Analytical Systems For NIREX Compliance

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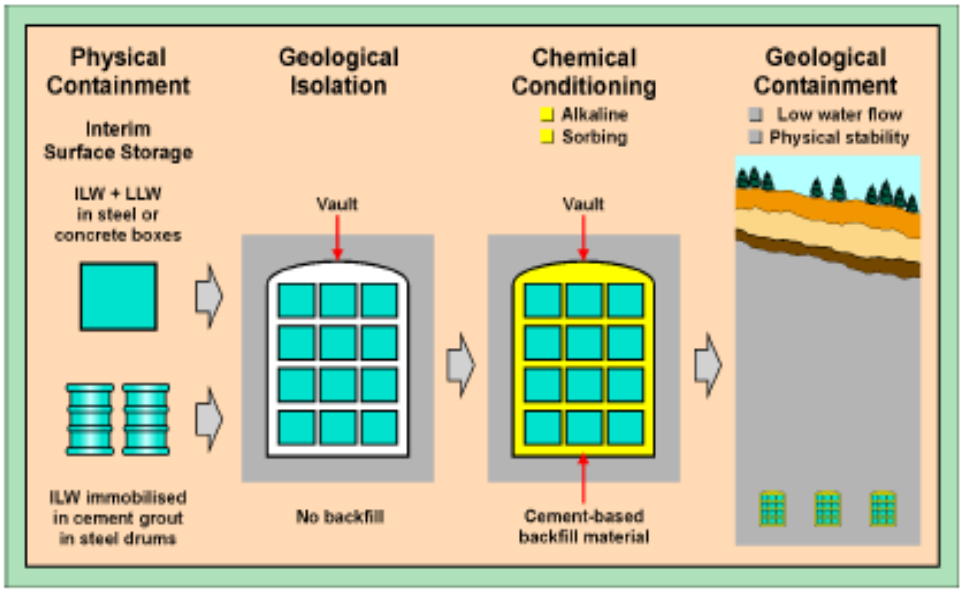
- Decommissioning of Magnox power stations creates lots of different types of wastes

Storage of ILW

- NIREX requires that the radionuclide inventory of these wastes be known as accurately as possible.



Aims and Objectives

- Required to design, develop and realise methods for the analyses of ^{79}Se and ^{99}Tc in various matrices associated with Magnox ILW
- Since extended to include ^{41}Ca and ^{93}Zr

Background to the Project

Magnox Electric contract requires the analyses of:

Selenium – 79

- Relatively low fission yield (0.045%) but long half-life (6.5×10^4 years)
- Importance increases with time
- Not yet included in the Magnox waste inventory

- Technetium – 99
  - High fission yield (6%) and long half life (2.1×10^5 years)
  - Not yet included in the Magnox waste inventory

Decay Equations

- Techentium-99 Decay

$$^{99}Tc \xrightarrow[\beta^- 294\ kev]{} {}^{99}Ru$$

- Selenium-79 Decay

$$^{79}Se \xrightarrow[\beta^- 160\ kev]{} {}^{79}Br$$

Matrices

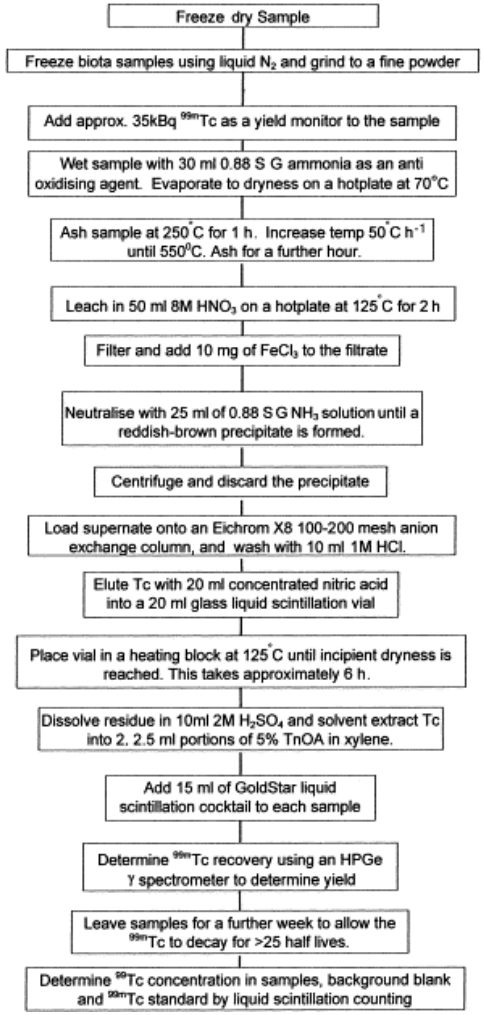
- Specifically examined the following matrices:
  - IonSiv IE-911 - cation exchange resin
  - AW500 - cation exchange resin
  - Alumina (Al_2O_3) - desiccant
  - Lewatit DN - organic cation exchange resin

Other Radionuclides Expected in Wastes

- Beta Emitters
  - Sr-90/Y-90
  - Ni-63
- Gamma Emitters
  - Cs-137
  - Eu-152
- Alpha Emitters
  - Th-232
  - Am-241
  - U-238

- Beta emitters a problem due to interferences in liquid scintillation counting
- Sr-90/Y-90 a major problem
  - High energy emission (546kev/2280kev) obscures Sr-79 (160kev) and Tc-99 (294kev) in counting window
  - Present in much greater quantities in the waste

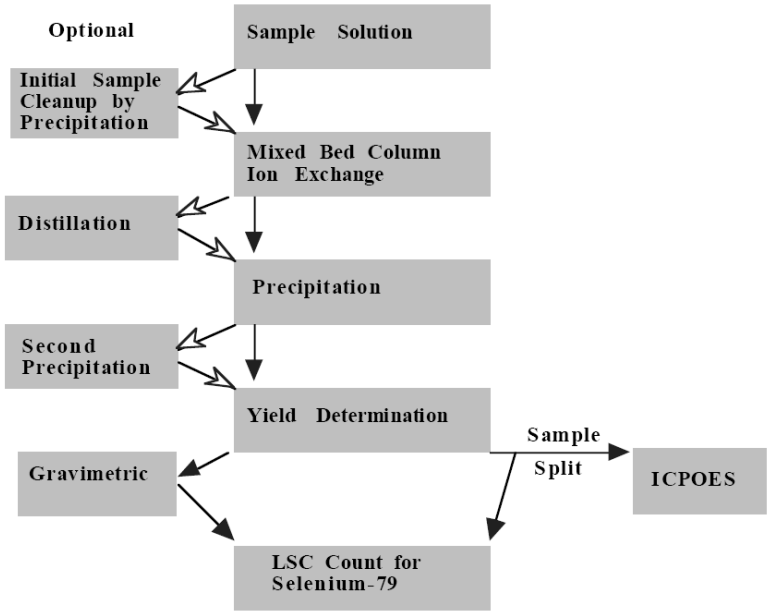
Example of a Technetium Method



- P.E. Warwick method for analysis of Technetium in environmental samples
- Use of precipitation, ion exchange and solvent extraction

F. Wigley, P. E. Warwick, I. W. Croudace, J. Caborn and A. L. Sanchez, Analytica Chimica Acta, Volume 380, 1, 1999, p73-82

Example of a Selenium Method



- DoE Method RP530
- Method uses ion exchange methods, with optional distillation and precipitation stages for sample clean up

Results

- Preparation of sample matrices
- Digestion methods for sample matrices
- Assessment of method ability to decontaminate interfering radio nuclides from solution
- Assessment of method yields

Digestion of Sample Matrices

- Proved to be the hardest task
- Technetium
  - 8M HNO_3 @ ~ 70-80^{o}C
- Selenium
  - Ionsiv-911 and Alumina – required digestion using NaOH
  - Due to selenate sorption

Technetium Yield and Decontamination

- Provides yields of 50-70%
- Decontamination of >99% for Ni-63, Se-75, Sr-90, E-152, Cs-137, Am-241

Selenium Yield and Decontamination

- Provides yields of 40 - 60%
- Decontamination of >99% for Ni-63, Se-75, Sr-90, E-152, Cs-137, Am-241

Extension to Calcium and Zirconium

- Magnox requested that a method be developed to determine ^{41}Ca and ^{93}Zr in concretes, gravels and sand

Zirconium Extraction

- E. Excoffier Method – use of Tributyl phosphate (TBP) impregnated on a resin
- A.G. Espartero method – use of 1-(2'-thenoyl)-3,3,3-trifluoroacetone (TTA) in xylene

1. Determination of Zr-93, Pd-107 and Cs-135 in Zircaloy Hulls Analytical Development on Inactive Samples – *E. Excoffier et al.*

2. Radiochemical Analysis of Zr-93 - *A.G. Espartero, et al.*

Methods Available for Ca-41 analyses in Concrete

- Sequential Determination of Ca-41/Ca-45 and Sr-90 in an Activated Concrete Core – *F. Rowlands, P. Warwick and I Croudace.*
- Radiochemical Analysis of Ca-41 and Ca-45 – *J.A. Suárez, M. Rodriguez, A. G. Espartero and G. Pina*
- Radiochemical Determination of Ca-41 in Nuclear reactor Concrete – *Xiaolin Hou*

Proposed Ca-41 Methodology Derived from Literature

- Follow F. Rowlands methodology
- Replace expensive Sr Spec resin ~ €2766 per 100 g
- Precipitation of Ca or Sr – as per *M. Rodríguez or Xiaolin Hou*

Conclusions

- Methods shown for 79Se and 99Tc provide adequate yields and decontamination to fulfil contractual obligations
- ^{41}Ca and ^{93}Zr methods are available in the literature
  - Need to apply to new matrices

Further Work

- Complete investigation in to ^{41}Ca and ^{93}Zr methods for suitability and contract fulfilment
- Upon completion two further radionuclides and matrices of interest will be assigned