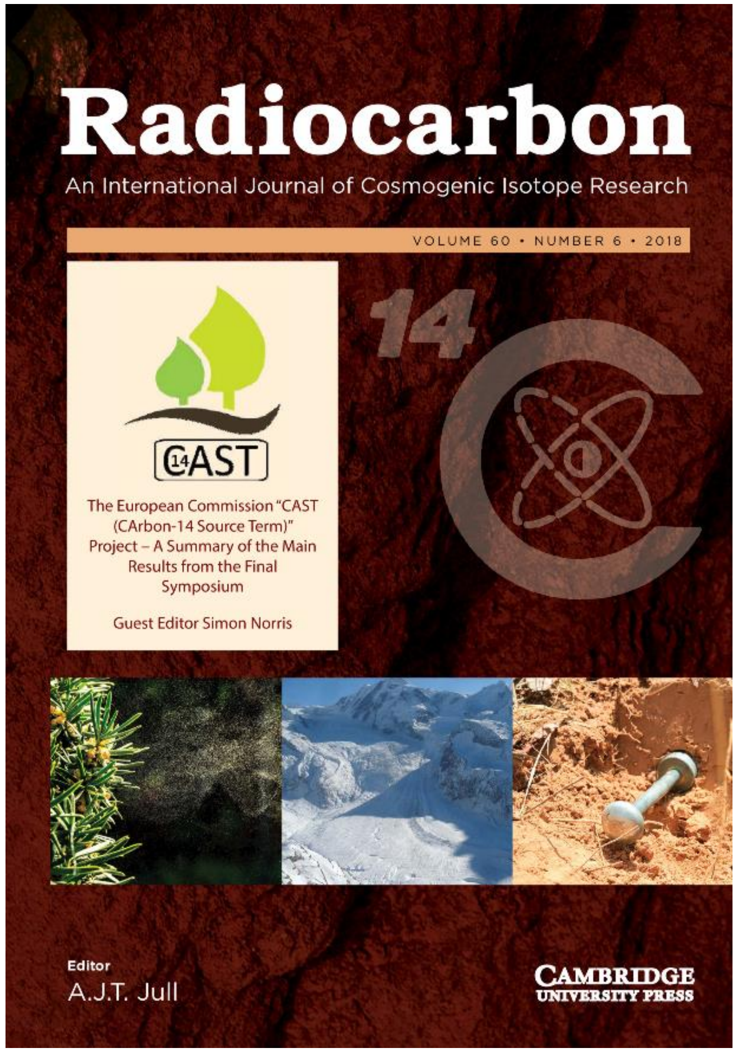
CAST

Interaction, Collaboration, Enhancement of Knowledge Base

Whole-project meetings London (2013), Brussels (2014), Bucharest (2015) & Lucerne (2016); many work-package meetings; Symposium in Lyon (2018)

Outreach

- CAST website available www.projectcast.eu
- CAST Radiocarbon journal special issue (https://www.cambridge.org/core/journals/radiocarbon/issue/B16E687954999C131670CC8705D8A2B0)
- 20+ papers
  - Irradiated steels
  - Irradiated Zircaloys
  - SIERs
  - Irradiated graphite
  - Safety assessments



Radioactive Waste Management

Conclusions

- "… to gain new scientific understanding …."
  - Clearly achieved
- "…. of relevance to safety assessment …"
  - Useful data generated for safety analyses and especially underlying information to support the safety case
- "… disseminated to stakeholders …."
  - Workshops, impressive number of reports / deliverables (>100), open symposium, Radiocarbon special issue …
- "… opportunity for early career researchers ..."

Thank you for your help!

- Christophe Davies (EC)
- Steve Williams (RWM – original coordinator)
- Jens Mibus (Nagra – CAST WP2 Leader)
- Sophia Necib (Andra – CAST WP3 Leader)
- Pascal Reiller (CEA – CAST WP4 Leader)
- Manuel Capouet (Ondraf/Niras – CAST WP6 Leader)
- Erika Neeft (Covra – CAST WP7 Leader)
- Fraser King (Integrity Corrosion Consulting, CAST Expert Review Group)
- Irka Hajdas (ETH, Switzerland, CAST Expert Review Group)