

2<sup>nd</sup> NKS-B Workshop on Radioanalytical Chemistry, Riso, Sept 2013,

## Application of Thermal Desorption Techniques to the Characterisation of Nuclear Decommissioning Wastes

Ian Croudace

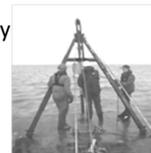
Phil Warwick

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University of Southampton  
National Oceanography Centre



# GAU Radioanalytical Laboratories

University company – undertaking research and consultancy



### Research & Development

Research on :  
Novel separation chemistries  
Radioanalytical techniques  
Instrument development  
Validation

### Consultancy services

Advice on sampling strategy & analytical programmes to :  
Government Agencies  
Nuclear industry  
Decommissioning services  
Waste disposal operators

### Analytical services

Commercial service to Industry  
Radionuclide analysis  
Elemental/ complexant analysis  
Opinions & Interpretations



### Industry training

Specialist training programmes  
CPD training  
Specialist analytical training  
End user awareness  
Guidance manuals  
KTS schemes

### PhD training

NDA & industry funded studentships  
Current research:  
Nuclear forensics  
Lab automation  
PRB technologies  
Environmental geochem  
Mass spectrometry  
Bioassay

## In the beginning ..... why an efficient thermal desorption instrument was needed?

1998-2002	GAU conducted a research study funded by the FOOD STANDARDS AGENCY in 1998 to investigate the fate of OBТ discharges from the Maynard Centre
1999	An efficient thermal desorption instrument was needed to allow the work to proceed

**Environmental Science & Technology**

**Evidence for the Preservation of Technogenic Tritiated Organic Compounds in an Estuarine Sedimentary Environment**

by M. Crockett, Philip R. Rowan, and James R. Martin

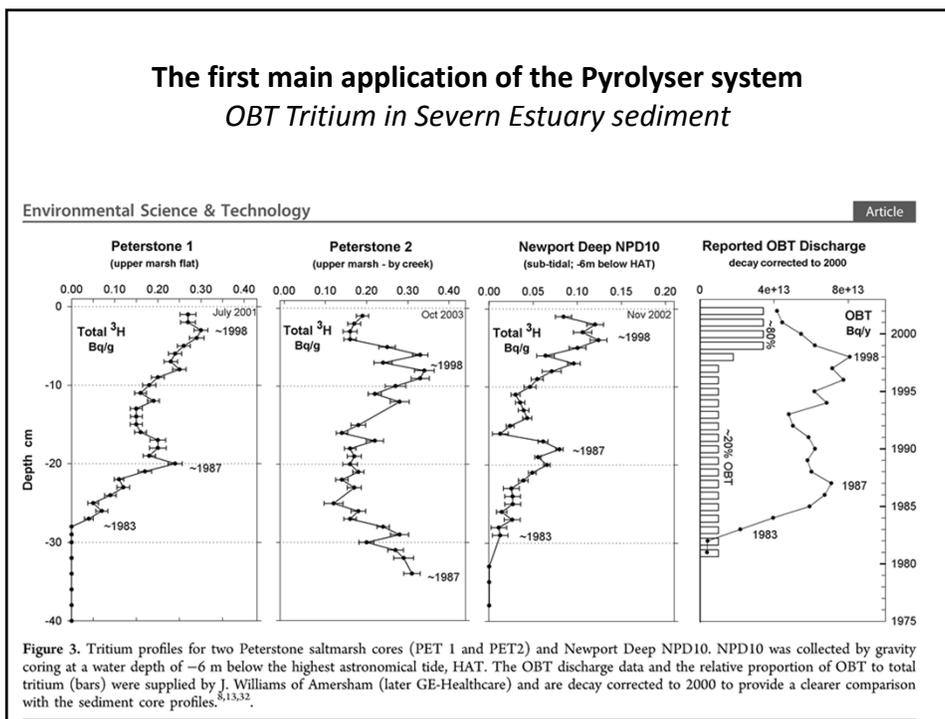
Environmental Science & Technology, 2000, 34(12), 2305-2312

OBТ discharged into estuary from 1980-2009

## Development of a novel thermal desorption instrument

1999	An efficient thermal desorption instrument was needed for the research work
1999	The multi-sample PYROLYSER-Trio was invented and commercialised

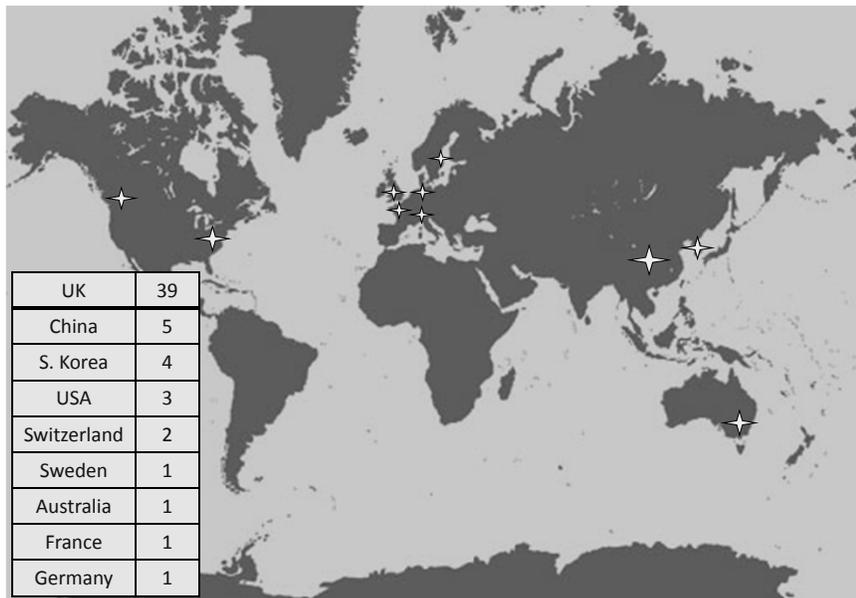
The diagram shows a horizontal tube with a sample boat at the front, followed by quartz wool on both sides, and a catalyst zone. A temperature profile graph below shows the temperature (°C) versus distance from the front of the furnace (cm). The graph indicates set points for the sample zone (90°C), mid-zone (90°C), and catalyst zone (300°C). A note states: 'Measurements made in the presence of airflow'.



## Development of a novel thermal desorption instrument

1999	An efficient thermal desorption instrument was needed to allow the work to proceed
1999	The PYROLYSER-Trio was invented and commercialised
2000-now	PYROLYSER widely adopted in the UK Magnox decommissioning programme Approximately 100,000 samples analysed over 10 years
2006-now	PYROLYSERS adopted worldwide

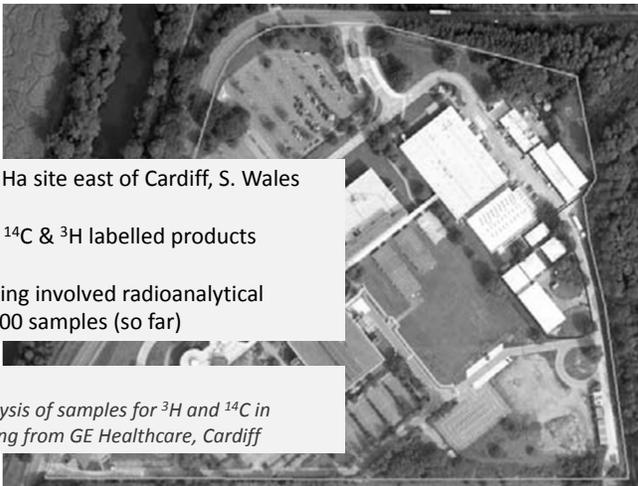
## Pyrolysers worldwide (57)



## Development of a novel thermal desorption instrument

1998-2003	GAU conducted a research study funded by the FSA in 1998 to investigate the fate of OBT discharges from the Maynard Centre (Cardiff)
1999	An efficient thermal desorption instrument was needed to allow the work to proceed - 'necessity is the mother of invention'
1999	The PYROLYSER-Trio was invented
2000-now	PYROLYSER widely adopted in the UK Magnox decommissioning programme >100,000 samples analysed in 10 years from Magnox sites
2006-now	PYROLYSERS adopted worldwide
2010-now	GE-Healthcare withdraws from radiopharmaceutical business and need to decommission their old manufacturing site
2010	GE-Healthcare commissions GAU to set up an on-site lab for $^3\text{H}$ and $^{14}\text{C}$ and also to provide analytical support during characterisation stage. Approx. 6000 samples analysed for $^3\text{H}$ and $^{14}\text{C}$

## GE Healthcare The Maynard Centre Decommissioning Project The UK's largest private sector decommissioning programme



The facility was built on a 15 Ha site east of Cardiff, S. Wales

1980-2009 - Manufactured  $^{14}\text{C}$  &  $^3\text{H}$  labelled products

2010 – now - Decommissioning involved radioanalytical characterisation of over 10,000 samples (so far)

### GAU Technical Document Used

*Sampling, preservation and analysis of samples for  $^3\text{H}$  and  $^{14}\text{C}$  in decommissioning materials arising from GE Healthcare, Cardiff*

GAU has analysed approx. 6000 samples (so far) for  $^{14}\text{C}$  &  $^3\text{H}$  during the decommissioning programme

## Applications to decommissioning

Accumulating the evidence PhD student ideal

- $^3\text{H}$  origin
- Thermal Desorption profiles
- Sample Composition effects
  - Concrete
  - Asbestos
  - Metals
  - Graphite
  - Plastic

## **Origin of $^3\text{H}$ contamination**

- Exposure to tritiated water (HTO) either as a liquid or vapour (Nuclear sites – particularly heavy-water reactors)
- *In-situ* production via neutron capture / ternary fission  
Nuclear sites
- HT gas - fusion and nuclear weapon fabrication sites
- Non-aqueous  $^3\text{H}$  (‘organically-bound  $^3\text{H}$ ’)  
e.g. radiopharmaceutical manufacture and use

## **Measurement of $^3\text{H}$ in solids**

1. Thermal desorption followed by LSC on bubbler soln.
2. Simple leaching (equilibration) with  $^3\text{H}$ -free water and measurement of  $^3\text{H}$  in aqueous phase / LSC
3. Sample digestion / distillation / LSC
4. He-3 mass spectrometry (specialised)

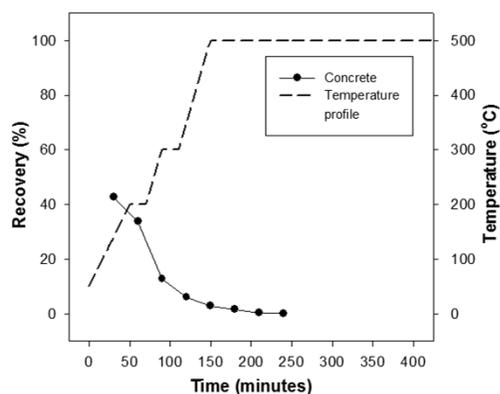
## $^3\text{H}$ Thermal Desorption Profiles

Single Total  $^3\text{H}$  thermal extraction or  
Multiple incremental  $^3\text{H}$  extractions

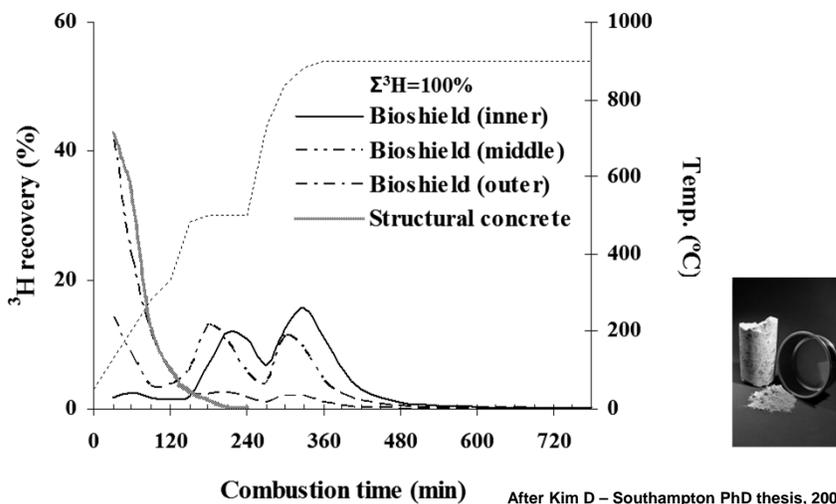
The T °C at which  $^3\text{H}$  desorbs from samples varies and depends on

- **origin of the  $^3\text{H}$**  (HT, HTO, OBT, *in-situ* formation)
- **chemical association of  $^3\text{H}$  in the sample** (hydroxide etc)
- **the sample composition** (concrete, metal, graphite etc)

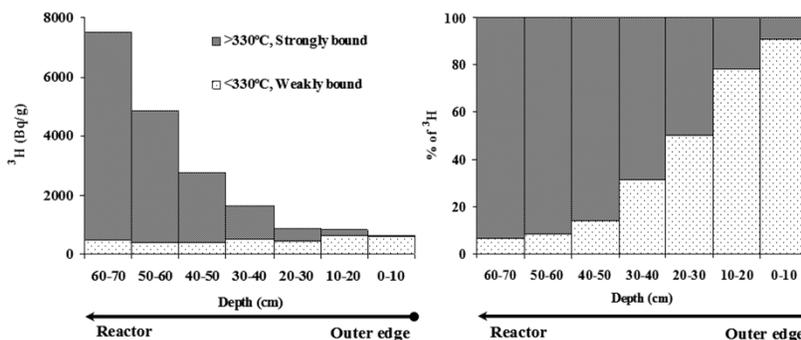
## $^3\text{H}$ desorption profiles from concrete exposed to HTO



### Desorption profiles for structural and bioshield concrete (heavy-water reactor site)



### Relative proportion of 'strongly bound' and 'loosely bound' $^3\text{H}$ in bioshield concrete

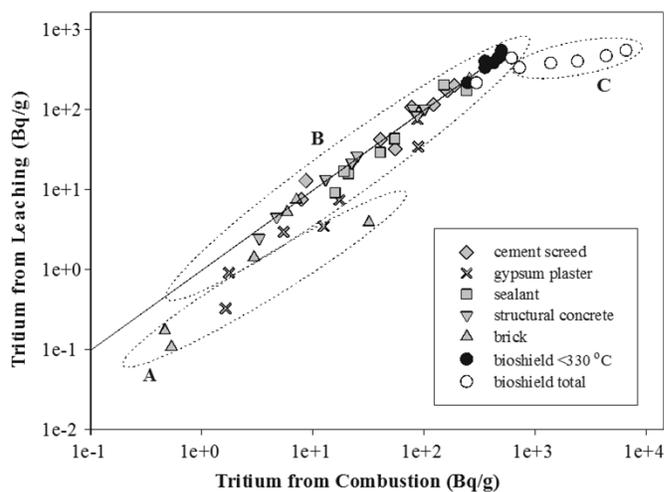


### $^3\text{H}$ extraction by leaching & thermal decomposition

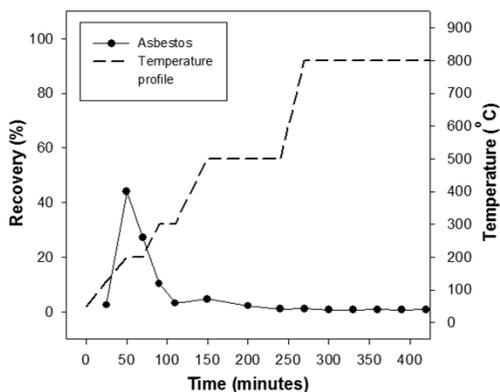
**A** – difficult to leach quantitatively

**B** – Comparable data

**C** – difficult to leach quantitatively



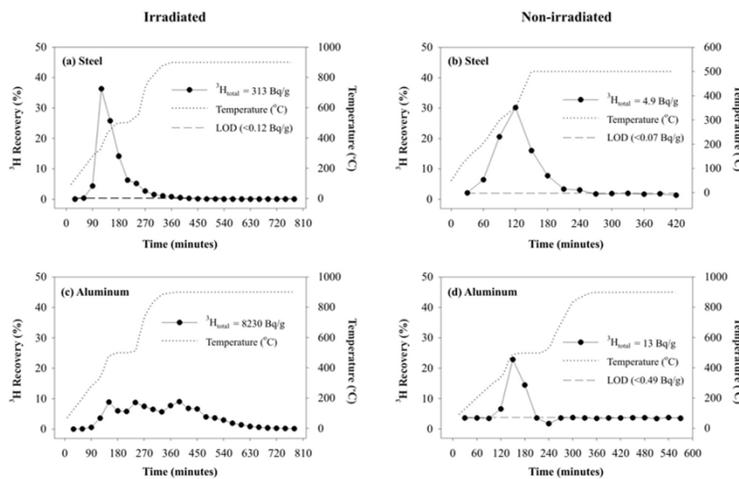
### $^3\text{H}$ evolution profiles from asbestos insulation from a Magnox reactor site



Asbestos exposed to HTO and no neutrons

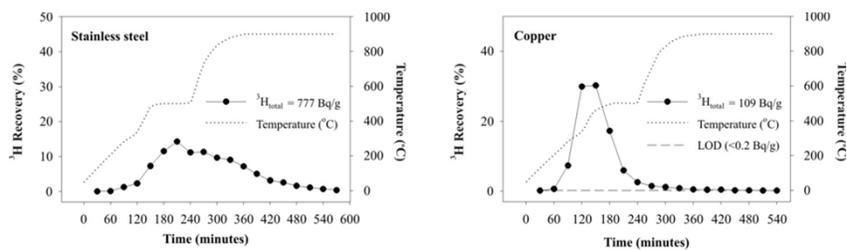


## $^3\text{H}$ desorption profiles from metals (I)



After Kim D – Southampton PhD thesis, 2009

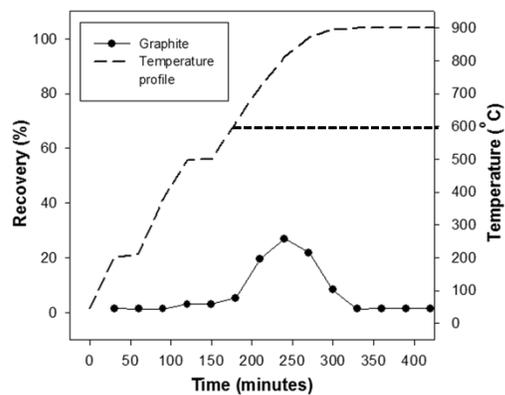
## $^3\text{H}$ desorption profiles from metal (II)



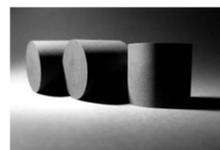
Non-irradiated metals

After Kim D – Southampton PhD thesis, 2009

## $^3\text{H}$ desorption profile from irradiated graphite

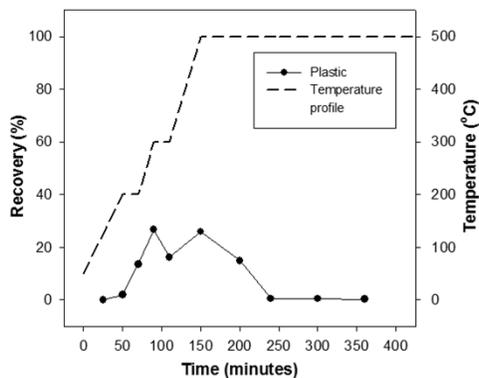


Graphite moderator  
(irradiated)



After Kim D – Southampton PhD thesis, 2009

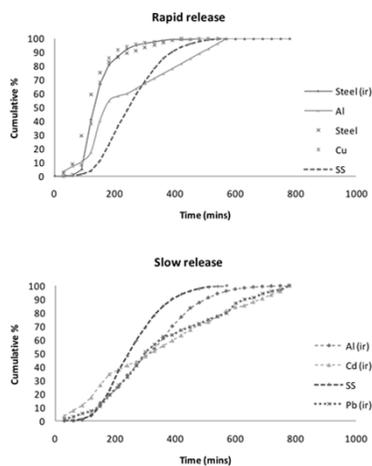
## $^3\text{H}$ in plastics



Polythene  
exposed to HTO

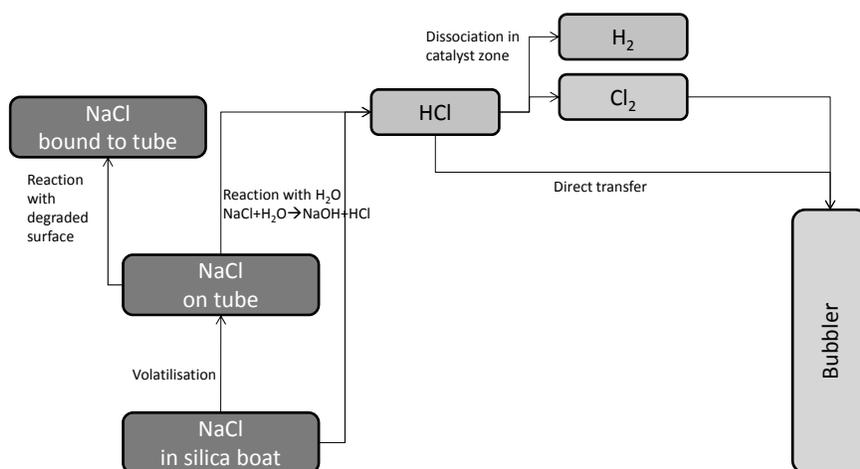
### Determination of thermal desorption profiles & cumulative tdp's provide an insight into the association of the $^3\text{H}$ in metals.

- $^3\text{H}$  lost at temperatures around  $100^\circ\text{C}$  is indicative of free  $^3\text{H}$ -water
- $^3\text{H}$  lost around  $300^\circ\text{C}$  indicates breakdown of hydroxide or oxyhydroxide phases
- $^3\text{H}$  lost at  $800\text{-}900^\circ\text{C}$  indicates a strongly bound form of  $^3\text{H}$  (e.g. n capture by Li)



### $^{36}\text{Cl}$ & $^{129}\text{I}$ extractions using the Pyrolyser

$^{36}\text{Cl}$  is present in nuclear graphite, concretes, ion exchange resins & desiccants



## Bubbler solution ( $\text{Na}_2\text{CO}_3$ ) passed through a Triskem silver loaded Cl-resin

- quantitative uptake of both isotopes by silver loaded Cl-resin
- $^{36}\text{Cl}$  is eluted quantitatively at any KSCN concentration
- $^{129}\text{I}$  remains on the resin at any KSCN concentration
- $^{129}\text{I}$  is eluted at elevated  $\text{Na}_2\text{S}$  concentrations

## Pyrolyser capability

Already proven  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{35}\text{S}$ ,  $^{36}\text{Cl}$ , and  $^{129}\text{I}$

- Lewis A., Warwick P.E. and Croudace I.W. (2005) Penetration of tritium (as HTO) into low carbon steel and remediation using abrasive cleaning. *J. Radiol. Prot.*, **25**, 1-8.
- Kim D.J., Warwick P.E. and Croudace I.W. (2008) Tritium speciation in nuclear reactor bioshield concrete and its impact on accurate analysis *Anal. Chem.*, **80**, 5476–5480.
- Dae-Ji Kim (2010, Korean Govt) Fundamental studies of methods for tritium analysis in environmental and construction materials. *PhD Thesis*
- Warwick P.E., Kim D., Croudace I.W., J. Oh (2010) Effective desorption of tritium from diverse solid matrices and its application to routine analysis of decommissioning materials. *Analytica Chimica Acta*, **676**, 93–102.
- Kim D., Croudace I.W. and Warwick P.E., (2012) The requirement for proper storage of nuclear and related decommissioning samples to safeguard accuracy of tritium data. *J. Hazard. Mater.*, **213-214**, 292–298.
- Croudace I.W., Warwick P.E., and Morris J.E. (2012) Evidence for the preservation of technogenic tritiated organic compounds in an estuarine sedimentary environment. *Environ. Sci. Technol.*, **46**, 5704–5712.
- Croudace I.W., Warwick P.E. and Kim D. (2011) Advances in tritium extraction methods to aid efficient waste characterisation, *Nuclear Future*, **7**, 48-53.
- Croudace I.W., Warwick P.E. and Kim D. (In prep) Tritium speciation in metals from nuclear sites and its impact of analytical strategy

W. J. Zhou, X. L. Hou, N. Chena, L. Y. Zhang, Q. Liu, C. H. Heb., M.Y. Luo, W. G. Liang, Y. K. Fan, Z.W. Wang, Y. C. Fu, H. B. Li

PRELIMINARY STUDY OF RADIOISOTOPE  $^{129}\text{I}$  APPLICATION IN CHINA USING XI'AN ACCELERATOR MASS SPECTROMETER  
INCS News, 25th issue, Volume VII, Number 1, January 2010

P E Warwick, A Zulauf, S Happel, I W Croudace: TRISKEM SUPPORTED

DETERMINATION OF  $^{36}\text{Cl}$  IN DECOMMISSIONING SAMPLES USING A PYROLYSER FURNACE AND EXTRACTION CHROMATOGRAPHIC SEPARATIONS.  
Presentation at the 11th ERA Symposium, 16/09/2010, Chester (UK)

## Conclusions

- Tritium may be present in a number of different forms depending on the source of  $^3\text{H}$  and sample composition and Thermal desorption instruments like the Pyrolyser efficiently provide  $^3\text{H}$  'speciation' and total activity information.
- Tritium desorption profiles provide insights into the kind of tritium in a sample and can guide the practical approach to use for specific materials.
- Temperatures in excess of  $800^\circ\text{C}$  are required to liberate  $^3\text{H}$  from graphite, metals and irradiated materials. For all other sample types tested,  $600^\circ\text{C}$  is generally sufficient.
- The thermal desorption process is successful for  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{35}\text{S}$ ,  $^{36}\text{Cl}$ , and  $^{129}\text{I}$ .
- It is expected that it could be extended to include  $^{99}\text{Tc}$  and  $^{210}\text{Po}$ .

## NEW FROM RADDEC

### HBO<sub>2</sub> Hyperbaric Oxidiser

designed to collect tritium from large masses of soft wastes  
and environmental samples



Thank you

### **$^3\text{H}$ sources in concretes**

- Adsorbed HTO > 105°C
- Dehydration of ettringite  $(\text{CaO})_6(\text{Al}_2\text{O}_3)(\text{SO}_3)_3 \cdot 32\text{H}_2\text{O}$  100 - 200°C
- Dehydration of portlandite  $\text{Ca}(\text{OH})_2$  > 450°
- Decomposition of structural OH groups > 500°C
  
- Form of  $^3\text{H}$  present will depend on source of  $^3\text{H}$   
adsorption of HTO or  
*in situ* production from neutron reactions with D, Li or B

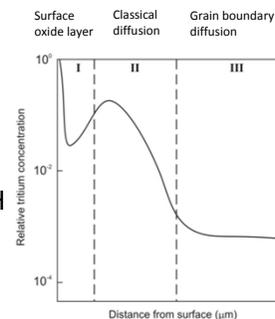
## Partitioning of $^3\text{H}$ in concrete

(exposure source HTO)

Compartment	Desorption temperature (°C)	% of total $^3\text{H}$
Capillary / porewater	< 200°C	77%
Water of crystallisation	200 – 450°C	15%
Calcium hydroxide (Portlandite)	450 – 550°C	7%
Calcium silicate hydrate	600 – 850°C	1%

## $^3\text{H}$ in metals – inferred from HT studies

- Surface oxyhydroxides (200 - 300°C)
- H diffused into metal lattice
- The form of  $^3\text{H}$  present depends on source of  $^3\text{H}$  (adsorption of HTO or in situ production via neutron activation of D or Li)



Generalised trend of  $^3\text{H}$  gas distribution in steel exposed to HT (after Perevezentsev et al, 2008)

Thermal decomposition temperatures for  $\text{Fe}(\text{OH})_3$  and  $\text{Cu}(\text{OH})_2$  are comparable at ca 275°C.

The similarity in profiles for **non-irradiated and irradiated steels** would suggest that the  $^3\text{H}$  retention mechanism is similar in both cases and probably associated with structural **oxyhydroxide** formation.

$^3\text{H}$  in **steel** is likely trapped in hydroxyl groups that will thermally decompose to yield tritiated water.

The first stage occurs at temperatures comparable to those required for the decomposition of  $\text{Fe}(\text{OH})_3$  or  $\text{Cu}(\text{OH})_2$  and the first  $^3\text{H}$  evolution stage for Al is comparable with steel and Cu metal. The second stage occurs at much higher temperatures (above 425°C) giving rise to the observed step change in the cumulative evolution profile.

For non-irradiated stainless steels, the thermal desorption of  $^3\text{H}$  required temperatures in excess of 500°C. This is most likely due to the penetration of  $^3\text{H}$  into the bulk metal requiring high temperatures to facilitate the liberation of the  $^3\text{H}$  along metal grain boundaries

The temperature of  $^3\text{H}$  desorption will depend on whether it is present in the metals as free water, water of crystallization, surface oxyhydroxides layer, structural OH groups or trapped along grain boundaries  $^3\text{H}$ .