Radiochemical analysis of $^{41}$Ca, $^{90}$Sr, $^{129}$I, and $^{36}$Cl in waste samples

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Main Radionuclides in the nuclear waste and used materials in the view of measurement

- **Gamma radionuclides**
  \[ ^{60}\text{Co}, \, ^{133}\text{Ba}, \, ^{137}\text{Cs}, \, ^{134}\text{Cs}, \, ^{106}\text{Ru}, \, ^{152,154,155}\text{Eu}, \]
  \[ ^{58}\text{Co}, \, ^{54}\text{Mn}, \, ^{59}\text{Fe}, \, ^{110m}\text{Ag}, \, ^{94}\text{Nb}. \]

- **Beta Emitter**
  \[ ^{3}\text{H}, \, ^{14}\text{C}, \, ^{36}\text{Cl}, \, ^{41}\text{Ca}, \, ^{55}\text{Fe}, \, ^{63}, ^{59}\text{Ni}, \, ^{93}\text{Zr}, \, ^{93}\text{Mo}, \, ^{90}\text{Sr}, \]
  \[ ^{99}\text{Tc}, \, ^{129}\text{I}. \]

- **Alpha emitter (transuranics)**
  \[ ^{238-241}\text{Pu}, \, ^{241}\text{Am}, \, ^{243,244}\text{Cm}, \, ^{237}\text{Np} \]
Waste samples and the relevant critical radionuclides for decommissioning

- **Graphite (reactor)**
  - $^3$H, $^{14}$C, $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{60}$Co, $^{152}$Eu

- **Concrete (normal or heavy)**
  - $^{41}$Ca, $^{60}$Co, $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{133}$Ba, $^{152}$Eu

- **Steel/stainless steel**
  - $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{36}$Cl, $^{93}$Zr, $^{93}$Mo, $^{94}$Nb, $^{60}$Co, $^{152}$Eu, transuranics

- **Aluminium**
  - $^{60}$Co, $^{63}$Ni, $^{55}$Fe, $^{36}$Cl

- **Lead**
  - $^{60}$Co, $^{63}$Ni, $^{55}$Fe

- **Water**
  - $^3$H, $^{14}$C, $^{63}$Ni, $^{99}$Tc, $^{129}$I, $^{90}$Sr, $^{60}$Co, $^{137}$Cs, transuranics

- **Ion exchange resin**
  - $^{55}$Fe, $^{63,59}$Ni, $^{14}$C, $^{99}$Tc, $^{36}$Cl, $^{93}$Zr, $^{93}$Mo, $^{94}$Nb, $^{90}$Sr, $^{129}$I, $^{137}$Cs, $^{60}$Co, $^{135}$Cs, transuranics
# 41Ca in the concrete

Activation products of calcium isotopes

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Target isotope Aboundance %</th>
<th>Reaction</th>
<th>Cross section, bar</th>
<th>Half life</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>41Ca</td>
<td>96.94</td>
<td>40Ca(n, γ)41Ca</td>
<td>0.41</td>
<td>1.03×10^5 y</td>
<td>EC</td>
</tr>
<tr>
<td>45Ca</td>
<td>2.086</td>
<td>44Ca(n, γ)45Ca</td>
<td>0.84</td>
<td>162.7 d</td>
<td>β-</td>
</tr>
<tr>
<td>47Ca</td>
<td>0.004</td>
<td>46Ca(n, γ)47Ca</td>
<td>0.7</td>
<td>4.54 d</td>
<td>β, γ</td>
</tr>
<tr>
<td>49Ca</td>
<td>0.187</td>
<td>48Ca(n, γ)49Ca</td>
<td>1.0</td>
<td>8.72 min.</td>
<td>β, γ</td>
</tr>
</tbody>
</table>

Energy of X-rays and Auger electrons : 0.3-3.6 keV
Determination: X-ray spectrometry (<0.08%)
LSC (10-20%)
Sr & Ca: Alkline earth element
Determination $^{41}$Ca in concrete

- Separation from matrix
  - Decomposition of heavy concrete by alkali fusion
  - Leaching Ca by acids
- Separation from active metals such as $^{60}$Co, $^{152}$Eu, $^{55}$Fe, $^{63}$Ni, $^{65}$Zn, $^{54}$Mn, $^{51}$Cr, etc.
  - Precipitation with Fe(OH)$_3$ by hydroxides at pH9
- Separation from other alkaline metals, such as $^{133}$Ba, $^{226}$Ra and $^{90}$Sr.
  - BaCrO$_4$ and SrCrO$_4$ precipitation
  - BaCl$_2$ and SrCl$_2$ precipitation in HCl solution
  - Ca(OH)$_2$ precipitation in NaOH solution

Concrete in the reactor

- Ordinary concrete
- Heavy concrete (50-70% BaSO$_4$ was added)
Decomposition of concrete for $^{41}\text{Ca}$ and other radionuclides

- For Ordinary concrete, silicates of calcium does not easily be decomposed by acids.
- For heavy concrete, some calcium exists as $\text{CaSO}_4$, which does not dissolve by acid.
- Alkaline fusion have to be used for the decomposition of concrete for the determination of calcium isotopes.

**Flowchart:**
- **Concrete**
  - Add $\text{Na}_2\text{CO}_3/\text{NaOH}$, fuse at 700 °C for 2-3 hours
- **Fused sample**
  - Leaching with water, filter through a filter paper and wash with water
- **Precipitate, $\text{CaCO}_3, \text{BaCO}_3$**
  - Dissolve with HCl
  - **Solution, $\text{CaCl}_2$**
  - Separation procedure
- **Filtrate, Na, K, Mg, Al, $\text{SO}_4^{2-}$ etc.**
Separation of Ca and Sr from other metals by hydroxides precipitation followed by carbonate precipitation

<table>
<thead>
<tr>
<th>Element / nuclide</th>
<th>Recovery, %</th>
<th>Element / nuclide</th>
<th>Decontamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>97.7±3.9</td>
<td>$^{137}$Cs</td>
<td>(4.5±0.3)×10^5</td>
</tr>
<tr>
<td>$^{85}$Sr</td>
<td>97.9±2.1</td>
<td>$^{60}$Co</td>
<td>(1.2±0.4)×10^5</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td>97.3±2.8</td>
<td>$^{152}$Eu</td>
<td>(8.5±0.5)×10^5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{59}$Fe</td>
<td>(2.5±0.1)×10^5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{63}$Ni</td>
<td>(2.5±0.2)×10^5</td>
</tr>
</tbody>
</table>
The new method for the separation of Ca from Sr and Ba

- Separation of Sr from Ca by Ca(OH)$_2$ precipitation
  - Ca(OH)$_2$: insoluble, $K_{sp} = 5.2 \times 10^{-6}$
  - Sr(OH)$_2$ and Ba(OH)$_2$: Soluble in alkine solution

Precipitate Ca as Ca(OH)$_2$ at 0.5 – 0.8 mol/l NaOH, repeat 3 times, 85% Ca can be recovered, and the decontamination factor for Sr and Ba are higher than $5 \times 10^4$
Separation of Ca from Sr and Ba by 3 repeated steps of Ca(OH)$_2$ precipitations at different NaOH concentrations

<table>
<thead>
<tr>
<th>[NaOH] mol/l</th>
<th>Decontamination factor, 3 precipitations</th>
<th>Recovery of Ca, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
<td>Sr</td>
</tr>
<tr>
<td>0.10</td>
<td>6.54×10$^4$</td>
<td>6.54×10$^4$</td>
</tr>
<tr>
<td>0.15</td>
<td>6.33×10$^4$</td>
<td>5.17×10$^4$</td>
</tr>
<tr>
<td>0.20</td>
<td>5.37×10$^4$</td>
<td>4.97×10$^4$</td>
</tr>
<tr>
<td>0.30</td>
<td>5.01×10$^4$</td>
<td>4.57×10$^4$</td>
</tr>
<tr>
<td>0.40</td>
<td>4.62×10$^4$</td>
<td>4.47×10$^4$</td>
</tr>
<tr>
<td><strong>0.50</strong></td>
<td><strong>4.71×10$^4$</strong></td>
<td><strong>4.42×10$^4$</strong></td>
</tr>
<tr>
<td>0.60</td>
<td>4.71×10$^4$</td>
<td>4.37×10$^4$</td>
</tr>
<tr>
<td>0.80</td>
<td>4.51×10$^4$</td>
<td>4.10×10$^4$</td>
</tr>
<tr>
<td>1.50</td>
<td>4.19×10$^4$</td>
<td>3.77×10$^4$</td>
</tr>
<tr>
<td>2.00</td>
<td>3.81×10$^4$</td>
<td>3.18×10$^4$</td>
</tr>
</tbody>
</table>
Procedure for simultaneous determination of $^{41}\text{Ca}$

Concrete

Leaching with HCl + HNO$_3$ at heating, filter

Residue, Silicate, BaSO$_4$

Filtrate, (metals, Ca, Sr, etc)

Add Fe carrier, Add NaOH to pH9, centrifuge

Precipitate, M(OH)$_x$

For $^{55}\text{Fe}$ and $^{63}\text{Ni}$

Add Na$_2$CO$_3$, centrifuge

Supernatant, Ca, Sr, Ba

Supernatant, Sr, Ba, Ra

Add NaOH to 0.5 mol/l, centrifuge

Precipitate $^{41}\text{Ca}$(OH)$_2$

Dissolve with HCl, add Fe$^{3+}$, and NaOH to pH9, centrifuge

Precipitate, Co, Eu, Fe

Precipitate, Ca, Ba, Sr, Ra CO$_3$

Add NaOH to 0.5 M, centrifuge, repeat

LSC measurement
Spectra of $^{41}$Ca in heavy concrete from DR-2

Sample Spectrum

Spectrum of $^{41}$Ca in concrete

Sample Spectrum

Spectrum of $^{41}$Ca, $^{55}$Fe and $^{63}$Ni in concrete
Quench correction for LSC of $^{41}$Ca

\[ y = 0.1211x - 80.073 \]

\[ R^2 = 0.9771 \]
Features of Method for $^{41}$Ca

- A separation of $^{41}$Ca from concrete is easy to operate
- Good decontamination from interferring radionuclides ($>10^4$)
- The chemical yields of the separation procedures for $^{41}$Ca is 80-90%.
- The detection limits for $^{41}$Ca is 0.020 Bq.

Hou X.L., Radiochim Acta, 2005
Sampling of concrete and graphite from Danish reactor, DR-2
Results of $^{41}$Ca in concrete from Danish reactor, DR-2
\(^{90}\text{Sr in water, graphite, resin, concrete}\)

- One of main fission products (Y=5.8%)
- Beta emitter, measured by GM detector or LSC.
- It has to be separated from other radionuclides before measurement.
- For some waste, it may contain \(^{89}\text{Sr}\) (50.5 d), it can be also measured by LSC with \(^{90}\text{Sr}\).
Analytical Procedure for $^{90}\text{Sr}$

Sample

Carbonate precipitate from water → Ash and Acid leaching from solid sample

Decomposed sample or Coprecipitate

Separation of Sr from Ca, Cs, metals and transuranics

Separation of Sr from Ra and Ba

Measurement of $^{89}\text{Sr}+^{90}\text{Sr}$

Measure $^{89}\text{Sr}$ by Cherenkov radiation
Decomposition of solid sample

Graphite, resin

Ashing at 700-800 °C

residue

solution

Separation procedure

Concentre

Add Na₂CO₃/NaOH, fuse at 700 °C for 2-3 hours

Fused sample

Leaching with water, filter through a filter paper and wash with water

Precipitate, SrCO₃, BaCO₃

Dissolve with HCl

Solution, CaCl₂

Separation procedure

Fitrate, Na, K, Mg, Al, SO₄²⁻ etc.
Method for the Separation of Sr

- solvent extraction
- liquid membrane extraction
- extraction chromatography (Sr-Spec resin)
- ion-exchange chromatography
- strontium rhodizonate precipitation
- $\text{Sr(NO}_3\text{)}_2$ precipitation in 70% HNO$_3$
  (can be used for separation of Sr from a large amount of Ca)
## Solubilities of Ca, Sr, Y Ba and Ra compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂</td>
<td>insoluble, Ksp = 5.2 × 10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>Sr(OH)₂</td>
<td>soluble in alkine solution</td>
<td></td>
</tr>
<tr>
<td>SrCl₂, BaCl₂, RaCl₂</td>
<td>soluble in water</td>
<td></td>
</tr>
<tr>
<td>SrCl₂</td>
<td>soluble in HCl &lt; 9.5 mol/L solution</td>
<td></td>
</tr>
<tr>
<td>BaCl₂, RaCl₂</td>
<td>insoluble in HCl &gt; 9 mol/l</td>
<td></td>
</tr>
<tr>
<td>Y₂(SO₄)₃</td>
<td>soluble in water</td>
<td></td>
</tr>
<tr>
<td>Sr(Ba, Ra)SO₄</td>
<td>insoluble in water</td>
<td></td>
</tr>
</tbody>
</table>
The new method for the separation of Sr

Separation of Sr from Ca:
  Ca(OH)$_2$ precipitation

Separation of Sr from Ba and Ra
  Ba(Ra)Cl$_2$ precipitation in concentrated HCl solution

Separation of $^{90}$Y from Sr, Ra and Ba
  Sr(Ra, Ba)SO$_4$ precipitation
### Separation of Sr from Ca by Ca(OH)$_2$

<table>
<thead>
<tr>
<th>$^{85}$Sr added (Bq)</th>
<th>Ca added (g)</th>
<th>$^{85}$Sr (Bq)</th>
<th>Recovery of Sr (%)</th>
<th>Ca in supernatant (g)</th>
<th>Ca decontamination (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Precip.</td>
<td>Supern.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>50.00</td>
<td>31.6</td>
<td>1058.4</td>
<td>97.0</td>
<td>0.18</td>
</tr>
<tr>
<td>1050</td>
<td>31.00</td>
<td>38.1</td>
<td>1037.7</td>
<td>96.4</td>
<td>0.14</td>
</tr>
<tr>
<td>1050</td>
<td>10.00</td>
<td>30.6</td>
<td>1029.6</td>
<td>97.1</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Concentration of NaOH in the solution: 0.5 mol/L
# Separation of Sr from Ba by $\text{BaCl}_2$ and $\text{BaCrO}_4$

<table>
<thead>
<tr>
<th>[HCl], mol/l</th>
<th>Tracers added (Bq)</th>
<th>Supernat. $^{85}\text{Sr}$ (Bq)</th>
<th>Precipitate $^{85}\text{Sr}$ (Bq) *</th>
<th>Recovery of Sr, %</th>
<th>Decontam. of Ba, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>1050</td>
<td>1510</td>
<td>918.8±14.2</td>
<td>2.0±3.4</td>
<td>99.8±0.3</td>
</tr>
<tr>
<td>9.0</td>
<td>1050</td>
<td>1510</td>
<td>484.7±18.4</td>
<td>2.1±2.4</td>
<td>98.8±0.3</td>
</tr>
<tr>
<td>9.5</td>
<td>1050</td>
<td>1510</td>
<td>43.8±9.4</td>
<td>62.4±5.9</td>
<td>94.1±0.6</td>
</tr>
<tr>
<td>10.0</td>
<td>1050</td>
<td>1510</td>
<td>40.5±7.2</td>
<td>331.2±11.1</td>
<td>68.5±1.5</td>
</tr>
<tr>
<td>10.5</td>
<td>1050</td>
<td>1510</td>
<td>28.6±4.2</td>
<td>743.4±18.4</td>
<td>29.5±1.3</td>
</tr>
<tr>
<td>11.0</td>
<td>1050</td>
<td>1510</td>
<td>7.9±4.8</td>
<td>846.3±21.2</td>
<td>21.1±1.1</td>
</tr>
<tr>
<td>$\text{BaCrO}_4$</td>
<td>1050</td>
<td>1510</td>
<td>15.3±5.7</td>
<td>49.0±7.8</td>
<td>95.3±0.7</td>
</tr>
</tbody>
</table>

* Average and standard deviation of two determinations
Separation of Y from Ra, Sr, and Ba by sulphate precipitation

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Added</th>
<th>Supernat.</th>
<th>Precipitate</th>
<th>Recovery of Y, %</th>
<th>Decontam.of Sr, Ba, Ra %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y, mg</td>
<td>11.10</td>
<td>10.95±0.22</td>
<td></td>
<td>98.6±2.0</td>
<td></td>
</tr>
<tr>
<td>$^{85}$Sr, Bq</td>
<td>1050</td>
<td>8.7±2.4</td>
<td>1042±38</td>
<td></td>
<td>99.2±0.2</td>
</tr>
<tr>
<td>$^{133}$Ba, Bq</td>
<td>1510</td>
<td>2.2±1.8</td>
<td>1511±21</td>
<td></td>
<td>99.9±0.1</td>
</tr>
<tr>
<td>$^{226}$Ra, Bq</td>
<td>33.0</td>
<td>0.14±0.26</td>
<td>32.87±0.47</td>
<td></td>
<td>99.6±1.4</td>
</tr>
</tbody>
</table>
Separation procedure of $^{90}$Sr

Add $^{85}$Sr, SrCl$_2$, pH 8-10, add (NH$_4$)$_2$CO$_3$, stand overnight

Supernatant

Precipitate (SrCO$_3$, Ca, Ra, Ba, transuranics)

Add HNO$_3$ to dissolve, Fe$^{3+}$, add NaOH to 0.5 mol/L, centrifuge

Supernatant, Sr

Precipitate (Ca(OH)$_2$, Fe, transuranics)

Supernatant, Y-90

Add H$_2$C$_2$O$_4$, centrifuge

Precipitate, $Y_2(C_2O_4)_3$ H$_2$O

$\beta$ Measurement of Y-90, calculation of Sr-90

Fig. 1 Beta spectrum of Sr sample separated from DR1 sample

Fig. 2 Cherenkov radiation of Sr sample separated from one DR1 sample
Combined procedure for simultaneous determination of $^{41}\text{Ca}$ and $^{90}\text{Sr}$

Concrete

1. Add Ca, Ba, Sr, $^{85}\text{Sr}$, Fe, Co, Eu, leaching with *aqua regia*, filter

   - Filtrate, (metals, Ca, Sr, etc)
   - Residue, (Silicate, BaSO$_4$)

   Filtrate, (metals, Ca, Sr, etc)

2. Add NaOH to pH 9, centrifuge

   - Precipitate, M(OH)$_x$
   - Supernatant, Ca, Sr, Ba, Cs, K

   (60Co, 152Eu, 55Fe, 63Ni, transuranics, etc.)

3. Add Na$_2$CO$_3$, centrifuge

   - Supernatant, Ca, Sr, Ba, Cs, K
   - Precipitate, (Ca, Ba, Sr, Ra)CO$_3$

4. Dissolve with HCl, add NaOH to 0.5 mol/L, centrifuge

   - Discard
   - LSC for $^{41}\text{Ca}$ measurement
   - ICP-OES for Ca

5. Dissolve with HCl, add Sr, Ba, Fe, Co, Eu, add NaOH to pH 9, centrifuge

   - Precipitate, Co, Eu, Fe,
   - Supernatant, Ca, Sr, Ba, Ra

6. Add NaOH to 0.5 mol/L, centrifuge

   - Precipitate, Co, Eu, Fe,
   - Supernatant, Ca, Sr, Ba, Ra

7. Dissolve with HCl

   - Precipitate $^{41}\text{Ca}$
   - LSC for $^{41}\text{Ca}$ measurement
   - ICP-OES for Ca

8. Add Y, keep 3 weeks for ingrowth of $^{90}\text{Y}$, add Na$_2$SO$_4$, centrifuge

   - Supernatant, $^{90}\text{Y}$

9. Add NH$_4$OH, centrifuge

   - Precipitate, Y(OH)$_3$

10. Dissolve with HCl, add H$_2$C$_2$O$_4$, filter

    - $\text{Y}_2$(C$_2$O$_4$)$_3$ precipitate

    - LSC or GM counter measurement of $^{90}\text{Y}$
### Analytical Method for $^{129}$I and their detection limits

<table>
<thead>
<tr>
<th>Method</th>
<th>Detection limit (atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid scintillation</td>
<td>$10^{12}$ (1 mBq)</td>
</tr>
<tr>
<td>$\gamma$-spectrometry</td>
<td>$10^{14}$ (0.1 Bq)</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>$5 \times 10^{11}$</td>
</tr>
<tr>
<td>Radiochemical neutron activation analysis</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Accelerator mass spectrometry (AMS)</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

$^{129}$I ($1.57 \times 10^7$ y)

- $\beta^-$, 196 keV, 100%
- $^{129m}$Xe, 8.88d
- IC, 96.6%
- $\gamma$, 39.6 keV, 3.4%

$^{129}$Xe (stable)
Separation procedure of iodine in solid samples

Solid samples
- decompose sample by combustion, acid digestion, or alkali fusion

solution
- Extracting with CCl₄,
- Back-extracting with H₂SO₃, repeat

Iodide separated
- convert to MgI₂ or AgI

Iodine Sample
- Measurement by LSC
- Gamma measurement
- AMS
- RNAA
Separation of $^{129}\text{I}$ from solid waste by combustion method

- Flask 1: $^3\text{H}$, $^{129}\text{I}$, $^{99}\text{Tc}$
- Flask 2,3: $^{14}\text{C}$, $^{129}\text{I}$
Schematic diagram of acid digestion system for separation of $^{36}\text{Cl}$ and $^{129}\text{I}$

1-Heating mantle; 2-three-necked flask; 3-sample in acid mixture; 4-bubbling tube; 5-separating funnel for adding acids; 6,7-reflux condenser; 8-receiver; 9-wash bottle containing water; 10, 11-absorption bottles containing 0.4 mol/l NaOH
Separation of $^{129}$I from solid waste by Alkali fusion

Solid samples (concrete)
- add NaOH/Na$_2$CO$_3$, iodine carrier, fusion at 600°C for 2 h

Fusee cake
- Leaching with H$_2$O, filter to remove residue (precipitation)

Solution with $^{129}$I
- Convert iodine to iodide, extract with CCl$_4$, abck extract with NaSO$_3$

Separated Iodine
Beta spectrum of $^{129}\text{I}$ by LSC

Sample Spectrum

- $^{129}\text{I}$ β counts in SP11
- background counts in SP12
Determination of $^{36}\text{Cl}$

- $^{36}\text{Cl}$ is long-lived radionuclides ($3 \times 10^5$ yrs)
- $^{36}\text{Cl}$ decays mainly by pure beta emission of $E_{\text{max}}=708.6$ keV.
- $^{36}\text{Cl}$ measurement is normally carried out by LSC and AMS.
Determination of $^{36}$Cl and $^{129}$I in graphite --- Sample decomposition

• Ashing at 900°C: ---iodine and part of Cl are lost.

• Decomposition at 900°C with O$_2$ and trapping iodine in NaOH solution: ---good recovery for iodine, but not good for chlorine

• Leaching with acid (HNO$_3$) at heating: --- not complete remove iodine and Cl from graphite, and loss of the leached iodine.

• Digestion with HNO$_3$ and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine

• **How to Do?**
Determination of $^{36}$Cl and $^{129}$I in graphite

--- Sample decomposition

- Graphite can be completely dissolved in a mixture of acids: $\text{HNO}_3+\text{H}_2\text{SO}_4 +\text{HClO}_4$

- The optima ratio of mixture is:
  
  \[ \frac{\text{H}_2\text{SO}_4}{\text{HNO}_3:\text{HClO}_4} = 15:4.1 \]

- A closed dissolution system is used for dissolve graphite in heating, Cl on the condenser tube and trap solution, while iodine mainly in the trap solution.
Schematic diagram of dissolution system of graphite for determination of $^{36}$Cl and $^{129}$I

1-Heating mantle; 2-three-necked flask; 3-sample in acid mixture; 4-bubbling tube; 5-separating funnel for adding acids; 6,7-reflux condenser; 8-receiver; 9-wash bottle containing water; 10, 11-absorption bottles containing 0.4 mol/l NaOH
Determination of $^{36}\text{Cl}$ and $^{129}\text{I}$ in concrete
--- Sample decomposition

- Leaching with acid (HNO$_3$) at heating: --- not complete removal of iodine and Cl from graphite, and loss of the leached iodine.

- Digestion with HNO$_3$ and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine

- Alkaline fusion using NaOH and Na$_2$CO$_3$, dissolution of fused cake in water, the supernatant is used for $^{129}\text{I}$ and $^{36}\text{Cl}$: ---- sample is completely decomposed and iodine and Cl are released. Iodine and Cl are not lost in alkaline medium
Determination of $^{36}$Cl and $^{129}$I in stainless steel

--- Sample decomposition

- Stainless steel is normally dissolved with HCl or HCl+HNO$_3$: could not be used for $^{36}$Cl because of too much Cl in HCl is introduced.

- Single acid, HNO$_3$, could not dissolve stainless steel.

- 10M H$_2$SO$_4$ with H$_3$PO$_4$ is successfully used for dissolve stainless steel for $^{129}$I and $^{36}$Cl: sample is completely decomposed and iodine and Cl are released.
Separation of Cl from matrices and other radionuclides

Specific precipitation of Cl\(^-\) with Ag\(^+\) (AgCl) can be used to selectively separation of Cl from matrix and other radionuclides (except iodine and bromine).

Iodine (\(^{129}\)I) should be first separated from the solution before AgCl precipitation.

\(^{129}\)I can be separated by solvent extraction using CHCl\(_3\)

No need to separate Br, since no long-lived radioisotopes of Br in the waste and environmental samples.

The separated AgCl can be dissolved in NH\(_4\)OH and mixed with scintillation cocktail for LSC: But less AgCl can be used and high quench effect. How to improve?
Separation of Ag⁺ and Cl⁻ in anion exchange chromatography

- 100mg Cl, 0.2 M NH₄NO₃-0.6 M NH₄OH eluting
- 200mg Cl 0.2 M NH₄NO₃-0.6 M NH₄OH eluting
- 50 mg Cl, 0.1 M NH₄NO₃-0.6 M NH₄OH eluting
- 100 mg Cl, 0.1 M NH₄NO₃-0.6 M NH₄OH eluting
Combined Analytical procedure for $^{36}$Cl and $^{129}$I

**Graphite, steel**

- Add stable Cl and I carriers, dissolve with acids, combine the absorption solutions and dissolved solution
- Add NaHSO$_3$, transfer to a separation funnels, add CCl$_4$, HNO$_3$, and NaNO$_2$ to extract, repeat the extraction
- Organic phase, $^{129}$I
  - Back-extract with NaHSO$_3$ solution, repeat extraction and back-extraction
  - Aqueous phase, $^{129}$I
    - LSC for $^{129}$I
    - ICP-MS for I
- Aqueous phase
  - Washes, Ag$^+$ etc.
  - AG 1×4 column
    - Effluent, $^{36}$Cl
      - Evaporate, dissolved with H$_2$O
      - ICP-MS for Cl
      - LSC for $^{36}$Cl
    - Eluting with 0.1 M NH$_4$NO$_3$-0.6 M NH$_4$OH

**Heavy Concrete**

- Add stable Cl and I carriers and NaOH and Na$_2$CO$_3$, fuse at 500 °C, leaching with H$_2$O, centrifuge to separate the supernatant
- Add NaHSO$_3$, transfer to a separation funnels, add CCl$_4$, HNO$_3$, and NaNO$_2$ to extract, repeat the extraction
- Organic phase, $^{129}$I
  - Back-extract with NaHSO$_3$ solution, repeat extraction and back-extraction
  - Aqueous phase
    - Washes, Ag$^+$ etc.
    - AG 1×4 column
      - Effluent, $^{36}$Cl
        - Evaporate, dissolved with H$_2$O
        - ICP-MS for Cl
        - LSC for $^{36}$Cl
    - Eluting with 0.1 M NH$_4$NO$_3$-0.6 M NH$_4$OH

*Hou et al., Anal. Chem., 2007*
Recovery of Cl and decontamination factors for other elements and radionuclides in the chemical separation procedure

<table>
<thead>
<tr>
<th>Element</th>
<th>AgCl precipitation</th>
<th>Anion exchange</th>
<th>Whole procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (recovery, %)</td>
<td>96.5</td>
<td>98.3</td>
<td>94.7±3.2</td>
</tr>
<tr>
<td>I ($^{125}$I)</td>
<td>1.4 x10$^3$</td>
<td>5.4 x10$^3$</td>
<td>2.9 x10$^6$</td>
</tr>
<tr>
<td>S</td>
<td>1.5 x10$^3$</td>
<td></td>
<td>5.6 x10$^6$</td>
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<tr>
<td>tritium</td>
<td>2.1 x10$^3$</td>
<td></td>
<td>4.8 x10$^6$</td>
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<tr>
<td>$^{14}$C (CO$_3^{2-}$)</td>
<td>1.5 x10$^3$</td>
<td></td>
<td>2.8 x10$^6$</td>
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<tr>
<td>Co ($^{60}$Co)</td>
<td>1.9 x10$^3$</td>
<td>8.5 x10$^3$</td>
<td>8.5 x10$^6$</td>
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<tr>
<td>Eu ($^{152}$Eu)</td>
<td>4.7 x10$^3$</td>
<td>6.5 x10$^3$</td>
<td>9.9 x10$^6$</td>
</tr>
<tr>
<td>Cs ($^{137}$Cs)</td>
<td>3.8 x10$^3$</td>
<td>5.1 x10$^3$</td>
<td>7.9 x10$^6$</td>
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<tr>
<td>Ba ($^{133}$Ba)</td>
<td>6.7 x10$^3$</td>
<td>4.9 x10$^3$</td>
<td>5.6 x10$^6$</td>
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<tr>
<td>Sr ($^{85}$Sr)</td>
<td>4.7 x10$^3$</td>
<td>8.3 x10$^3$</td>
<td>8.7 x10$^6$</td>
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<tr>
<td>Ni ($^{63}$Ni)</td>
<td>5.9 x10$^3$</td>
<td>9.8 x10$^3$</td>
<td>9.8 x10$^6$</td>
</tr>
<tr>
<td>Fe ($^{55}$Fe)</td>
<td>1.9 x10$^3$</td>
<td>8.8 x10$^3$</td>
<td>8.1 x10$^6$</td>
</tr>
</tbody>
</table>
Performance of the procedure for $^{36}\text{Cl}$

- Recovery of Cl: >70%
- Decontamination factors for most of radionucleides: $>10^6$
- Detection limit using LSC: 14 mBq
- Decommissioning samples, concrete, graphite, stainless steel, aluminum, lead, have been successfully analysed for $^{36}\text{Cl}$
Distribution of $^{36}\text{Cl}$ in the concrete core from Danish research reactor DR-2 with comparison to $^{55}\text{Fe}$, and $^{63}\text{Ni}$
Concentrations of $^{36}$Cl in samples from the graphite thermal column, aluminum tanks and lead shielding in the concrete core from DR-2 reactor

<table>
<thead>
<tr>
<th>Sample</th>
<th>Code</th>
<th>$^{36}$Cl, Bq/g mean±SD</th>
<th>$^{63}$Ni, Bq/g</th>
<th>$^{36}$Cl/$^{63}$Ni Activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>5.5 Yi</td>
<td>0.18±0.03</td>
<td>5.76</td>
<td>0.030</td>
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<tr>
<td>Graphite</td>
<td>5.5 Yy</td>
<td>3.58±0.13</td>
<td>102</td>
<td>0.035</td>
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<tr>
<td>Graphite</td>
<td>5.5 li</td>
<td>22.6±1.5</td>
<td>499</td>
<td>0.045</td>
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<tr>
<td>Graphite</td>
<td>5.5 ly</td>
<td>6.61±0.52</td>
<td>74.9</td>
<td>0.088</td>
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<tr>
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<td>7.5 Yi</td>
<td>6.37±0.48</td>
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<td>0.048</td>
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<tr>
<td>Graphite</td>
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<td>5.57±0.54</td>
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<tr>
<td>Graphite</td>
<td>7.5 li</td>
<td>39.9±3.4</td>
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<td>0.053</td>
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<tr>
<td>Graphite</td>
<td>G</td>
<td>3.33±0.28</td>
<td>61.2</td>
<td>0.054</td>
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<tr>
<td>Aluminum</td>
<td>B1</td>
<td>0.027±0.003</td>
<td>15.6</td>
<td>0.0017</td>
</tr>
<tr>
<td>Aluminum</td>
<td>B2</td>
<td>0.023±0.03</td>
<td>15.5</td>
<td>0.0015</td>
</tr>
<tr>
<td>lead</td>
<td>B4</td>
<td>0.0032±0.0012</td>
<td>2.58</td>
<td>0.0012</td>
</tr>
</tbody>
</table>
Combined analytical procedure for $^{36}$Cl, $^{129}$I, $^{41}$Ca, $^{63}$Ni and $^{55}$Fe

**Aqueous phase,**
- Add CCl$_4$, HNO$_3$ to pH2, add NaNO$_2$ to extract, repeat.
- Add AgNO$_3$, centrifuge
- Add NaHSO$_3$ solution to back-extract iodide
- Add 25% NH$_3$ to dissolve AgCl, add HNO$_3$ to pH2, centrifuge, washing precipitate with H$_2$O, repeat precipitate
- Repeat extraction and back-extraction
- Add NaOH to pH10 and evaporate to 3 ml

**Precipitate, AgCl**
- Add Ag(NH)$_3$Cl, centrifuge
- Load to column
- AG 1x4 column, NO$_3^-$ form
- Eluate $^{36}$Cl
- Evaporate to 3 ml

**Solution, Ag(NH)$_3$Cl**
- Wash with 25% H$_3$ solution
- Elute with 0.2 M NH$_4$NO$_3$/0.6M NH$_4$OH solution

**Eluate $^{129}$I solution**
- Washing with 25% H$_3$ solution
- Elute with 3 M HNO$_3$
- Precipitate $^{41}$Ca
- Supernatant, Sr, Ba
- Add HCl to dissolve

**Eluate $^{41}$Ca solution**
- LSC measurement for $^{36}$Cl, $^{129}$I, $^{41}$Ca, $^{63}$Ni, $^{55}$Fe

**Supernatant, Ca, Sr, Ba**
- Dissolve with HCl, Add NaOH to pH9, centrifuge

**Precipitate $^{41}$Ca**
- Supernatant, Sr, Ba
- Evaporate, dissolved with HCl, loading with 6 M HCl
- Elute with H$_2$O
- Evaporate to dryness, dissolve with $H_3PO_4$

**Eluate $^{63}$Ni**
- Evaporate with 0.2 M NH$_4$Cit, Eluting with 3 M HNO$_3$
- Add Fe, Ni, Ca, Sr and I carriers and hold-back carriers, NaOH, Na$_2$CO$_3$, fuse at 500 ºC, leaching with water, centrifuge, washing precipitate with 0.2 M Na$_2$CO$_3$ for 4 times

**Precipitate (metals, Ca, Sr,)**
- AG 1x4 column
- Washing with 4 mol/l HCl
- Eluting with 0.5 mol/l HCl
- Evaporate, dissolved with HCl, loading with 6 M HCl
- Washing with 0.2 M NH$_4$Cit, Eluting with 3 M HNO$_3$
- Supernatant, Sr, Ba
- Evaporate, dissolved with HCl, loading with 6 M HCl
- Washing with 0.2 M NH$_4$Cit, Eluting with 3 M HNO$_3$
- Add Fe, Ni, Ca, Sr and I carriers and hold-back carriers, NaOH, Na$_2$CO$_3$, fuse at 500 ºC, leaching with water, centrifuge, washing precipitate with 0.2 M Na$_2$CO$_3$ for 4 times

**Concrete**
- Add NaOH to pH9, centrifuge
- Precipitate M(OH)$_3$