EC 428 ECCN= N

CArbon-14 Source Term
CAST

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Carbon-14 release from irradiated stainless steel

Outline

- Samples
- Leaching experiments
- Analytical methods
- Results to date (to 60 weeks)
  - C-14 liquid phase
  - C-14 gas phase
  - Co-60 liquid phase
- Interim conclusions
- Ongoing work
- Reporting

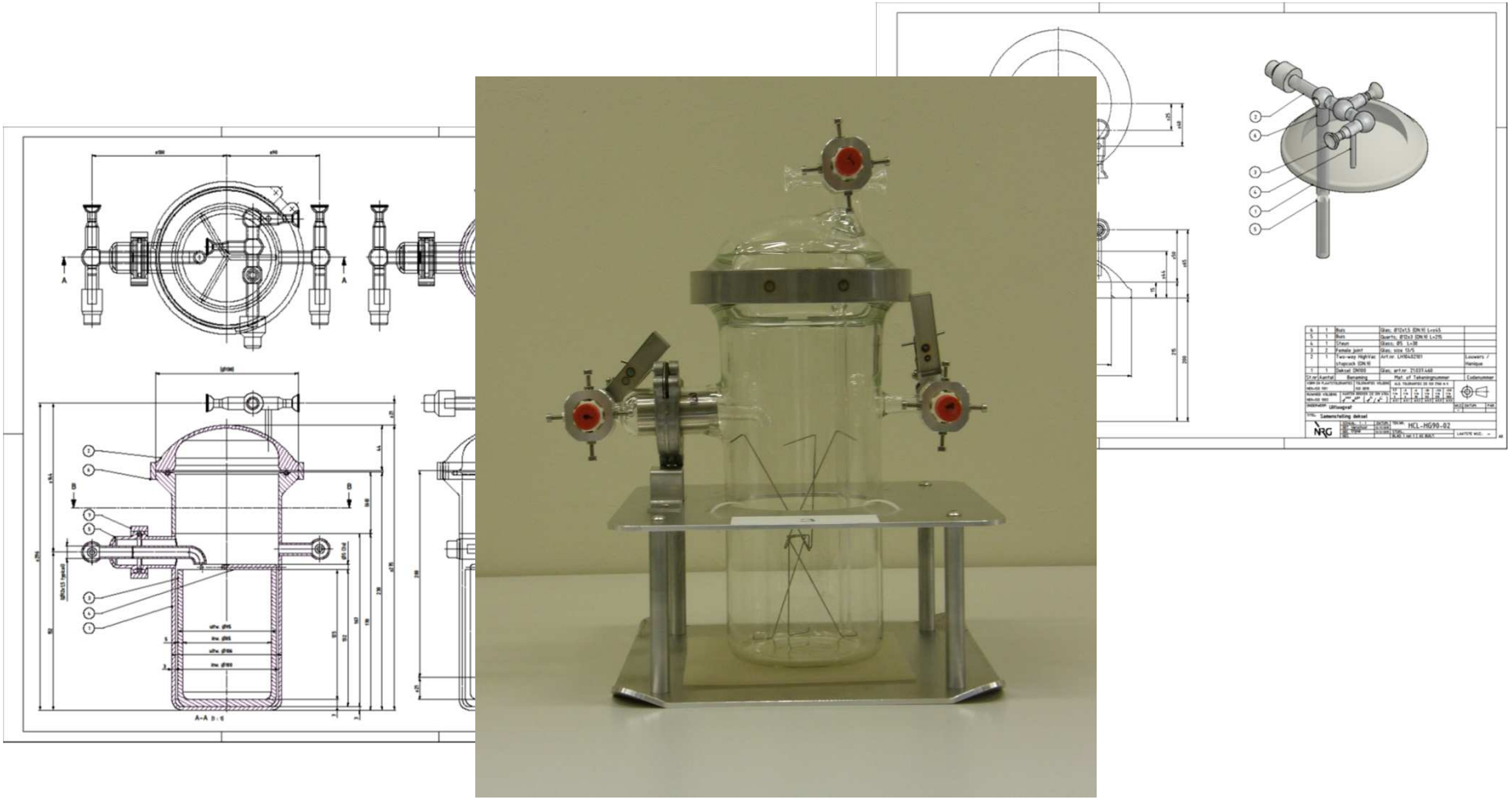
Samples

- 316L(N) austenitic stainless steel from single sheet
- 6 CT specimens irradiated at HFR, Petten – SIWAS O7 experiment (2dpa, 80°C, 5 28-day cycles) in 1996/97
- C-14 and Co-60 inventory assessed by ORIGEN calculations
- Unirradiated steel from same sheet
- 3 experiments each with 3 CT specimens

Container	**1**	**2**	**3**
Mass (g)	228	221	222
Geo.S.A. (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 mm^3

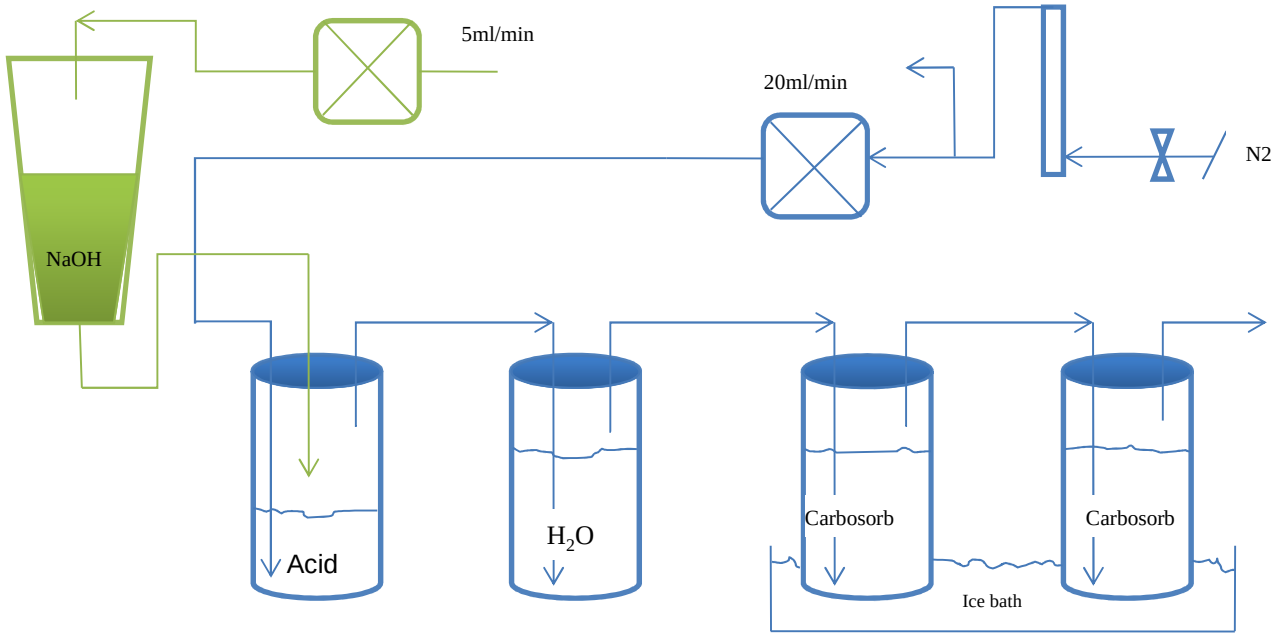
Final container design



CT specimen support

Liquid phase analysis

- Co-60 by gamma spectrometry, Canberra High purity Ge detector
- C-14 inorganic measurement done by acidification of solution and release of C-14 as $^{14}CO_2$, measured by LSC (Packard TriCarb 3180 TR/SL)

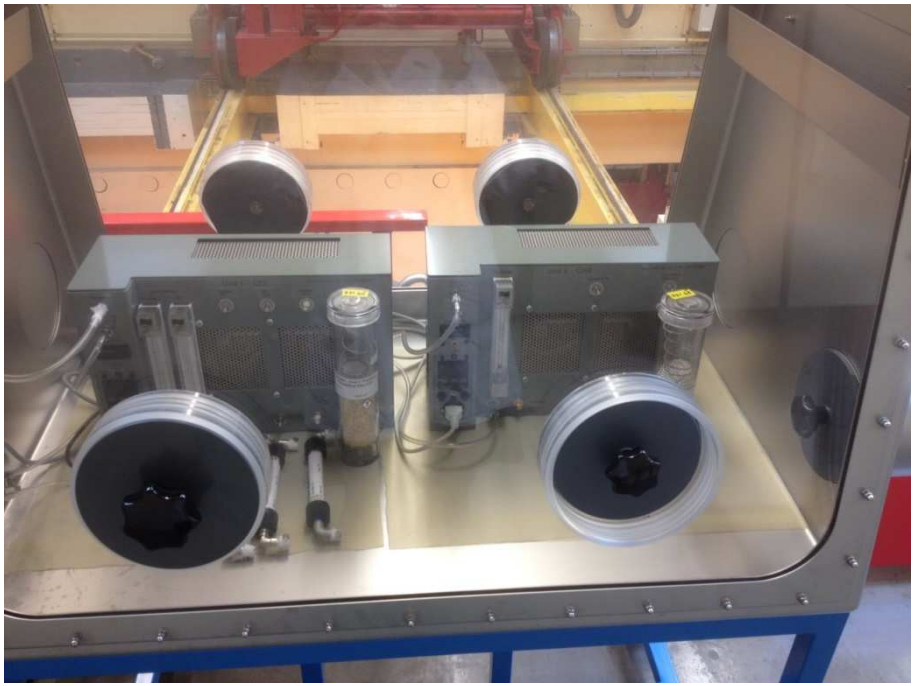


Gas phase sampling apparatus

- Designed and made at RCD in UK
- Captures $^{14}CO_2$, ^{14}CO and $^{14}CH_4$ fractions by selective oxidation/ absorption on 3 soda lime columns
- Concern over potential CO sorption to metal surfaces
  - replaced all nickel-based fittings with stainless steel
- Efficiency and selectivity of 2 catalysts were measured
  - CO 94.5% (CuO)

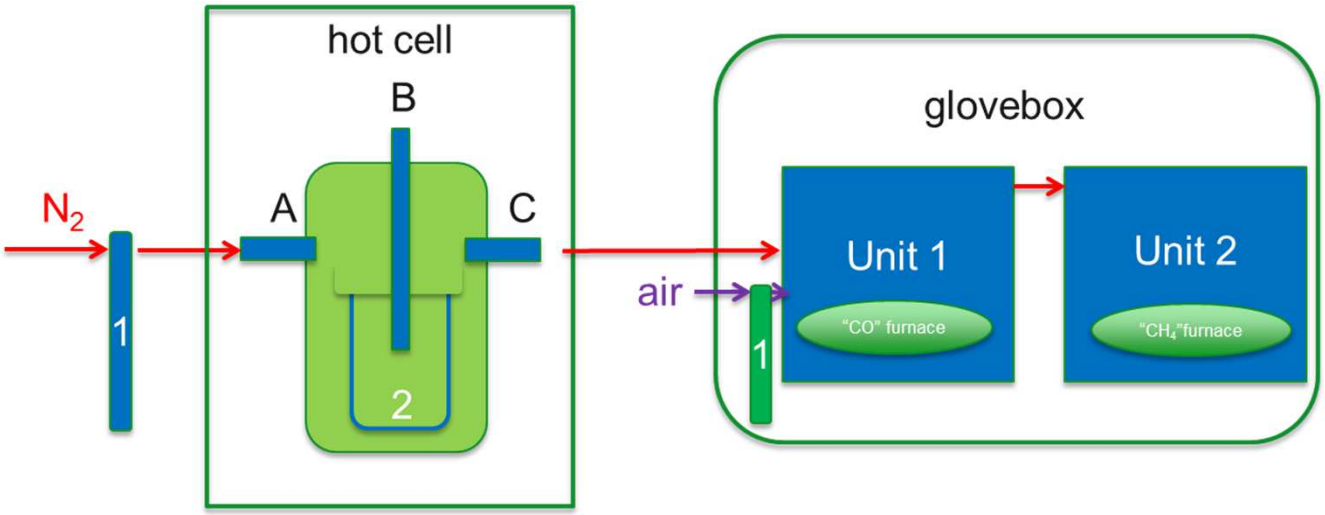
  remainder oxidised on CH_4 catalyst
  - CH_4 95% (Pt)

  with <2% removed after CO catalyst



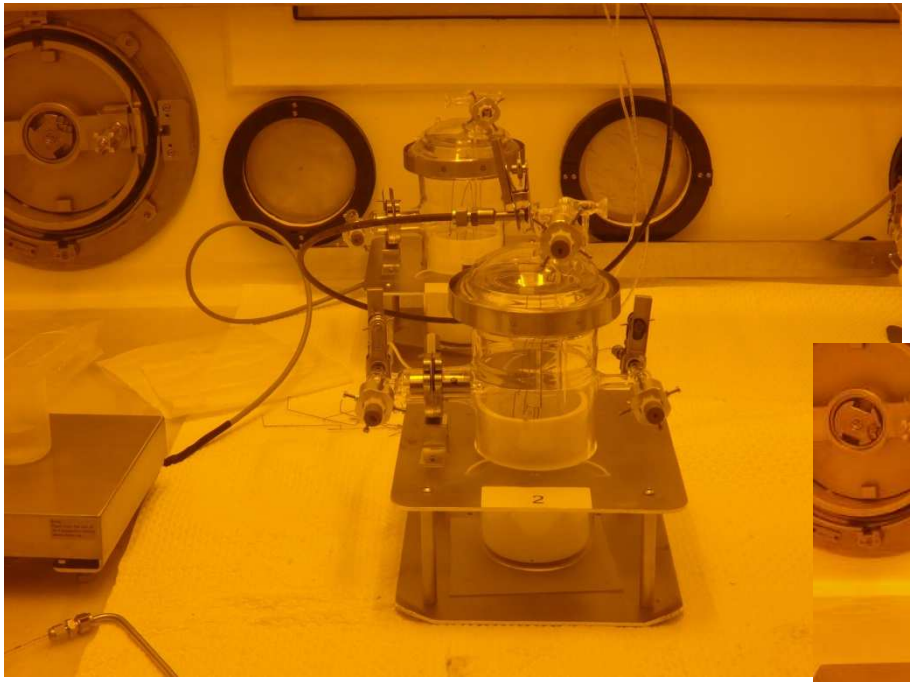
Leaching experiments

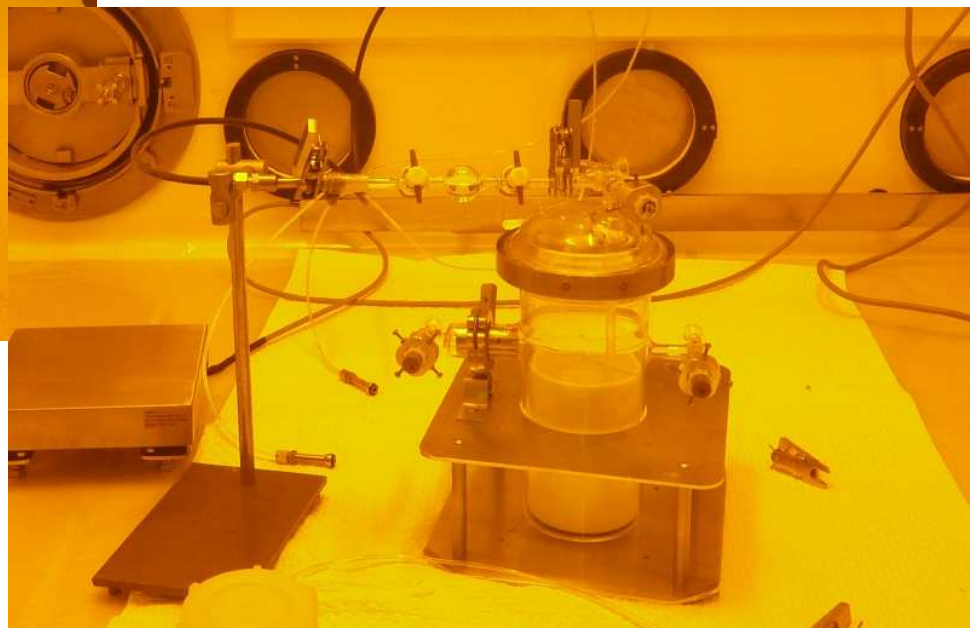
- Leaching in 600 ml 0.1M NaOH (pH 13) under N_2 at the ambient temperature in the hot cell (~30°C)
- Gas and solution phase sampled periodically
  - purge with N_2 for collection of gas phase C-14, with selective capture and oxidation of $^{14}CO_2$, ^{14}CO and ^{14}C-hydrocarbons ($^{14}CH_4$) as CO_2
  - then collect solution sample via dip leg for γ-spec (Co-60) and C-14



Setup for tests: *1* is soda lime column for removing C-14 from N_2 feed, *2* is leaching container where *A* is N_2 inlet, *B* is dip leg and *C* is N_2 outlet, *Unit 1* and *Unit 2* are the parts of RCD rig

Leaching experiments

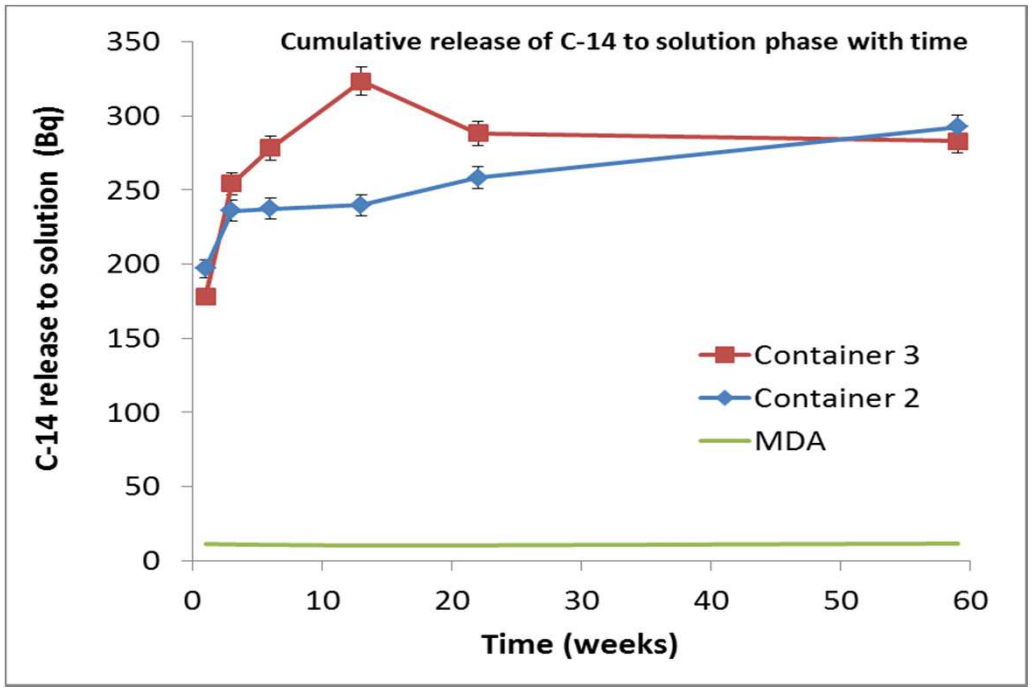




Progress with experiments

- Experiments started 31 May to 2 June 2016
  - Added 600 ml 0.1M NaOH via dip leg
- Sampling after 1, 3 and 6 weeks and 3, 5 & 13 months
  - Purged vessel with nitrogen for 7 hours
    - Collected gas phase C-14 in RCD samplers
    - Sequential oxidation and capture of $^{14}CO_2$, ^{14}CO and ^{14}C-hydrocarbons ($^{14}CH_4$) as CO_2 on soda lime columns
  - Collected ~7ml (from week 6 ~15ml) solution sample via dip leg
- Analysis
  - Co-60 and inorganic C-14 in solution to 13 months (NRG)
  - C-14 gas phase to 13 months (RCD)

Results – C-14 inorganic solution phase

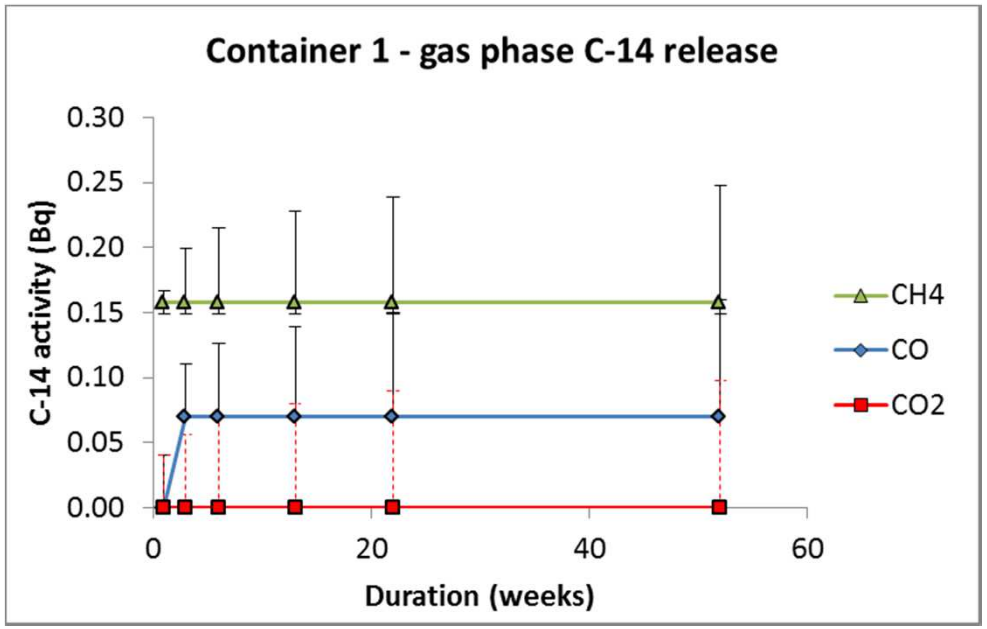


Containers 2, 3
49 MBq C-14

C-14 release from Container 2: corrosion rate ***~ 3nm/yr****, at congruent release of C-14 with corrosion and uniform C-14 distribution through steel*

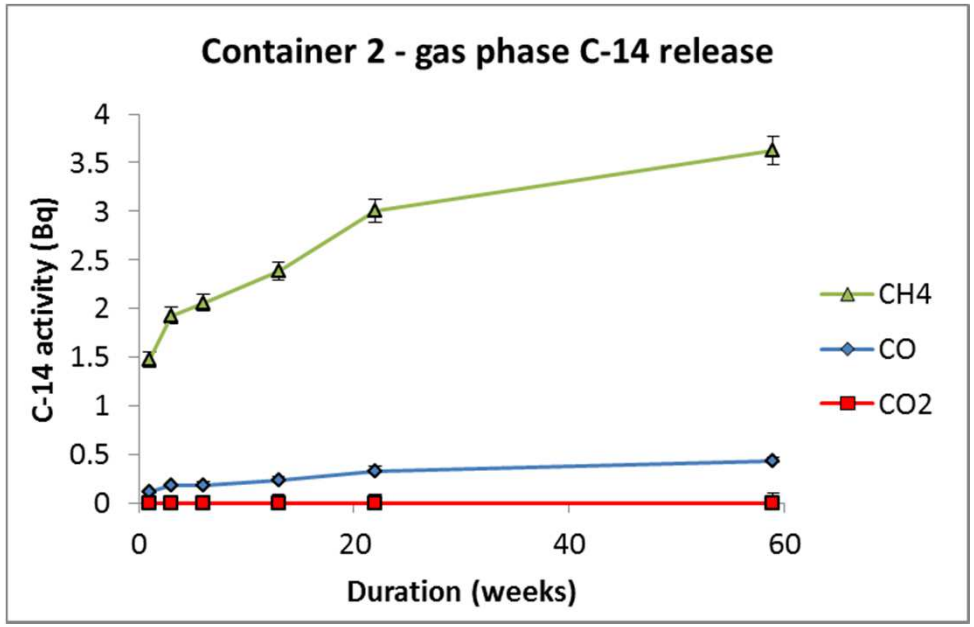
- Fast initial C-14 release, then rate decreases
- Container 2 – C-14 activity still increasing at steady rate
- Container 3 – C-14 activity has changed little between 6 and 60 weeks, with an unexplained peak after 13 weeks
- Container 1 – no C-14 measurable

Results – C-14 gas phase
Container 1 – unirradiated steel



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

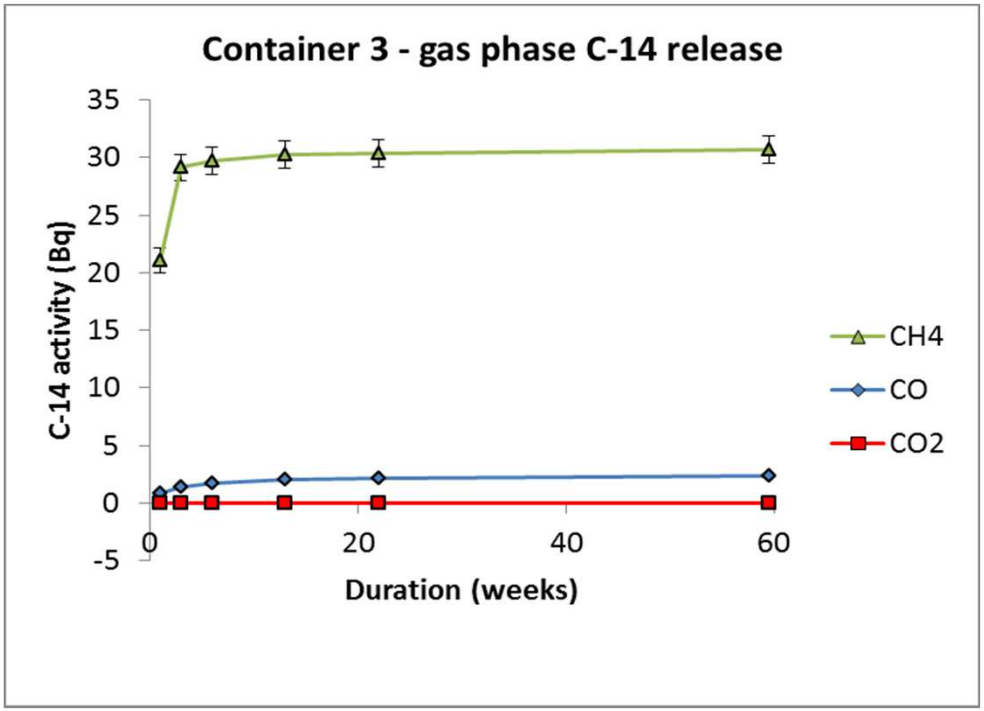
Results – C-14 gas phase
Container 2 – irradiated steel



- C.f.
  292 ±8 Bq to solution phase over 13 months

- **Majority C-14 release to gas phase as hydrocarbons**
- ~10% CO or volatile oxygenated organic compounds
- No measurable gas phase CO_2

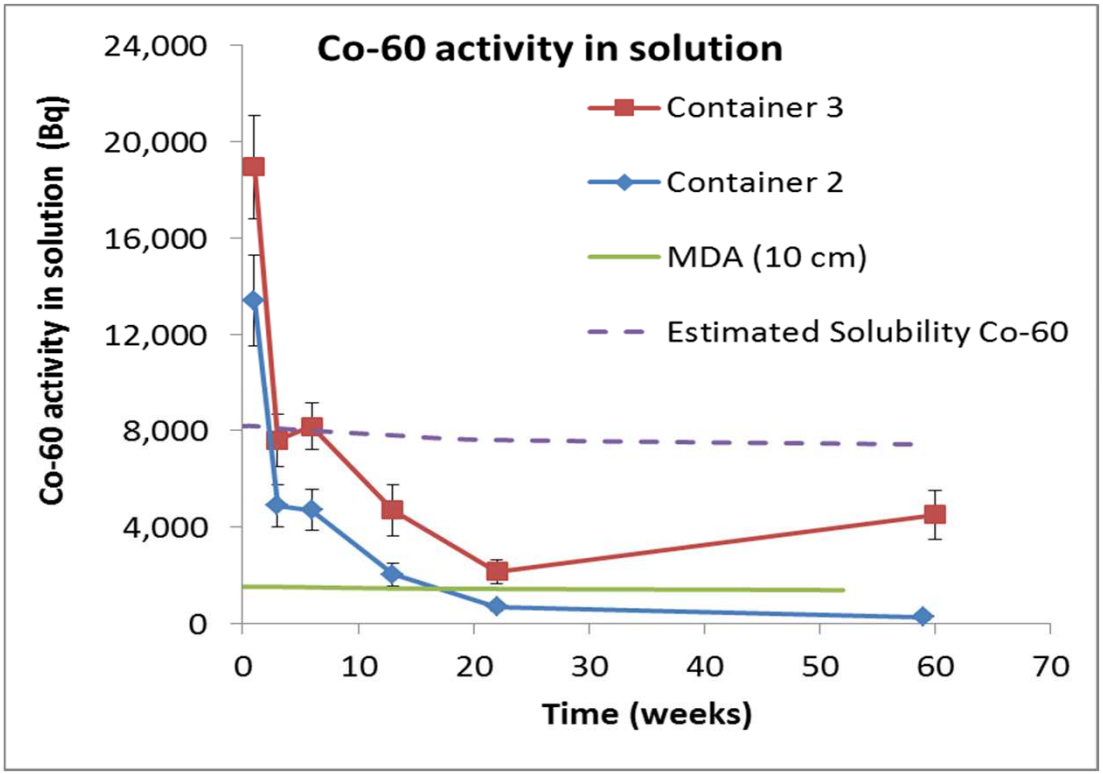
Results – C-14 gas phase
Container 3 – irradiated steel



- C.f.
  283 ± 8 Bq
  C-14 to solution phase over 13 months

- **Majority C-14 release to gas phase as hydrocarbons**
- ~6% CO and/or volatile oxygenated organic compounds
- No measurable gas phase CO_2

Results – Co-60 solution phase



Container 2,3
16 GBq Co-60

- High Co-60 activity in leachates after 1 week
  - 1 part in 10^6 of Co-60 inventory
- Then solution activity decreases
  - possible solubility limitation and/or sorption

Additional tests

- 2 tests of Co-60 sorption/solubility:
  - Setup filled with NaOH (600 g) and Co-60 spike (11,2 kBq)
  - Samples taken at T0 and after 6 weeks, under N_2 atm., RT
  - Test 1 – without stainless steels
  - Test 2 - with stainless steels

Period	Experiment without steel	Experiment with steel
	Co -60 activity (Bq/g solution)	
T0	19.22±0.51	21.26±0.53
T6 weeks	22.33±0.59	20.92±0.55

Conclusions I

- 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

Conclusions II

- 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

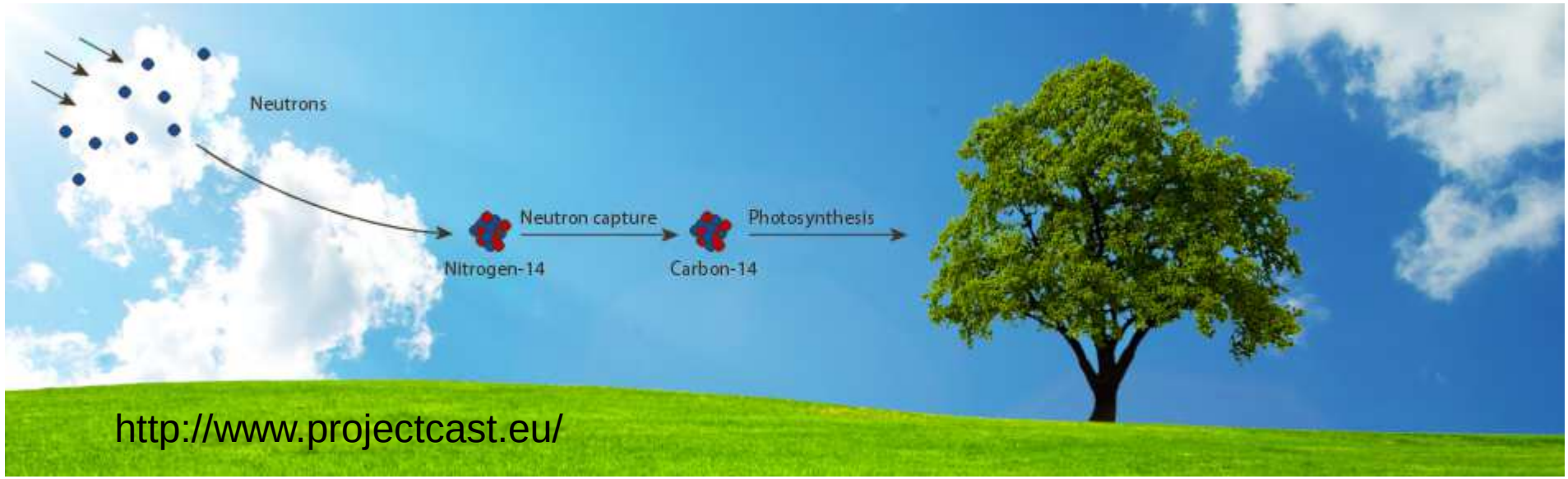
Ongoing work (outside CAST scope)

- Experiments extended with one year
- Leaching experiments continuing
  - 2 years sampling – June 2018
    - Results July –August 2018
- Experiments terminated after 2 years
  - vessels acid washed to recover deposits for γ-spec
- Some of the solution samples taken during periodic sampling will be analysed for total C-14 total by pyrolysis

Reporting

- D2.8 - NRG Final Report on *C-14 release and speciation from irradiated stainless steel under alkaline reducing conditions*
- Contribution to D2.18 - WP2 synthesis report
- Final Report to RWM drafted
- Work presented at KONTEC 2017 http://www.kontec2017.de/en/home

CArbon-14 Source Term (CAST) project



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