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Analytical strategy for measurement of ^{14}C in leachate of irradiated zirconium alloy hulls

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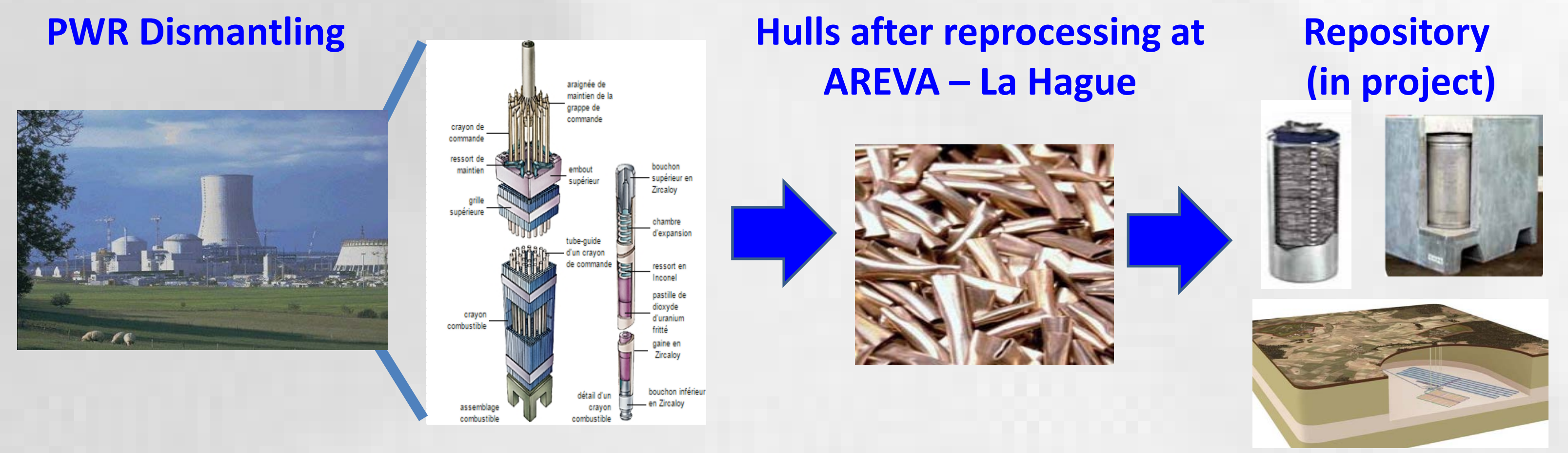
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Background

With a half-life of **5,730 years**, **Carbon-14 (¹⁴C)** is a **key radionuclide in safety assessments** for geological disposal of long-lived waste. In zirconium alloy claddings, neutron activation of ¹⁴N, impurity element of these alloys, is the main source of ¹⁴C. $^{14}_7\text{N} + ^1_0\text{n} \rightarrow ^{14}_6\text{C} + ^1_1\text{p}$

¹⁷O coming from the UO₂ (or (U-Pu)O₂) oxide fuel and from water coolant is also a significant precursor of ¹⁴C in the zirconia oxide layers formed in reactor on the internal and external sides of cladding respectively. $^{17}_8\text{O} + ^1_0\text{n} \rightarrow ^{14}_6\text{C} + ^4_2\text{He}$

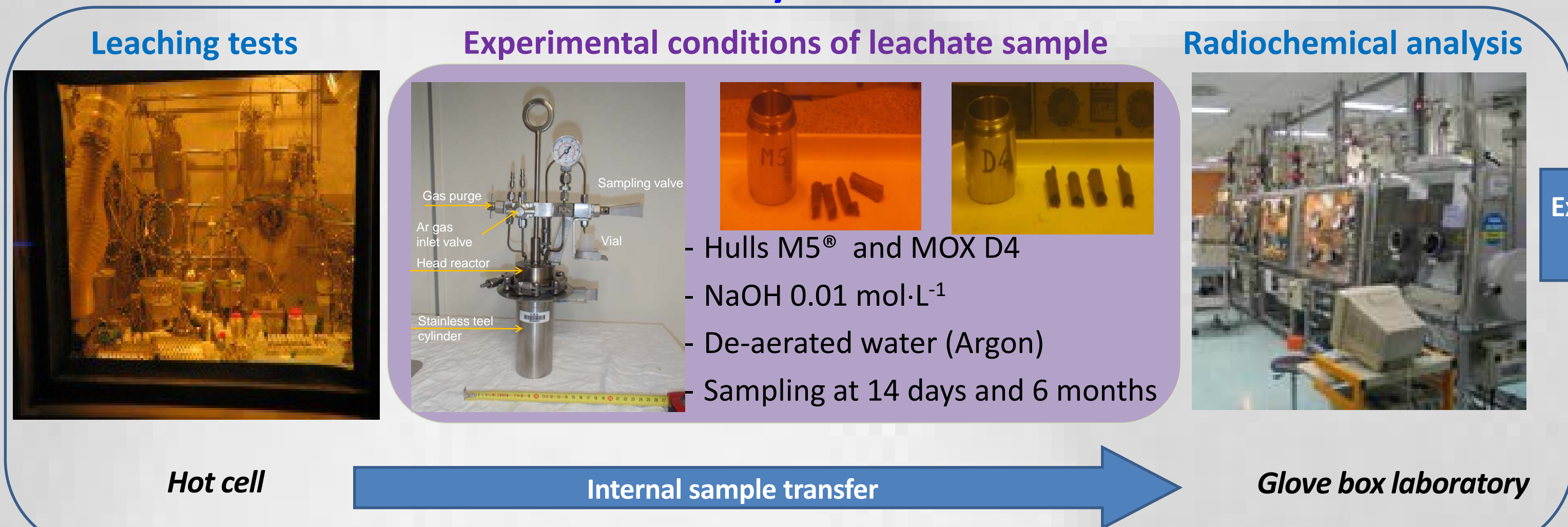


Objectives and analytical process

Work Package 3 (WP3) is related to **Zircaloy** in the CAST (Carbon-14 Source Term) project. It aims to obtain a better understanding ¹⁴C behaviour in waste Zr fuel claddings under disposal conditions with regard to ¹⁴C inventory (and origins), release from waste packages and speciation of released ¹⁴C.

Zircaloy-based alloy hulls, M5-type hull (UOX) and D4-type hull (MOX), supplied by AREVA-La-Hague, have been leached in a basic solution simulating the pH of cementitious water (NaOH solution, pH 12, anoxic conditions) in the hot cells of ATALANTE facility (CEA Marcoule). These samples come from the reprocessing of irradiated spent fuel in PWR reactors. Leachates have been analyzed to allow detection and quantification of organic and inorganic compounds in solution.

ATALANTE facility at CEA Marcoule



Analysis of Carbon-14

LASE

Step 1: Total ¹⁴C determination

Pyrolysis of the sample on a tri-tube pyrolysis furnace followed by liquid scintillation counting
DL = 0.5 Bq/mL (0.2 mL of sample)



Step 2: Method for organic and inorganic ¹⁴C partition



- ✓ Acidification with H₃PO₄ (25 %) of a small volume of the leachate solution,
- ✓ N₂ gas bubbles in the solution to drag CO₂,
- ✓ Collect of inorganic carbon in a NaOH solution,
- ✓ Organic carbon is kept in the vessel.

=> The method has been tested with a mixture of an inorganic molecule and an organic molecule labelled with ¹⁴C: Na₂CO₃ et C₆H₁₂O₆.

Samples	Inorganic ¹⁴ C	Organic ¹⁴ C
Na ₂ ¹⁴ CO ₃	85 %	0 %
¹⁴ C ₆ H ₁₂ O ₆	0 %	100 %
Na ₂ ¹⁴ CO ₃ + ¹⁴ C ₆ H ₁₂ O ₆	70 %	100 %

Organic ¹⁴C: Pyrolysis followed by LSC or AMS measurement of a small volume of solution, which is kept in the vessel,

Inorganic ¹⁴C: Total ¹⁴C * - organic ¹⁴C
* ¹⁴C Total: Pyrolysis followed by LSC or AMS measurement of a small volume of the leachate solution.

Step 3: Results for M5-type hull and D4-type hull leachates

Samples	Total ¹⁴ C Bq.g ⁻¹ of hull	Organic ¹⁴ C Bq.g ⁻¹ of hull	Inorganic ¹⁴ C Bq.g ⁻¹ of hull	Partition Organic / Inorganic %
Blank (in hot cell)	< 0.3 Bq.g ⁻¹ (DL LSC)	0.75 ± 0.44 Bq.g ⁻¹ *	< 0.3 Bq.g ⁻¹ (DL LSC)	Not possible
M5-type hull 14 Days	186 ± 12	85 ± 12	101 ± 12	46/54
M5-type hull 6 Months	192 ± 6	83 ± 12	110 ± 12	43/57
D4-type hull 14 Days	40 ± 6	7 ± 1*	33 ± 1	17/83
D4-type hull 6 Months	48 ± 8	6 ± 2*	42 ± 2	13/87

✓ Total ¹⁴C of leachate D4-type hull >> Total ¹⁴C of leachate D4-type hull

✓ Inorganic ¹⁴C of leachate D4-type hull >> inorganic ¹⁴C of leachate M5-type hull

* AMS value

➔ No evolution between 14 days and 6 months for ¹⁴C released in leachate.

LRMO

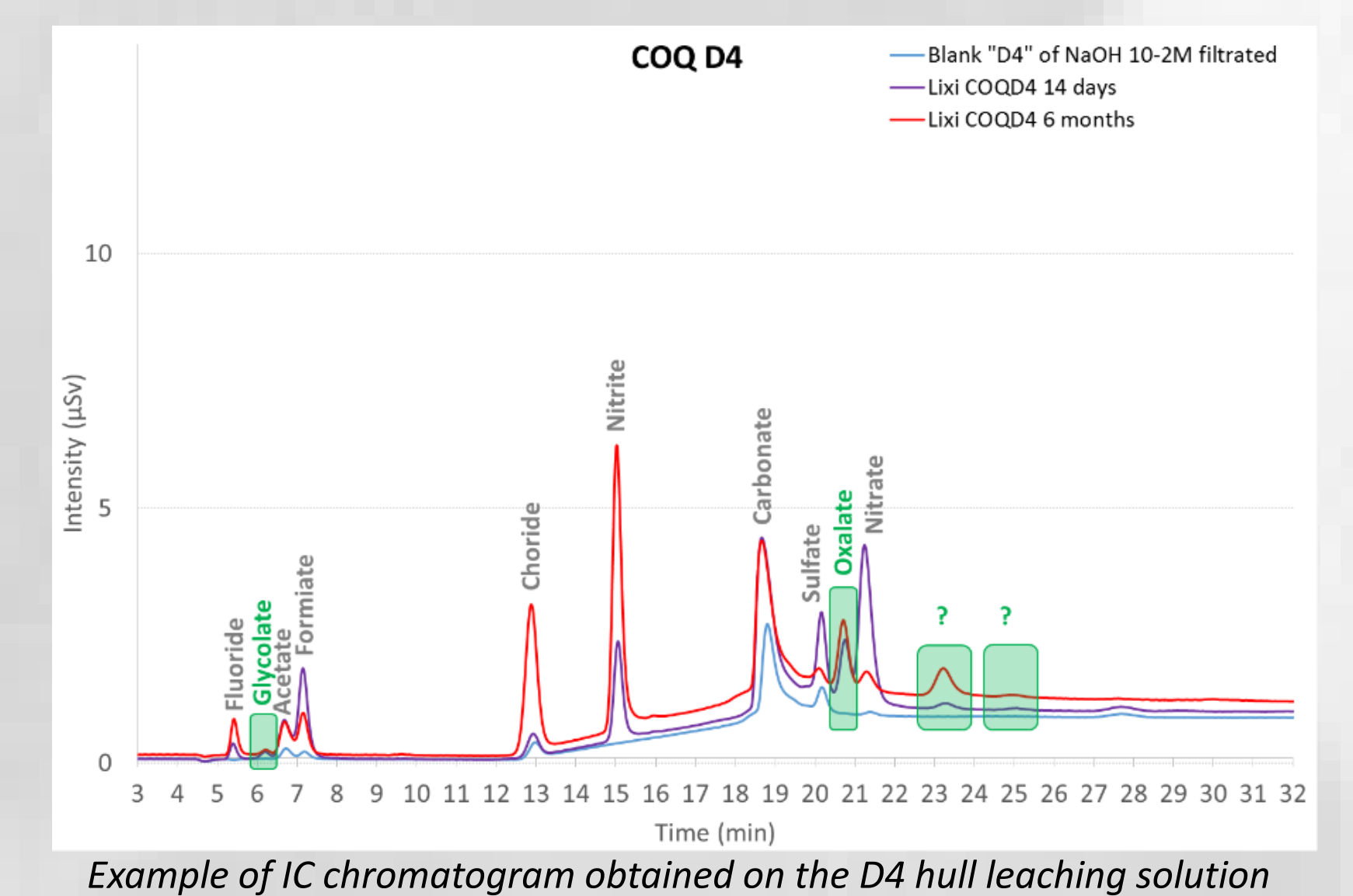
Step 1: Organic (TOC) and inorganic (TIC) carbon total concentrations

Samples	TOC mgC.L ⁻¹	TIC mgC.L ⁻¹
Blank "M5" NaOH	6	7
M5-type hull 14 days leachate	11	18
M5-type hull 6 months leachate	5	29
Blank "D4" NaOH	< 1	2
D4-type hull 14 days leachate	9	18
D4-type hull 6 months leachate	5	31

1. TIC > TOC concentrations due to carbonation of solutions

2. TOC concentration after 14 days > after 6 months ?
A contamination due to manipulation for 14 days sample or an evolution and/or a degradation of organic compounds in alkaline conditions after one month

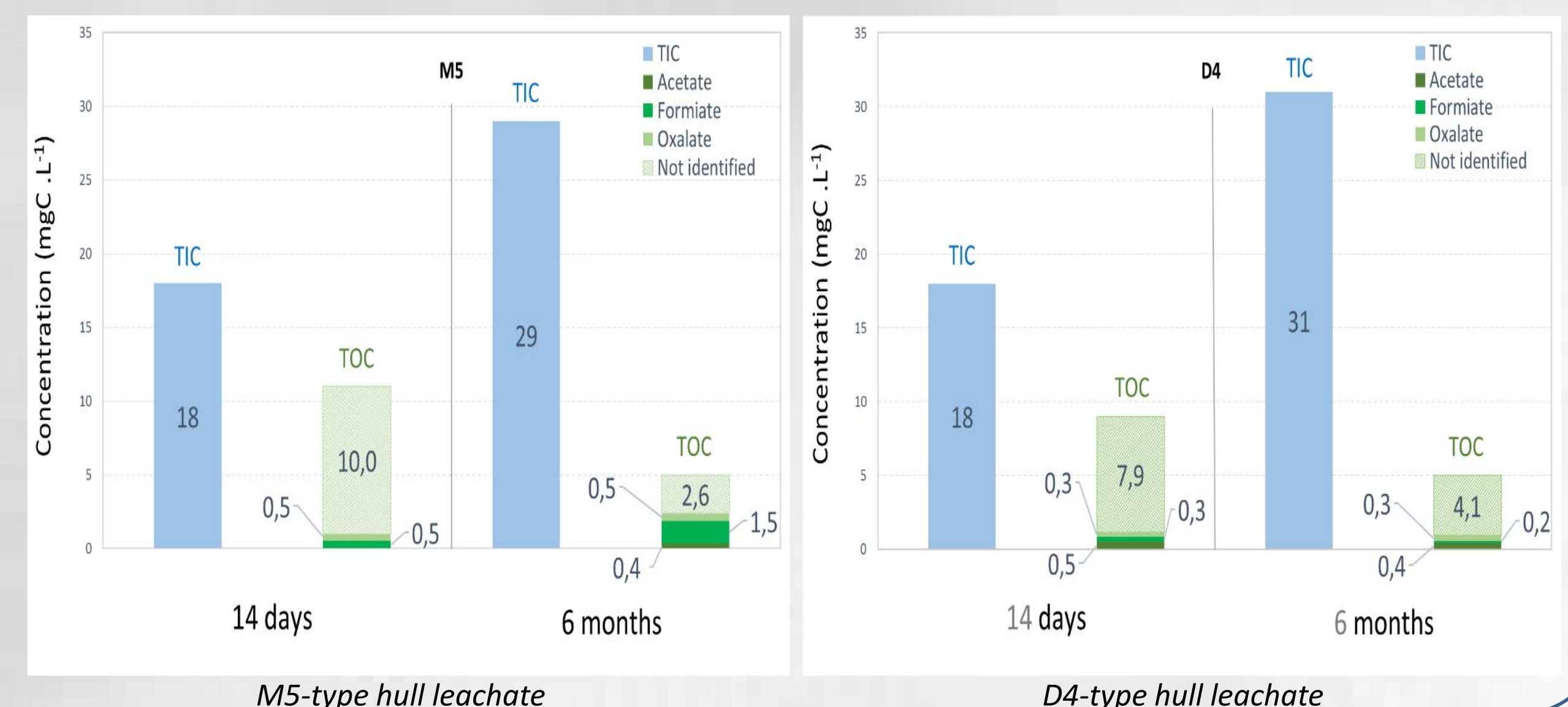
Step 2: Identification and quantification of carboxylic acids by ionic chromatography (IC)



- Inorganic anions:** only one with inorganic carbon (TIC) : CO₃²⁻
- Organic anions:**
 - Acetate/formate in blank solutions (contamination?)
 - Glycolate/oxalate come only from hull leaching solutions
- Other organic/inorganic unidentified compounds**

Step 3: Carbon mass balance

Difficult to conclude on TOC concentrations coming only from hull leaching
TOC in blanks and samples solutions very close to each other. Blanks have not strictly followed the same experimental conditions!



Conclusions

- ¹⁴C could be quantified in the leachate of M5-type and D4-type hulls; the partition of organic/inorganic ¹⁴C has been measured :
 - Releases of total ¹⁴C and organic ¹⁴C by M5-type hull higher than by D4-type hull,
 - Less than 20 % of organic ¹⁴C released after 6 months for the D4-type hull against 50 % for M5-type hull,
 - The organic ¹⁴C represents less than 3.10⁻⁴ % of TOC for M5-hull and 3.10⁻⁵ % of TOC for D4-hull .
- From theory calculations, diffusion coefficient of ¹⁴C within Zr-metal and Zirconia is very low. However, measurements of ¹⁴C in solution indicate its possible diffusion through Zr metal and/or Zr oxide layer by other mechanism such as diffusion through the grain boundaries.
- For the organic carbon, only two carboxylic acids (glycolic and oxalic acids) have been detected and/or quantified in the leachate.