CArbon-14 Source Term, CAST

Analytical strategy for the measurement of carbon 14 in alkaline solution

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Introduction

Carbon-14 is

- a long-lived radionuclide (5,730 y)
- radionuclide of interest regarding the safety for the management of intermediate level wastes (ILW).

In PWR reactor, ^{14}C is found in stainless steel and zircaloy cladding due to neutron activation mainly by $^{14}N(n,p)^{14}C$ and $^{17}O(n,\alpha)^{14}C$ reactions.

Steel and cladding are planned to be placed in deep geological formation, within steel canister and stored in cement container. A cementitious environment will dominate the repository site. Therefore, the release of carbon-14 in aqueous media and its diffusion within the repository site is an important issue for safety assessment.

Aims

Among the inventory of carbon-14 released during leaching process, organic and inorganic carbon is formed and is recovered in alkaline aqueous media. The aims of this work was to characterize carbon-14 organic fraction and to provide its speciation, with a focus on carboxylic acids having a short carbon chain ≤ 5.

Characterization of carboxylic acids with a low carbon chain length is of importance since they are preferentially released compounds from zircaloy alloys and steels.

The chemical composition of the leaching solution depends on the origin and the nature of the leached irradiated materials.

Besides the investigation of ^{14}C target molecules, the leaching solution contains activation products (e.g. ^{60}Co, ^{63}Ni, ^{55}Fe…), fission products (e.g. ^{137}Cs, ^{99}Tc, ^{90}Sr ^{125}Sb…), and actinides (e.g. ^{235}U, ^{239}Pu), which are present at a significant activity level compared to ^{14}C. The second objective of this work was to provide a simple method of purification without altering organic carbon-14 molecules.

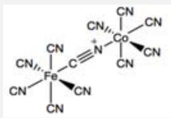
Method

Main objectives:

i) Reduce the total activity in leachates
ii) Remove beta-emitting radionuclides that interfere with the measurement of C-14 activity ⇒ LSC
iii) Limit the potential contamination of analytical instruments ⇒ AMS

solution (^{60}Co, ^{137}Cs, ^{125}Sb, …) NaOH, pH 12
→ Filtration PTFE 0.45 µm
→ Decontamination of leaching solution: Inorganic ion exchanger $K_2[CuFe(CN)_6]$ without organic binding. Extraction of major RNs
→ TIC/TOC
→ αβγ
→ Ion chromatography
→ Ion exclusion column (TFA eluent) / Anion column ($NaOH/Na_2CO_3$ eluent)
→ Collection of fractions
→ γ measurement
→ Liquid scintillation counting
→ AMS measurement

Inorganic ion exchanger for cesium extraction



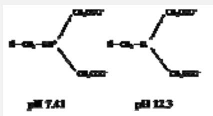
Structure of potassium hexacyanocobalt(II) ferrate(II) resin and the organic binding polymer based on polyacrylonitrile PAN

- Good candidate for rapid, efficient and quantitative fixation of cesium
- High exchange capacity
- Stable for the entire pH range from acidic to alkaline
- Weak interaction with nonmetallic ions
- Resistant to ionizing radiation

Retention of Cs-137 and C-14 labeled carboxylic acids after 1 hour contact with $K_2[CuFe(CN)_6]$ without binding polymer resin (initial activity for Cs-137 and C-14 labeled carboxylic acids 100 Bq).

Radionuclides	% retention
Cs-137	> 99%
C-14 formate	< 1%
C-14 propionate	< 0.5%
C-14 butyrate	< 0.5 %
C-14 oxalate	< 4%

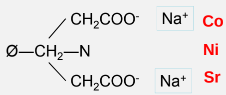
Chelex-Na resin for transition metal extraction



Structure of Chelex 100 resin

- Good candidate for efficient and quantitative fixation of cobalt and nickel
- High exchange capacity
- Stable for the entire pH range from acidic to alkaline
- Weak interaction with organic anions species
- Resistant to ionizing radiation used for extraction and pre-concentration of radionuclides

In the sodium form, Chelex 100 acts as a cation exchanger and allows the elimination of polyvalent transition metals ⇒ Co, Ni, Fe, Cr and Mn.



Radionuclides	% retention
Co-60	95%
Ni-63	97%
C-14 formate	1%
C-14 propionate	7%
C-14 butyrate	2%
C-14 oxalate	2%

Chelex-Fe(III) resin for antimony extraction

Chelex 100 in ferric form:

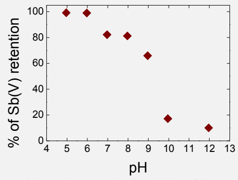
⇒ arsenic (III) and (V) efficiently removed from aqueous solution
⇒ arsenic/antimony: similarities in the coordinating properties
⇒ to remove antimony

Antimony:

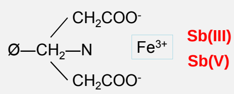
⇒ Sb(III) for oxygen-depleted media and Sb(V) under oxic conditions
⇒ For antimony diluted solutions, SbO_3^- is the main species present in alkaline conditions

Preparation of

⇒ Chelex 100 doped with Fe(III)
⇒ Oxidation of a solution of $SbCl_3$ dissolved in ultrapure water in the presence of goethite as a catalyst



Evolution of the retention for Sb(V) at different pH values ranging from 5 to 12



pH 5-6: Efficient retention of Sb(V)

pH > 6: Drastic drop of Sb(V) retention

pH>10: Decomposition of Chelex-Fe(III) by forming hydroxide complexes.

Radionuclides	% retention
Sb(V)	> 99%
C-14 formate	4%
C-14 propionate	25%
C-14 butyrate	48%
C-14 oxalate	91%

Conclusions

RETENTION		KCFC	Chelex-Na	Chelex-Fe
Carbon-14	Formate	No	Weak	High
	Propionate			
	Butyrate			
	Oxalate			
Cs-137		High		
Co-60			High	
Ni-63				
Sb(V)				High pH5-6

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