Intercalibration Exercise for Difficult-To-Measure Radionuclides in Activated Steel

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Content

- Context
- Phases of the project
  - 1st phase - Preparation
  - 2nd phase - Radiochemical analysis
  - 3rd phase – Methodology and analysis of the results
- Conclusions

Context

Context

- Difficult-to-measure (DTM) vs easy-to-measure radionuclides
  - Term used in the decommissioning field
  - What makes them difficult?
  - Formation of scaling factors
- Lack of reference materials
- Validation of radiochemical analysis via intercalibration exercise
- NKS platform
  - Nordic countries have decommissioning projects
  - “DTM Decom” project for DTM analysis in activated steel

nks
Nordic nuclear safety research

Phases of the project

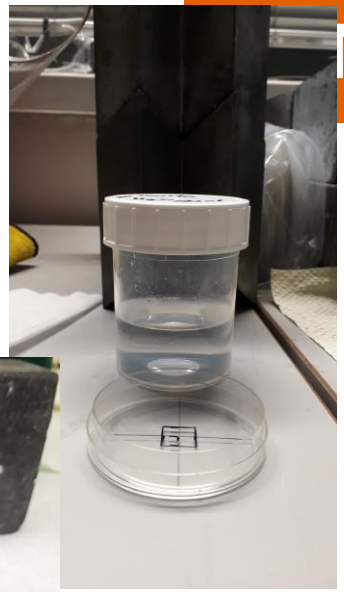
1st phase - preparation

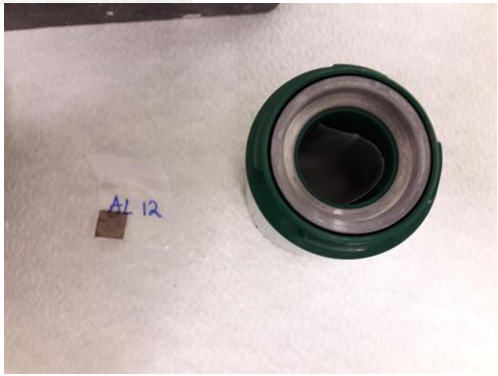
- Participants
  - Finland – VTT (coordinator), Fortum power and heat, Helsinki University
  - Sweden – Cyclife
  - Denmark – Danish technical University
  - Norway – IFE Halden and Kjeller
  - France – CEA Saclay (self funded)
- Online kick-off meeting in February
  - Material to be studied - activated reactor pressure vessel steel
  - Each participant to receive 2-3 samples
  - Main DTMs of interest ^{55}Fe and ^{63}Ni
  - Optional ^{14}C, ^{59}Ni, (^{60}Co)

1st phase - preparation

- Sample preparation
  - One RPV steel bar (10 cm x 1 cm x 1 cm) cut to ~0.2 mm slices
  - Oxide layer removal, weight after air drying
  - Homogeneity studies using gamma spectrometry (ISOCS)
    - Sample holder
    - 3 cm above detector to reduce coincidence
    - 1.8% RSD% of Co-60 in 20 sample measurements

      → homogenous
- Sending of the samples
  - 2-3 samples to each partner
  - Sending as UN2910 shipment
  - Participant received the packages in May 2019
  - Radiochemical analysis time May-September 2019



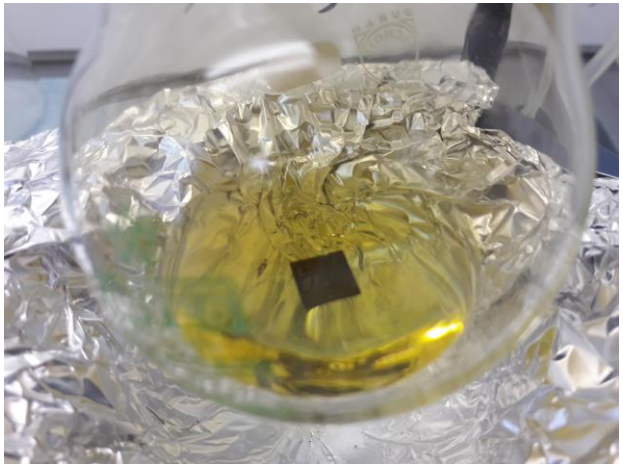


2nd phase – radiochemical analysis

- Main steps of the radiochemical analysis of ^{55}Fe and ^{63}Ni

Step 1 - Decomposition of the solid

Carriers	• Some added carriers • Some added also hold back carriers
Hot plate	• conc HNO3:HCl (2:1) • Aqua regia
Heating mantle + round bottom flask	• when ^{14}C was analysed • 5M H_2SO_4 + conc HNO_3 • H_2O:HNO_3:HCl + $HClO_4$
Microwave	• HNO_3:HF:HCl



2nd phase – radiochemical analysis

- Main steps of the radiochemical analysis of ^{55}Fe and ^{63}Ni

Step 2 - separation of analytes

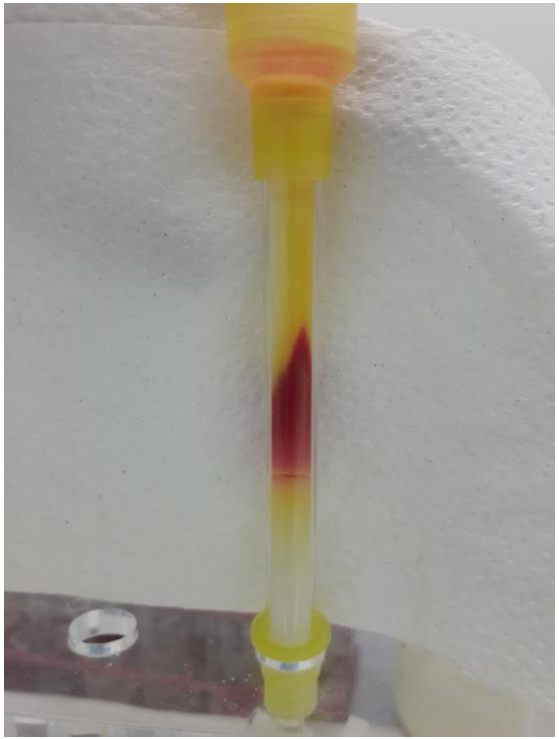
Solution	• Small fraction (0.3 ml to 1 ml) of the acid digestion solution • Whole solution
Carriers	• Some added carriers • Some added hold back carriers
Separation via hydroxide precipitation	• NaOH or NH_4OH to precipitate Ni and Fe (or only Fe) • Separation of Fe and Ni using anion exchange resin (AG 1x4 resin) • Separation of Fe and Ni using anion exchange resin (Dowex 1x4) in 9:1 acetone : 6 M HCl mixture (removal of Co)
Removal of silver and separation via TRU resin	• solution to dryness and diluted with HNO_3 • silver precipitated as AgCl with 0,1M HCl • Fe and Ni separated using TRU resin

2nd phase – radiochemical analysis

- Main steps of the radiochemical analysis of ^{55}Fe and ^{63}Ni

Step 3 - Purification of fractions

Fe fraction	• Some used 2nd AG resin • Evaporated to dryness • Dissolved mainly 1M H_3PO_4
Ni fraction	• Purified using Ni-resin (1 or 2 times) • Evaporated to 0.5 ml – 2 ml

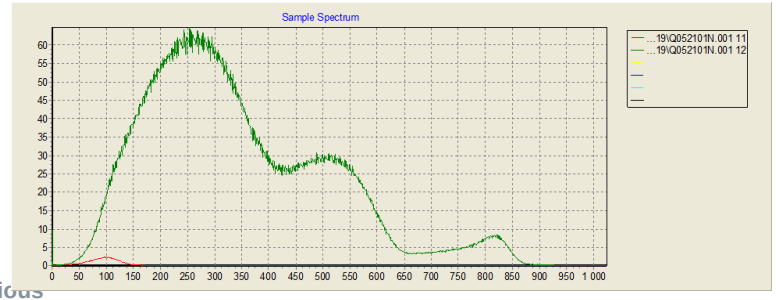


2nd phase – radiochemical analysis

- Main steps of the radiochemical analysis of ^{55}Fe and ^{63}Ni

Step 4 - Measurements

LSC fractions	• Measured using LSC • Standard solutions for quench correction or TDCR technique • Ultima Gold, HiSafe • Interference of Co-60 in Ni-63 fraction
Yield fractions	• Measured using ICP-MS, ICP-OES, MP-AES • Ni yield by spiking a replicate • Fe yield estimated to be 90%



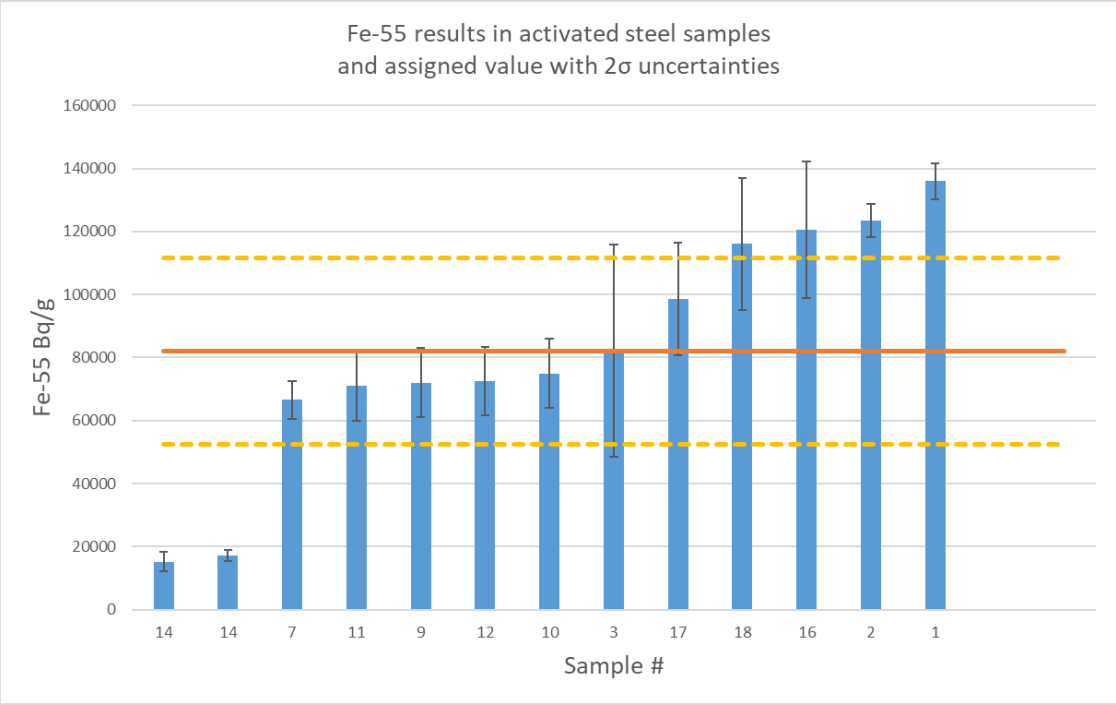
3rd phase – methodology

- Analysis based on ISO 13528 standard
- Variety of scoring strategies – most often participant's deviation from an assigned value is compared
- Assigned value x_{pt}
  - Use of real material and not a reference material with assigned values for analytes
  - Assigned value derived from the participant's results
  - Robust mean and standard deviation using Algorithm A
    - Transforms the original data by a process called winsorisation to provide an alternative estimators of mean and standard deviation
    - Expected proportion of outliers is below 20%
- Comparison of performance using z score

Z score	Analysis result
$z \leq 2.0$	Acceptable
$2.0 < z < 3.0$	Warning signal
$z \geq 3.0$	Unacceptable

3rd phase – analysis of the results

- ^{55}Fe results
  - 13 entries analysed
  - Assigned value: 82.0 ± 29.4 kBq/g (2σ)

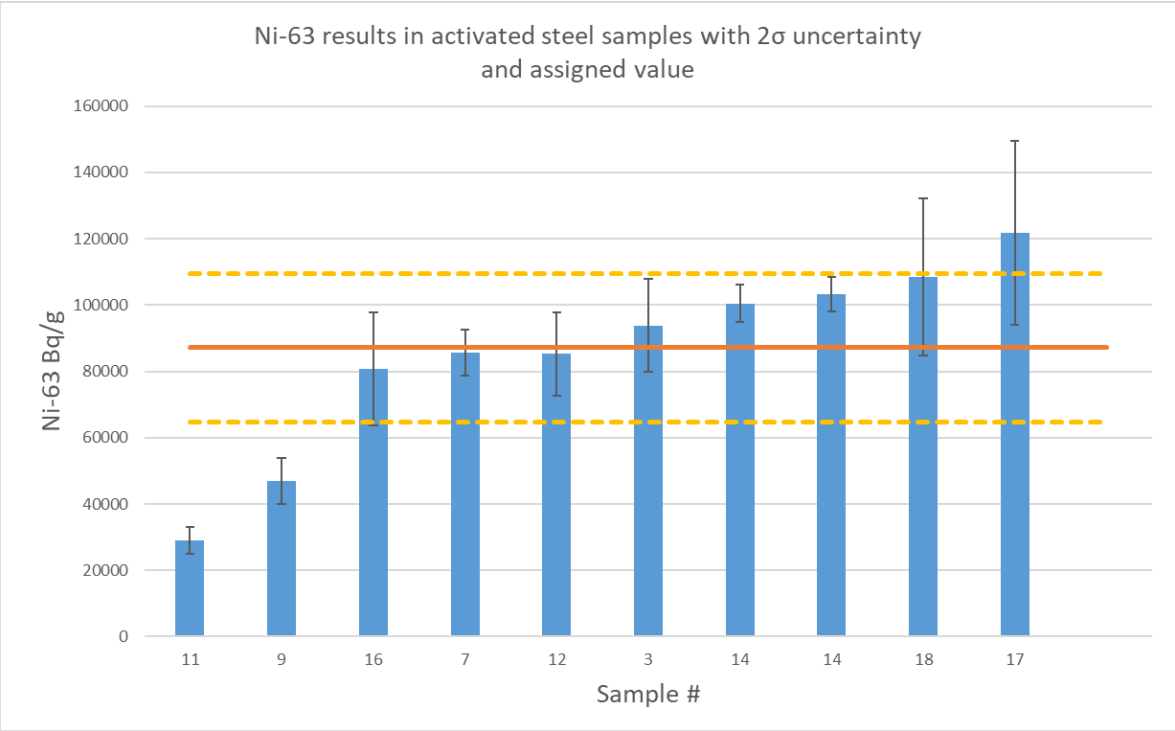


Sample #	Z score
1	3.7
2	2.8
3	0.0
7	1.0
9	0.7
10	0.5
11	0.7
12	0.6
14	4.4
14	4.5
16	2.6
17	1.1
18	2.3

Z score	Analysis result
z ≤ 2.0	Acceptable
2.0 < z < 3.0	Warning signal
z ≥ 3.0	Unacceptable

3rd phase – analysis of the results

- ^{63}Ni results
  - 10 entries analysed
  - Assigned value: 87.1 ± 22.4 kBq/g (2σ)



Sample #	Z score
3	0.6
7	0.1
9	3.6
11	5.2
12	0.2
14	1.5
14	1.2
16	0.6
17	3.1
18	1.9

Z score	Analysis result
$z \leq 2.0$	Acceptable
$2.0 < z < 3.0$	Warning signal
$z \geq 3.0$	Unacceptable

Conclusions

Conclusions

- Preparatory phase needs to be carefully designed
  - DTMs present
  - Sending of the sample
- Radiochemical analyses are similar with small differences
- Assigned value
  - all results were taken into the robust mean analysis
  - possible to make a sub selection of the results – would the results differ?
- Results will be published in NKS website DTM Decom final report and as a peer reviewed publication
- DTM Decom II on activated concrete on 2020 applied

Acknowledgements and references

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- Radiochemical analysis references

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beyond

the obvious

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