

Eva de Visser – Týnová¹, Stephen W. Swanton², Stephen J. Williams³, Marcel P. Stijkel¹, Alison J. Walker⁴, Robert L. Otlet⁴

¹ Nuclear Research & consultancy Group (NRG), P. O. Box 25, 1755 ZG Petten, The Netherlands *Corresponding author: E. de Visser-Týnová, e-mail: devisser@nrg.eu

² Wood, Building 150, Harwell Campus, Didcot, OX11 0QB, United Kingdom

³ Radioactive Waste Management, Building 587, Curie Avenue, Harwell Campus, Didcot, OX11 0RH, United Kingdom

⁴ RadioCarbon Dating Lockinge Ltd, Unit 1 Lockinge Stables, East Lockinge, Wantage, OX12 8QY, United Kingdom

EXPERIMENTAL

OBJECTIVES

The objective of this work is to measure the rate and speciation of carbon-14 release from irradiated stainless steel on leaching under high-pH anaerobic conditions, representative of a cement-based near field for intermediate- and some low-level wastes (ILW/LLW). In particular, this includes measurements of releases to the gas phase as well as to solution. The gas phase carbon-14 collection method allows for the discrimination of carbon-14 released as ¹⁴CO₂, ¹⁴CO (and volatile oxidized species) or ¹⁴C-hydrocarbons. The carbon-14 solution analysis method used to date has measured the inorganic carbon-14 release only. Work is in progress to measure the total carbon-14 release to solution that includes any dissolved organic carbon-14 species.

SAMPLES

- 316L(N) austenitic stainless steel from single sheet
- 6 compact tension (CT) specimens irradiated at HFR, Petten – SIWAS 07 experiment (2dpa, 80°C, 5 28-day cycles) in 1996/97
- C-14 and Co-60 inventory assessed by ORIGIN calculations
 - Co-60 in good agreement with γ -spec measurement
- 3 experiments each with 3 CT specimens
- Un-irradiated from same sheet

Container	1	2	3
Mass (g)	228	221	222
Geo.SA. (cm ²)	104.4	114.4	114.4
C-14 (Bq)	0.1	4.9E+07	4.9E+07
Co-60 (Bq)	0	1.6E+10	1.6E+10

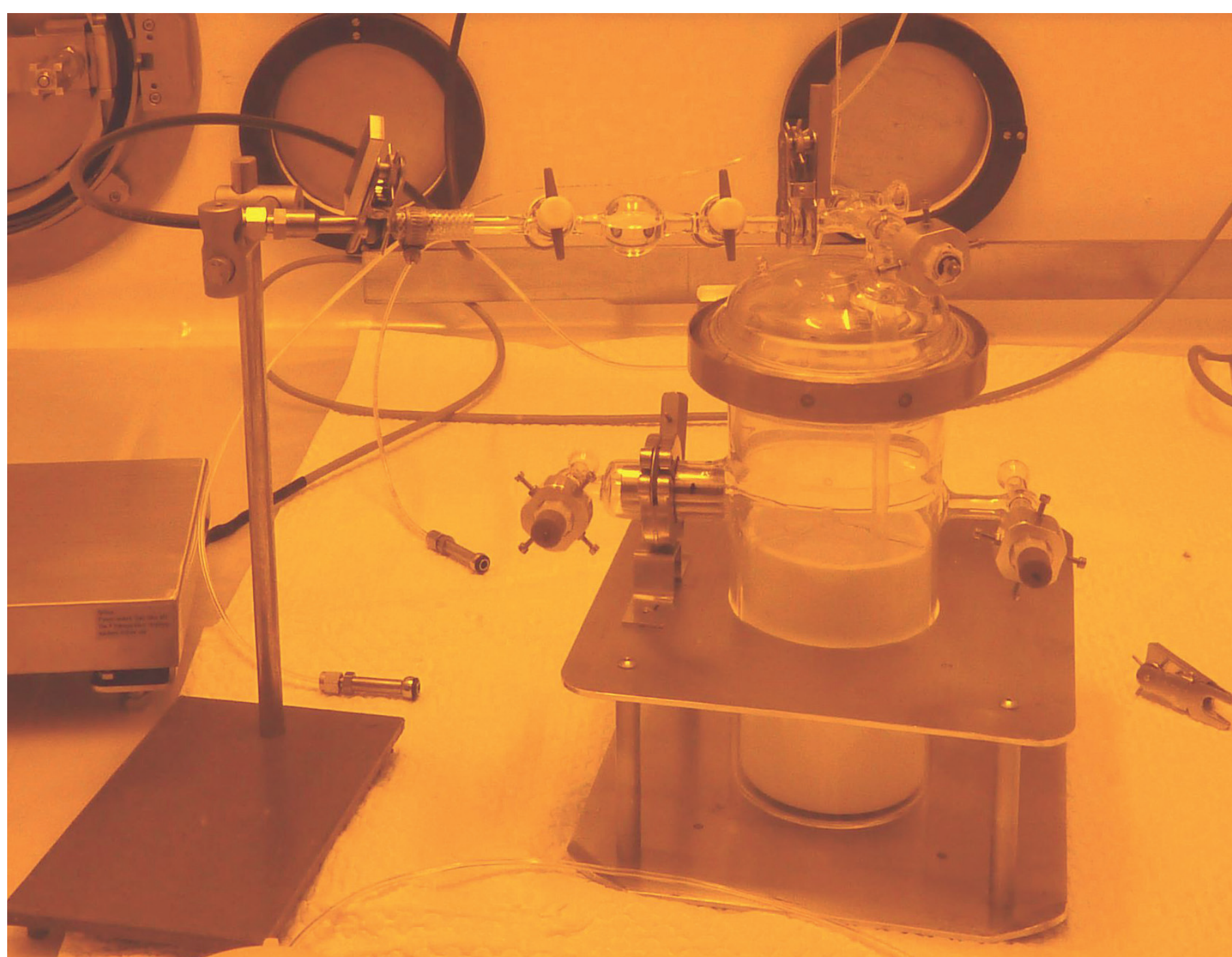


CT specimen
30x28.8x12 mm³

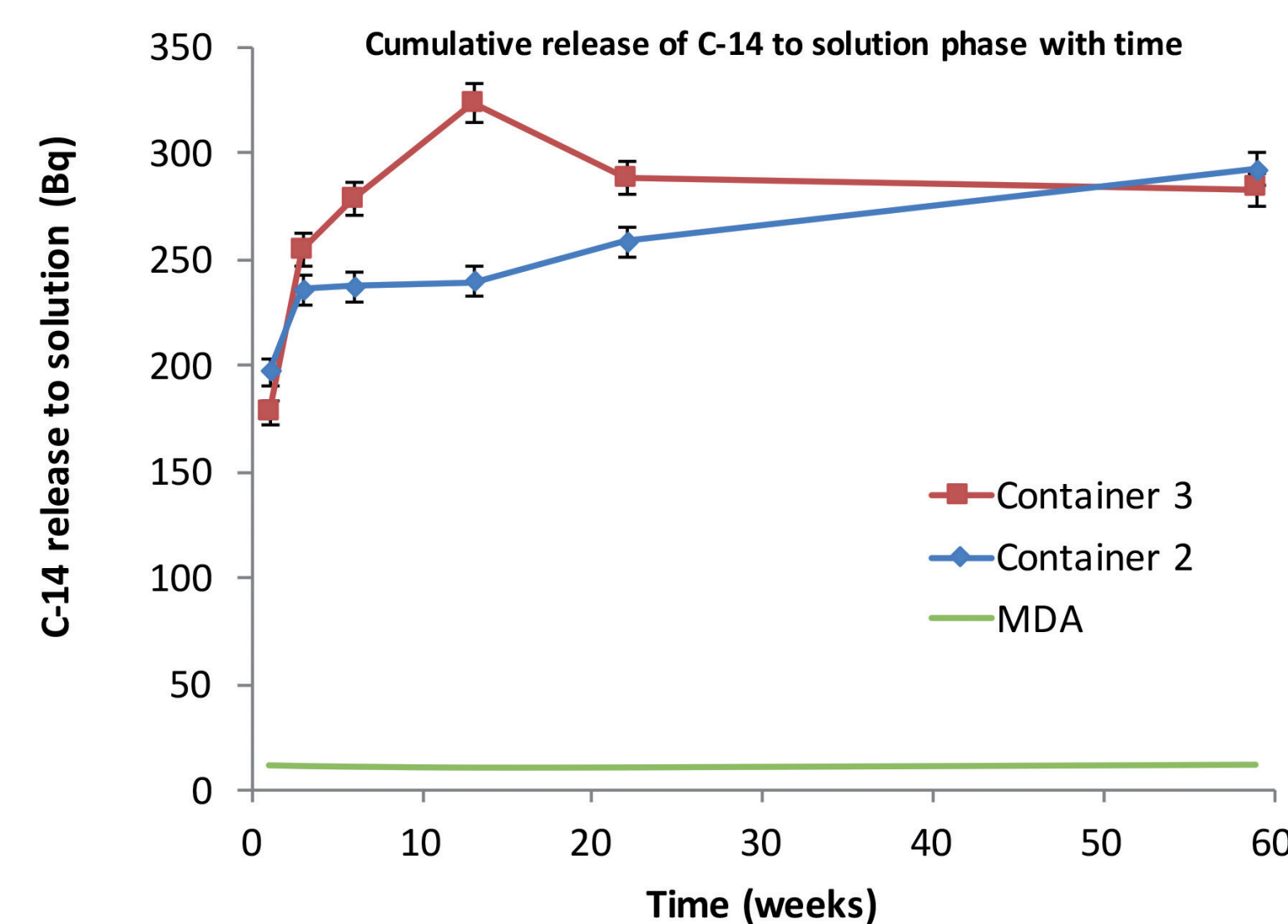
LEACHING EXPERIMENTS

- Leaching in 0.1M NaOH (pH 13) under nitrogen at the ambient temperature in the hot cell
- Duplicate experiments on irradiated steel samples
- Identical experiment on un-irradiated steel sample (same batch)
- Gas and liquid phase periodic sampling
 - 1 week, 3 weeks, 6 weeks, 3 months, 5 and 13 months
 - Gas phase purged and passed through RCD sampler system to selectively capture ¹⁴CO₂, ¹⁴CO (and volatile oxidized species) or ¹⁴C-hydrocarbons
 - 2 liquid samples for γ -spec (Co-60) and C-14 analysis (by NRG)
- Blank tests to measure C-14 background
- On termination, the container will be acid leached to recover any sorbed radionuclides for γ -spec analysis
- Experiments in progress for a period of 19 months; further sampling planned after 24 months

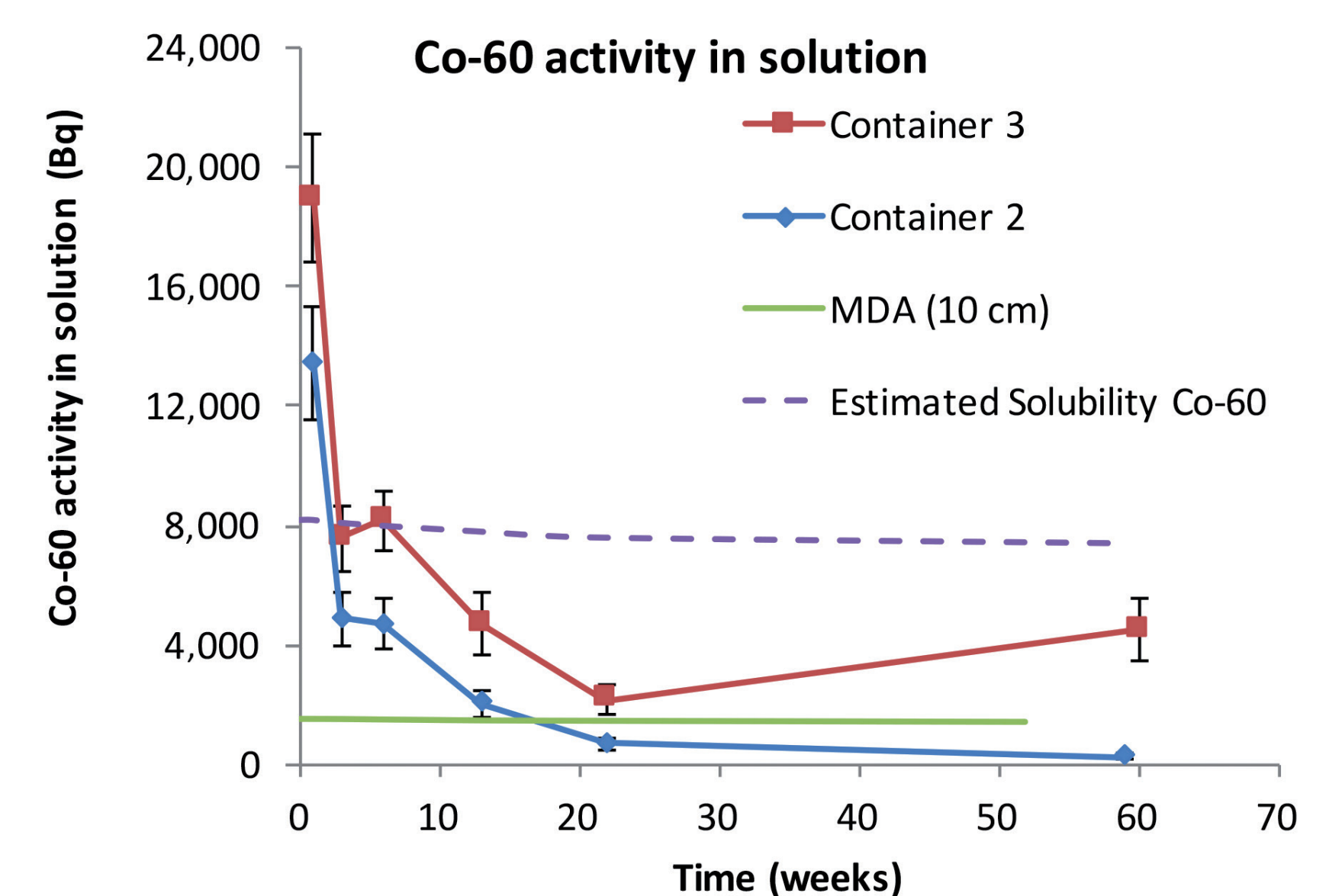
RESULTS



Leaching setup placed in the hot cell

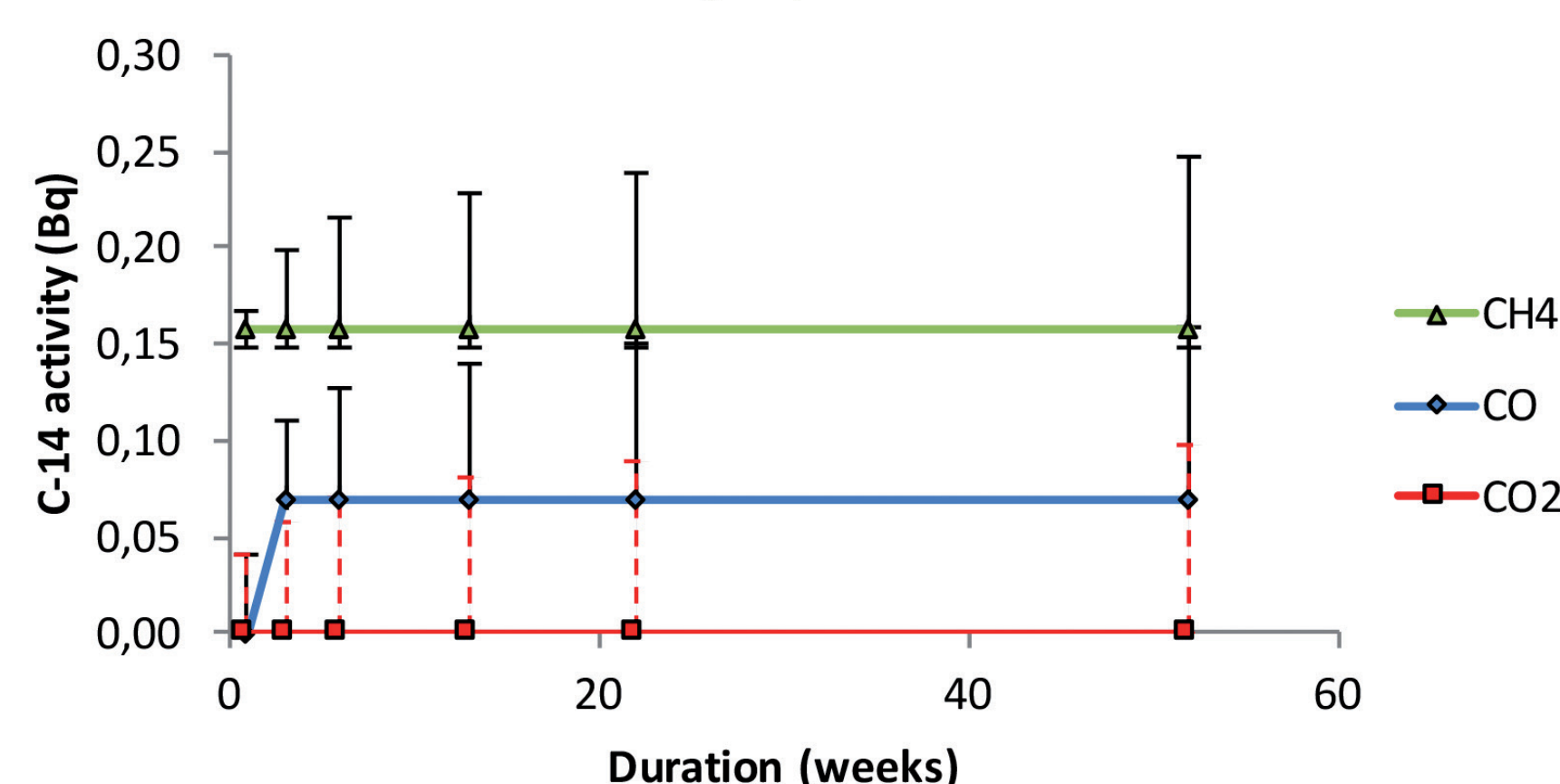


- Fast initial C-14 release, then rate decreases
 - Container 2 – C-14 activity still increasing at steady rate
 - Container 3 – C-14 activity has changed little between 6 and 60 weeks, with an unexplained peak after 13 weeks
 - Container 1 – no C-14 measurable



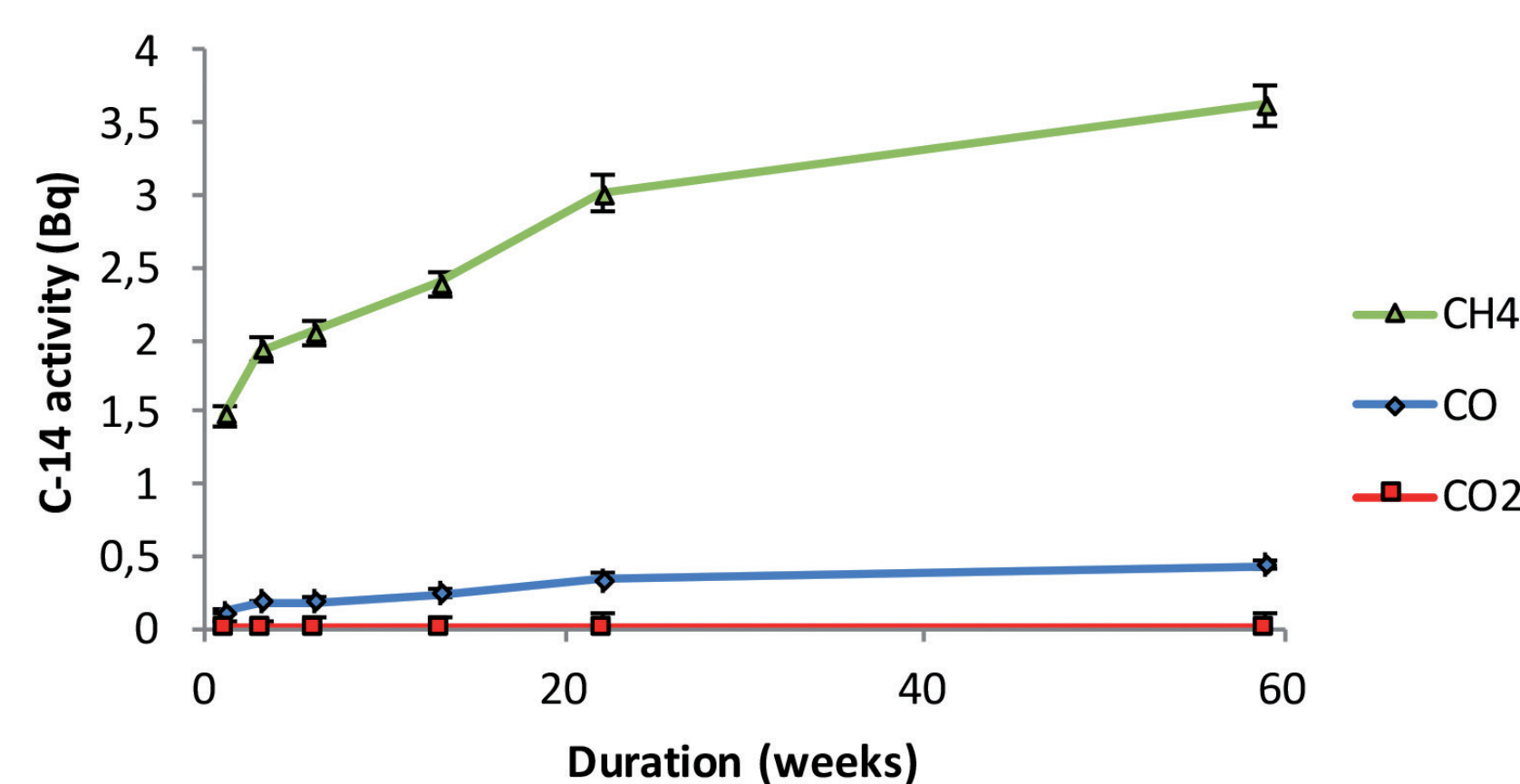
- High Co-60 activity in leachates after 1 week
 - 1 part in 10⁶ of Co-60 inventory
- Then solution activity decreases
 - possible solubility limitation and/or sorption to vessel walls

Container 1 - gas phase C-14 release



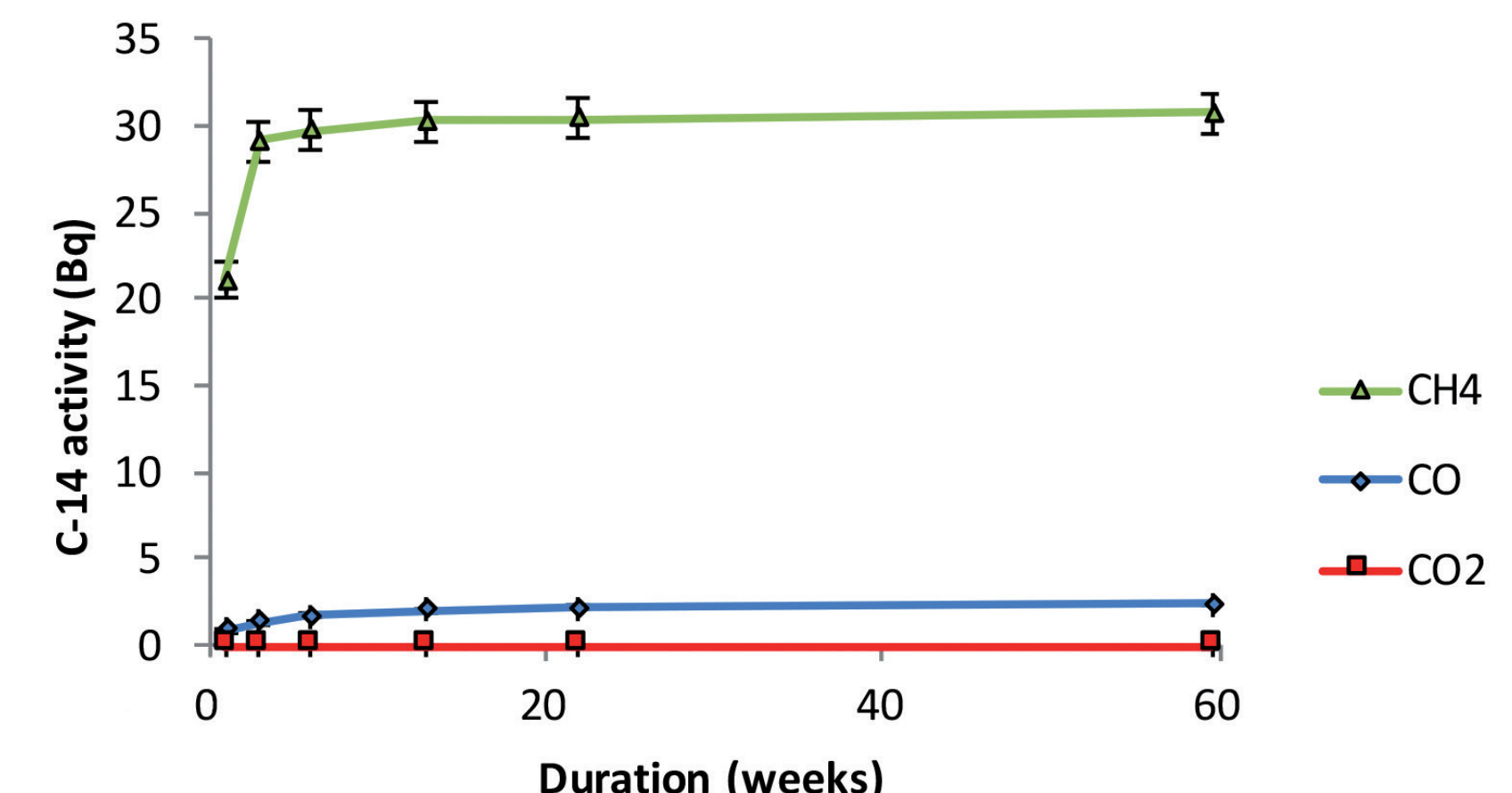
- Unirradiated samples
- LoD <0.04 Bq
- 2 analyses give positive C-14 measurement above LoD

Container 2 - gas phase C-14 release



- **Majority C-14 release to gas phase as hydrocarbons**
- ~10% CO or volatile oxygenated organic compounds
- No measurable gas phase CO₂

Container 3 - gas phase C-14 release



- **Majority C-14 release to gas phase as hydrocarbons**
- ~6% CO and/or volatile oxygenated organic compounds
- No measurable gas phase CO₂

INTERIM CONCLUSIONS

- There is a relatively fast initial release of accessible C-14 species from the surface of the steel on immersion in alkaline water
 - Predominantly to solution phase but also to gas phase
 - Higher proportion and rate of release to gas phase initially in Container 3
- Gas phase release predominantly hydrocarbons with up to 10% released as CO or volatile oxygenated compounds
- Rate of carbon-14 release declines beyond 3-6 weeks in both Containers 2 and 3
 - Release continues at measurable rate to both gas and solution phases in Container 2
 - Rate of release to the gas phase decreases more quickly in Container 3; little change in solution phase concentration between 6 and 60 weeks

- Reasons for differences in carbon-14 release between Containers 2 and 3 are not yet understood
- Release of Co-60 was investigated as a possible marker of the rate of steel corrosion, but is not suitable due to possible solubility limitation and/or sorption to the irradiated steel
- The experiments are still running; further sampling is planned after two years; once terminated, the leaching vessels will be emptied and the walls acid washed to recover deposits for cobalt-60 analysis by γ -spectroscopy
- Measurements of total carbon-14 in the solution phase are planned using a pyrolysis method to investigate whether some of the dissolved release occurs as organic species; at present, total releases of carbon-14 to solution may be underestimated