DTM-Decom II - Intercomparison exercise in analysis of DTM in decommissioning waste

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Abstract

An intercomparison exercise was carried out for difficult to measure radionuclides in activated concrete samples. The results were analysed accorging to ISO 13528 standard. The performance assessment was carried out using z score. Report includes an overview of the radioanalytical procedures, preliminary and final results, and preformance assessments.

Key words

Decommissioning, Difficult-to-measure radionuclides, intercomparison, activated concrete

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Final Report from the NKS-B DTM-Decom II activity

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1. Introduction

Analysis of decommissioning waste is challenged by the difficult-to-measure (DTM) radionuclides. The difficulties begin in the sampling phase due to representativeness and integrity of the sample. For example, large amounts of material, such as biological shield concrete, may be available but its heterogeneity can cause problems. The radiochemical analysis of DTM is challenged by other interfering radionuclides and often also the digestion of the material. Therefore, collaborative discussions and knowledge sharing between radioanalytical laboratories on the radiochemical analysis of DTM have been carried out in the proposed three-year NKS project of DTM analysis in decommissioning waste. The first year of DTM Decom I project focused on DTM analysis of activated steel [Leskinen et al. 2020b, 2020c]. The second year, namely DTM Decom II, was dedicated to DTM analysis of activated concrete. The main focus was on the DTM analysis of Fe-55, Ni-63, H-3, and C-14 whereas analysis of Ca-41, Cl-36, Eu-152, and Co-60 were optional. This report presents the references used in the DTM analysis of activated concrete, overview of the radiochemical methods, measurement results and statistical analysis of the results. Third year of the DTM analysis in decommissioning waste is proposed to focus on DTM analysis of spent ion exchange resin (DTM Decom III, funding decision pending).

2. Overview of DTM Decom II

The project began with a kickoff meeting in which the studied activated concrete was introduced and the main and optional DTMs for analysis were decided. The main DTMs of interest were chosen to be Fe-55, Ni-63, H-3 and C-14. Ca-41 and Cl-36 were optional DTMs and Eu-152 and Co-60 were optional gamma emitters. Also a survey of the current capabilities of the participating laboratories was carried out (Table 1). The analysis time span from June to October 2020, when a preliminary meeting was held in order to discuss the difficulties in the DTM analysis. Aftewards, partners had the possibility to re-evaluate their results and carry out further experiments until November when the final meeting was held. The final results are presented in this report.

Table 1. Capabilities of the participating laboratories on analysis of DTMs in activated concrete in the beginning of the project

Affiliation	Readiness of DTM analysis
VTT	National project on going for analysis of H-3, C-14, C-41, Fe-55 and Ni-63 in activated concrete
IFE Kjeller	Method under development for analysis of Ni-63 and Fe-55 in activated concrete.
DTU	Methods for determination of H-3, C-14, Cl-36, Ca-41, Fe-55, Ni-63, Mo-93, Tc-99, I-129, Cs-135 and actinides are ready to be used, the method of Cs-41 is mainly for concrete, but the methods of other radionuclides are used for all types of nuclear samples, and also for environmental samples. The speciation analysis methods for H-3, C-14, Tc-99 and I-129 are also ready to be used.
CEA	Routine analysis for H-3, C-14, Fe-55, Ni-63, Cl-36 and Ca-41 in radioactive concretes. CEA has routine analysis for radioactive liquids and concretes with low and intermediate level of radioactivity.
HU	Participant in an on-going national project, where HY will determine 41-Ca, 55-Fe and 63-Ni from an activated concrete.
Cyclife	Routine analysis for C-14 in concrete samples. H-3, Fe-55, Ni-63 and Cl-36 in concrete under development.
Fortum	Routine capabilities include Ni-63 and Fe-55 measurements from spent resin, evaporator waste and swipe samples. Method is also found to be suitable for analysis in stainless steel from NPPs with sample pretreatment different than for the routine analysis.
IFE Halden	Method under development for analysis of Ni-63 and Fe-55 in activated concrete.

3. Preparation, homogeneity and sending of the samples

3.1. Sample preparation

A large amount of activated concrete core (biological shield) was drilled and the powder was mixed prior to division to eight 20 g samples (Figure 1). As seen in Figure 1, the 20 g of powdered samples exhibited initially different volumes. However, packing of the powdered concrete was carried out in order to establish proper geometry information for the ISOCS measurements (sample height). The measured dose rate of each sample did not differ from background.

A preliminary measurement results for Ca, Fe and Ni contents in a representative inactive biological shield concrete was provided to the partners (approximately Ca 90 mg/g, Fe 20 mg/g and Ni < 1 mg/g) prior to the analysis phase. The results represented the studied material giving an order of magnitudes of the stable elements in the concrete.

Figure 1. Examples of studied samples in a liquid scintillation vials (20 g)

3.2. Homogeneity and sending of the samples

Each sample was measured twice by placing them on top of an HPGe detector of an ISOCS (In-Situ Object Counting System). The same measurement geometry was ensured by placing the sample carefully in the centre of the detector. The efficiency calibrations were carried out using Geometry composer. Initially, the homogeneity was determined by calculating the relative standard deviation of the Eu-152 results (Figure 2). As the RSD was 1.7%, the samples were considered to be homogenous.

According to the ISO13528 standard, the homogeneity can be assessed using Equation 1. Therefore, s_s was calculated from sample averages, between-test-portion ranges, general average, standard deviation of sample averages, within-sample deviation and between-sample standard deviation using the Figure 2 results. The Equation 1 was true when the robust standard deviation of participant results were used as σ_{pt} (see chapter 8.7). Therefore, the samples were homogenous also according to the ISO standard.

$$s_s \leq 0.3\sigma_{pt} \tag{1}$$

Where
s_s = between-sample standard deviation
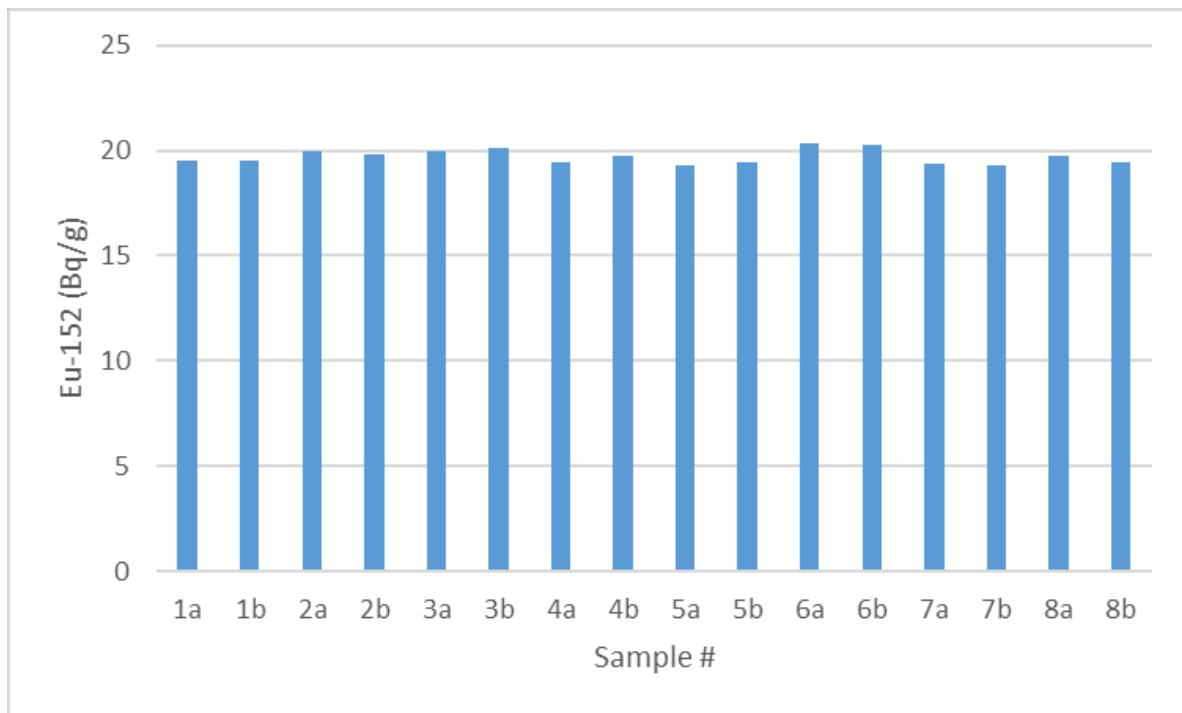σ_{pt} = robust standard deviation of participant results

Figure 2. Eu-152 activity concentrations in the eight activated concrete samples measured twice (a and b) at VTT

4. Radiochemical analysis

Participants carried out the radiochemical analyses based on either internal or published procedures [Gautier et al, 2015, 2020; Eichrom Method 2014; Ervanne 2009; Hou, 2005, 2005b, 2018; Hou et al., 2005a, 2005b, 2007; Itoh et al., 2002; Leskinen et al., 2020a; Nottoli et al., 2013, Triskem international method 2013]. The procedures had similar steps, which are summarised in following subsections.

Radiochemical analysis began with decomposition of the solid matrix which was carried out using different acid mixtures on a hot plate or in a microwave oven. The carriers and hold back carriers were added if needed. The acid digestions on a hot plate were:
- Acid leaching with conc. HCl and HNO_3
- *Aqua regia* refluxed in 190 °C for 2.5 hours, residue filtered
- Acid leaching using 8 M HNO_3 followed by *aqua regia*
- HNO_3, HF and $HClO_4$ mixture followed by HNO_3 and $HClO_4$ treatment
- 9M HCl, several HF cycles, mixture HNO_3, HCl and HF

The acid digestions using microwave oven were:
- Conc. HNO_3, HF and HCl in 220 °C for 30 min followed by evaporation
- Conc. HNO_3, HCl and HF followed by evaporation and treatment with HNO_3

4.1. Radiochemical analysis of Fe-55 and Ni-63

Majority of the laboratories carried out hydroxide precipitation with NaOH or NH_4OH in order to precipitate Fe and Ni from the solution prior to Fe and Ni separation using anion exchange resin. One laboratory precipitated and removed AgCl prior to their TRU resin (Eichrom Technologies) separation of Fe and Ni. One laboratory carried out anion exchange resin separation of Fe and Ni straight after acid digestion. Purified Fe fractions were evaporated to

dryness and the residue dissolved into 1M H_3PO_4 and measured using LSC. All partners further purified Ni fraction with Ni resin (Eichrom Technologies) once or twice. The purified Ni fractions were evaporated to lower volumes and measured using LSC. The efficiencies of Fe-55 and Ni-63 LSC measurements were determined using elaborated quench curves and TDRC technique. The yields were determined by measurement of stable Ni and Fe using UV-Vis, ICP-OES, ICP-MS, MP-AES and standard addition. In one case for Fe measurement, the yield was estimated to be 90%.

4.2. Radiochemical analysis of H-3 and C-14

The H-3 and C-14 analysis were carried out using thermal oxidation e.g. a Pyrolyser or an Oxidiser. Due to low amount of C-14 giving below limit of detection results using the thermal oxidation, one laboratory carried out the C-14 analysis using a closed system on a heating mantle. The sample was acid digested in a closed system in which CO_2 was released and trapped into CarboSorb or CarbonTrap. The H-3 and C-14 samples were measured using LSC. The measurement efficiencies were determined using standard solutions for quench correction or TDCR technique. The yields were experimental estimations.

4.3. Radiochemical analysis of Ca-41

Three laboratories carried out the analysis of Ca-41 which was listed as an optional DTM. The procedures contained sequential precipitations of Ca as carbonates and hydroxides. One partner utilised heating of the solution (95-98 °C, 1 h) in the first carbonate precipitation after initial removal of transit elements as hydroxides at pH 8-9. One laboratory used oxalate precipitation instead of carbonate precipitation. Separation of the supernatant and precipitates were carried out using centrifugation. After the final hydroxide precipitation, the residue was either dissolved into HCl, evaporated to dryness ($CaCl_2$), dissolved in water (3-4 ml) and mixed with liquid scintillation cocktail or the precipitate was dissolved in 4 M HCl and the pH of the solution was raised to 6-7 prior to mixing with liquid scintillation cocktail. The yield of Ca-41 was estimated by ICP-OES or MP-AES measurement of stable Ca and Ca-41 was measured using LSC.

4.4 Radiochemical analysis of Cl-36

Two laboratories carried out the analysis of Cl-36 which was listed as an optional DTM. The release of Cl-36 from the concrete was carried out with acid leaching with 8M HNO_3 or with combustion using a Pyrolyser. In the first case, chloride in the leachate was separated by AgCl precipitation followed by an anion exchange chromatographic purification. The separated chloride in NH_4Cl solution was mixed with scintillation cocktail. In the second case, the released chlorine trapped in a trapping solution (6 mM Na_2CO_3, method under development) was separated using AgCl precipitation, purified from silver using anion exchange resin similarly to the first case.

5. Analysis of Eu-152 and Co-60

Seven laboratories carried out the analysis of gamma emitters which were listed as optional gamma emitters. Majority of the analysis were carried out in solid form either in plastic or glass LSC vial or on a petri dish. All laboratories used high purity Germanium detectors placing the sample on top of the detector. Efficiency calibrations were carried out using calibration solutions with LVis (Gamma vision) with EFFTRAN coincidence correction, ISOCS,

LabSOCS or dual polynomial fitting. One participant utilised efficiency corrections based on experience due to lack of efficiency calibration for the LSC vial geometry.

6. Methodology

Statistical analysis of the results was carried out using the ISO 13528 standard similarly to DTM Decom project I [1-2]. The activated concrete studied was not a reference material and thus a robust statistical method was utilised for development of assigned value based on the participant's results. Robust mean and robust standard deviation were calculated using Algorithm A, which transforms the original data by a process called winsorization. This method provided alternative estimators of mean and standard deviation. Algorithm A is robust for outliers, when the expected proportion of outliers is less than 20%.

Performance assessment was carried out using z score. Z score (Eq. 2) is a recommended method in cases when participant's results are used for the calculation of assigned value. In cases where the robust standard deviation is large, another value for σ_{pt} can be used so that the results that are not fit for purpose will receive an action signal. The intercomparison exercise organiser can decide the value. In cases where the robust standard deviation was large ($1\sigma > 20\%$), the uncertainty of the assigned value (Eq. 3) was used as σ_{pt}. The analysis results with z score were marked as acceptable when $z \leq 2.0$, a warning signal was given for results with $2.0 < z < 3.0$, and results were unacceptable for $z \geq 3.0$.

$$z_i = (x_i - x_{pt}) / \sigma_{pt} \tag{2}$$

Where
x_{pt} = the assigned value
σ_{pt} = standard deviation for the proficiency assessment

$$u(x_{pt}) = 1.25 \times s^* / p^{0,5} \tag{3}$$

Where
s^* = robust standard deviation of the results
p = number of samples

7. Calculation of uncertainty and limit of detection

The participants used a variety of methods to calculate the measurement uncertainties. Some participants utilised only LSC counting uncertainties, since they were considered to be the main source of uncertainty. Some participants utilised some or all uncertainties originating from different steps of the analytical procedures e.g. LSC and yield measurement uncertainties and uncertainties of the digestion step, pipetting, weighting etc. In cases when the measured activities are low, such as in this project, emphasis was recommended to be given also for the blank measurements.

Also the limit of detection calculations varied among the participants. The participants utilised Currie's method, ISO 11929-1:2019 standard, French standards (NF M60-322 and NF M60-317) and estimations based on 3 times of the blank uncertainty in consideration of counting efficiency and chemical recovery.

8. Measurement results and statistical analysis

Table 2 summarises the different approaches taken for estimation or measurement of completeness of the acid digestions. The acid digestions were reported to be complete in several cases (except of silica residue) whereas in some cases down to 60% completeness of acid digestion was reported. Two participants carried out Ca, Fe and Ni analysis in the acid digested solutions (Table 3).

Table 2. Estimated completeness of acid digestion, elemental acid digestion yields and addition of Ca, Fe and Ni carriers

Sample #	Estimated completeness of the acid digestion (%)	Elemental acid digestion yield (%), measured/estimated (m/e)	Addition of carriers
1	100%	Ca	no
		Fe - not taken into consideration	3.5 mg
		Ni- not taken into consideration	1.5 mg
2	<100%, silica residue	Ca	No
		Fe 75-90% (e)	2 mg / 1 g concrete sample
		Ni 75-90% (e)	4 mg / 1 g concrete sample
3	Estimated to be 100%	Ca	no
		Fe - not taken into consideration	no
		Ni - not taken into consideration	0.05 mg
4	85%	Ca	
		Fe 71% (e from Ni)	no
		Ni 71% (m)	2 mg
5		Ca	
		Fe	
		Ni	
6	100%, silica residue	Ca 100%(m)	no
		Fe 100%(m)	no
		Ni < LOD (m)	2 mg
7	60% was dissolved	Ca 36%(m)	200 mg
		Fe 30%(m)	no
		Ni <LOD (m)	2 mg
8	100%, silica residue	Ca not analysed	no
		Fe 100%(e)	4 mg
		Ni 100%(e)	2 mg

Table 3.Original Ca, Fe and Ni composition in activated concrete

Sample #	Ca (mg/g) ± 2σ	Fe (mg/g) ± 2σ	Ni (mg/g) ± 2σ
4	51.2±10.2	20.8±4.2 (estimated from Ni yield)	0.0193±0.006
6	71.4±10.1	18.9±2.8	<LOD
Preliminary information on inactive concrete	90	20	<1

8.1. Fe-55 results

In total, 13 Fe-55 analysis results were submitted (Table 4) and 7 entries were above LOD. The minimum sample size to produce results above LOD was 3 g. However, the results above LOD varied significantly (0.112 - 8.1 Bq/g) and therefore, statistical analysis was not carried out.
The main reason for the variation was estimated to originate from the high amount of stable Fe in the concrete and acid digestion yield estimations (see Table 2 and 3). Additionally, sample 3 LSC measurements may have suffered from luminescence, quenching and spectral interferences. Luminescence can be minimised by keeping the sample in LSC cocktail in dark at least over night before measurement. The effect of quenching to counting efficiency can be overcome by carrying out the measurement with standard addition. The large uncertainty in sample 7 was also most likely caused by quenching and low activity.

Table 4. Sample numbers, size, yield, and activity of Fe-55 results.

Sample #	Sample size (g)	Yield (%)	Fe-55 activity (Bq/g)
1	3	90	0.37±0.02
1	3	95	0.34±0.02
1	3.5	101	0.35±0.02
2	10	64	1.59±0.94
3	5	90% (estimated)	8.1±0.2
4	5	83	<0.344
5	10		0.112±0.035
6	0.6	13	<0.5
6	0.6	18	<0.4
6	0.6	19	<0.4
7	10	57	2.6±4.1
8	0.5	32	<0.5
8	0.5	53	<0.3

8.2. Ni-63 results

In total, 13 Ni-63 analysis results were submitted (Table 5) and 3 entries were above LOD. The minimum amount of sample to produce measurable activity was 5 g. The low yield in sample 7 was caused by burning of the sample during evaporation causing possible loss of the analyte

and quenching. 10 iterations with Algorithm A were carried out and the assigned value for the Ni-63 activity concentration was calculated to be 0.967 ± 0.267 Bq/g (2σ). The assigned value is affected by the low number of entries but it was considered to fit for purpose. The robust standard deviation of the assigned value was 27.1% and therefore standard uncertainty of assigned value was utilised in the z score calculations. The results in table 5 show, that all the entries were in acceptable range.
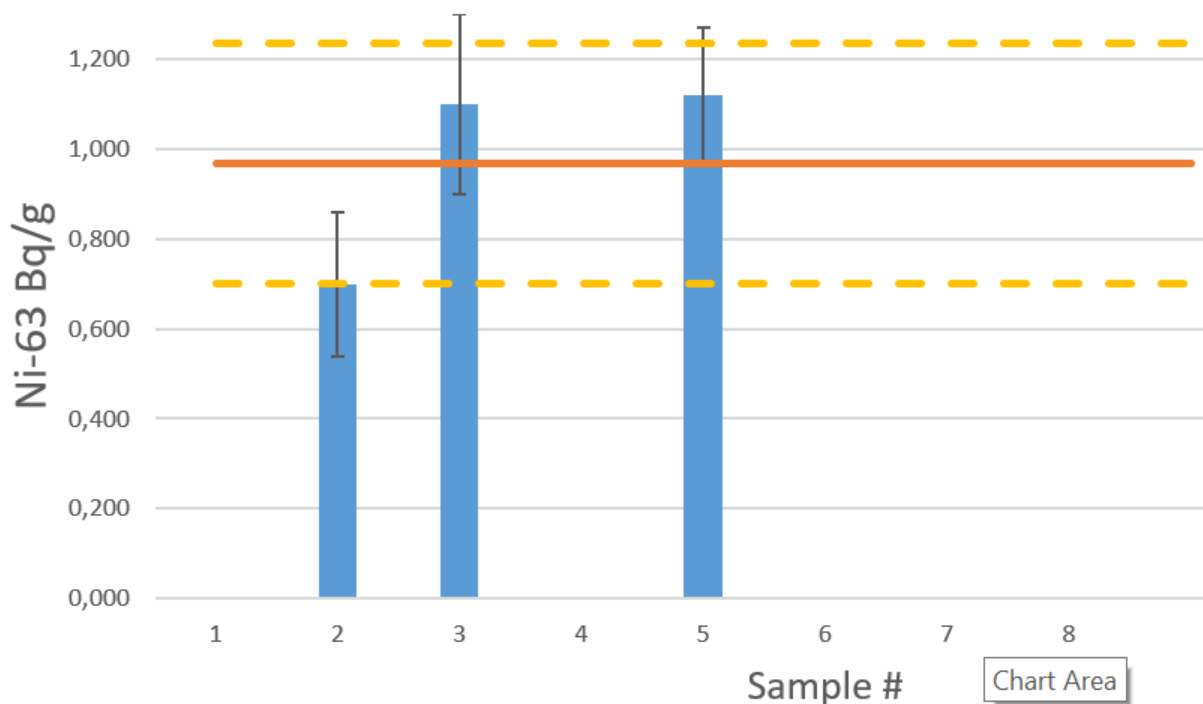

Figure 4. Ni-63 results in activated concrete samples and assigned value with 2σ uncertainties.

Table 5. Sample numbers, size, yield, activity and z scores of Ni-63 results.

Sample #	Sample size (g)	Yield (%)	Ni-63 activity (Bq/g)	z score
1	3	24	<0.1	-
1	3	83	<0.1	-
1	3.5	90	<0.1	-
2	10	24	0.70±0.16	2.0
3	5	99	1.1±0.2	1.0
4	5	30	<0.311	-
5	10		1.12±0.15	1.1
6	0.6	114	<0.6	-
6	0.6	102	<0.6	-
6	0.6	101	<0.6	-
7	10	77	<0.45	-
8	0.5	87	<0.09	-
8	0.5	85	<0.09	-

8.3. H-3 results

In total, 5 H-3 analysis results were submitted (Table 6). The assigned value for the H-3 activity concentration was calculated to be 54.9 ± 3.5 Bq/g (2σ). The robust standard deviation of the

assigned value was low (6.3%) and it was used in the z score calculations (Table 6). The results show that all the results were in acceptable range.
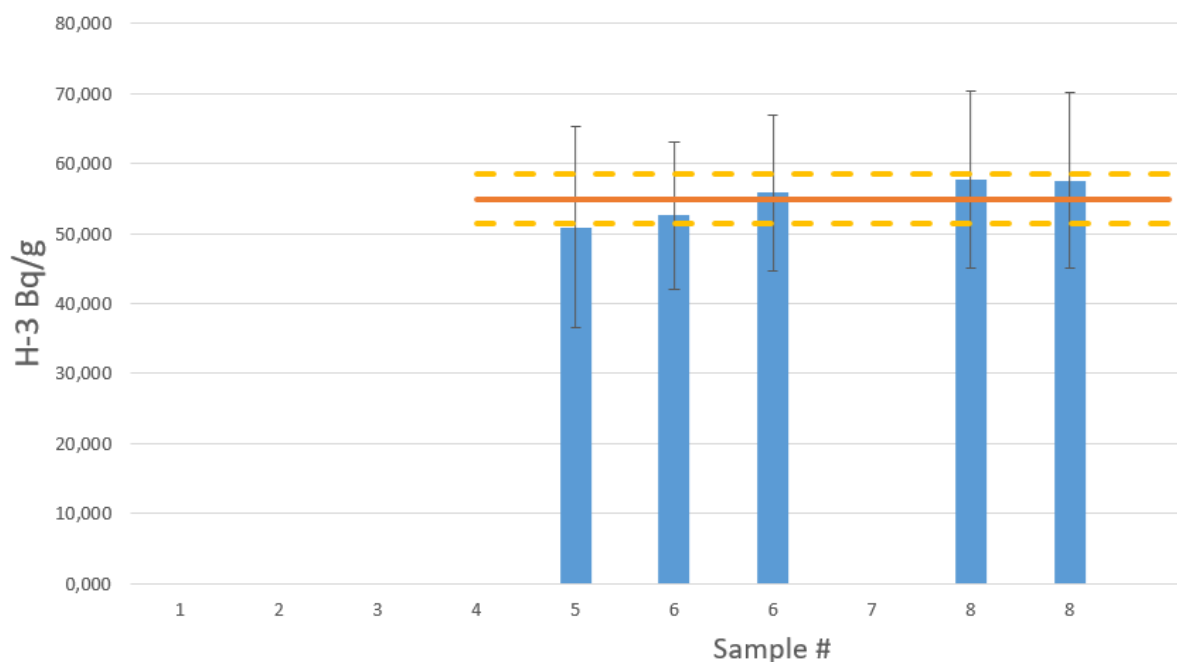

Figure 5. H-3 results in activated concrete samples and assigned value with 2σ uncertainties.

Table 6. Sample numbers, size, yield, activity and z scores of H-3 results.

Sample #	Sample size (g)	Yield (%)	H-3 activity (Bq/g)	z score
5	0.5		50.9 ±14.3	1.2
6	5	90	52.6 ±10.5	0.7
6	1	90	55.8 ±11.2	0.3
8	1	76	57.7 ±12.6	0.8
8	1	76	57.6 ±12.5	0.8

8.4. C-14 results

In total, 5 C-14 analysis results were submitted (Table 6). As the results show, 4 out of 5 results were below limit of detection. Therefore, statistical analysis of the results was not possible. Only utilisation of traditional acid digestion was able to produce results. However, more entries would be needed to verify the results as samples 6 and 8 below LOD were estimated to have 100% yields and twice to 10 times the amount of sample compared to sample 5.

Table 6. Sample numbers, size, yield, and activity of C-14 results.

Sample #	Sample size (g)	Yield (%)	C-14 activity (Bq/g)
5	0.5		0.072 ± 0.011
6	1	100	< 0.2
6	5	100	< 0.04
8	1	100	< 2.5
8	1	100	< 2.5

8.5. Cl-36 results

In total, 2 Cl-36 analysis results were submitted (Table 7) and only 1 entry was above LOD. Therefore statistical analysis of the results was not possible. The results show that Cl-36 activity concentration was measurable when 10 g of sample was used and below 0.4 Bq/g in 2 g sample size. The results also show a significant difference in the yields. In the case of sample 8, the method development was on going where as sample 5 was analysed with routine method.

Table 7. Sample numbers, size, yield, activity and z scores of Cl-36 results.

Sample #	Sample size (g)	Yield (%)	Cl-36 activity (Bq/g)
5	10	93-98	0.006 ± 0.001
8	2	5	<0.4

8.6. Ca-41 results

In total, 6 Ca-41 analysis were carried out (Table 8), but no results above LOD were submitted. Significant LSC spectral interference was observed for sample 5 and samples 6 suffered from formation of white color in the sample and liquid scintillation cocktail. There was a recommendation made in the preliminary meeting to inhibit white color formation by dissolving the final Ca precipitate in HCl and completely remove the acid with evaporation. The formed $CaCl_2$ is easy to dissolve in water and color should not appear. Also sample 7 suffered from significant quenching.

Table 8. Sample numbers, size, activity and z scores of Ca-41 results.

Sample #	Sample size (g)	Yield (%)	Ca-41 activity (Bq/g)
5	10	>93	Spectral interference
6	0.6	34	<0.3
6	0.6	24	<0.4
6	0.6	24	<0.4
6	1.8	33	<0.07
7	10	68	<0.5

8.7 Eu-152 results

In total, 7 Eu-152 analysis results were submitted prior to the final meeting (Table 9, Figure 9). The assigned value for the Eu-152 activity concentration was calculated to be 21.0 ± 1.7 Bq/g (2σ). The robust standard deviation of the assigned value was low (8.3%) and it was used in the z score calculations. One additional entry (sample 3) was submitted after the final meeting and it was not included in the assigned value determination. The z score results show that only one result is in unacceptable range ($z \geq 3$) and all the others in acceptable range ($z \leq 2$).
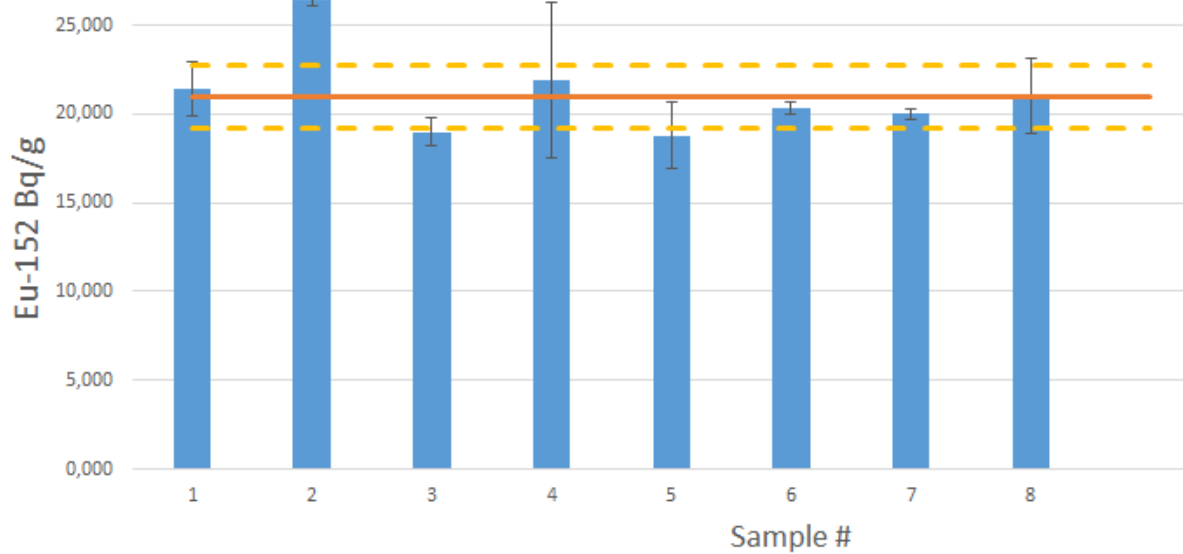
Figure 9. Eu-152 results in activated concrete samples and assigned value with 2σ uncertainties.

Table 9. Sample numbers, size, activity and z scores of Eu-152 results.

Sample #	Sample size (g)	Eu-152 activity (Bq/g)	z score
1	20	21.4±1.5	0.2
2	2	26.4±0.3	3.1
3	20	19.0±0.7	1.2
4	16	21.9±4.4	0.5
5	12	18.8±1.9	1.3
6	20	20.3±0.2	0.4
7	18	20.0±0.3	0.6
8	20	21.0±2.1	0.0

8.8. Co-60 results

In total, 7 Co-60 analysis results were submitted prior to final meeting (Table 10, Figure 10). The assigned value for the Co-60 activity concentration was calculated to be 0.262 ± 0.048 Bq/g (2σ). The robust standard deviation of the assigned value was below 20% (18.4%) and it was used in the z score calculations. Two additional entries (sample 2 and 3) were submitted after the final meeting and they was not included in the assigned value determination. The z score results show that all the results were in acceptable range.
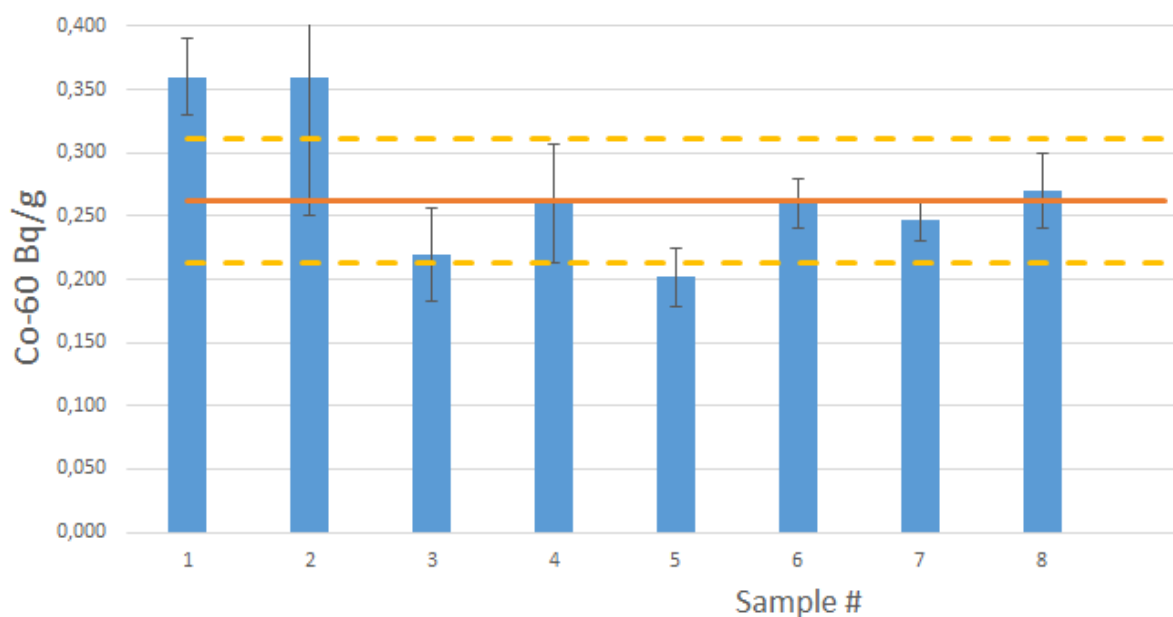
Figure 10. Co-60 results in activated concrete samples and assigned value with 2σ uncertainties.

Table 10. Sample numbers, size, activity and z scores of Co-60 results.

Sample #	Sample size (g)	Co-60 activity (Bq/g)	z score
1	20	0.36±0.03	2.0
2	2	0.36±0.11	2.0
3	20	0.22±0.04	0.9
4	16	0.26±0.047	0.0
5	12	0.020±0.002	1.2
6	20	0.26±0.01	0.0
7	18	0.247±0.017	0.3
8	20	0.27±0.03	0.2

9. Conclusions

DTM analyses were carried out for eight homogenous activated concrete samples. The focus was in Fe-55, Ni-63, H-3 and C-14 analysis, whereas Ca-41 and Cl-36 were optional. Additionally, analysis of gamma emitters Eu-152 and Co-60 was optional. The results were analysed according to the ISO 13528 standard when applicable. The assigned value, to which results were compared, was calculated from participant's results. The performance was assessed using z score which indicates result's deviance from the assigned value.

The Fe-55 results were affected by the low solubility (solubilisation) and high stable Fe content in the activated concrete. The combination of incomplete acid digestion and unknown original content of Fe in the acid digestion solution caused significant variance in the results and statistical analysis of the results was not carried out. Therefore, it can be concluded that in the case of low solubility matrices, the acid digestion yield and original concentration of stable analyte in the acid digestion solution are important parameters in calculation of radiochemical yield and consequently radiochemical yield correction of the activity results.

Contrary to analysis of activated steel in DTM Decom I, the Ni-63 analysis in activated concrete was not interfered by Co-60 due to its low activity concentration. Additionally, low stable Ni content in the original sample did not affect the yield calculations contrary to Fe-55 analysis. Even though the majority of the submitted results were below LOD, the statistical analysis was carried out for 3 Ni-63 entries resulting to assigned value of 0.967 ± 0.267 Bq/g (2σ) and all the z score values were in acceptable range.

The H-3 results were produced using thermal oxidation and the assigned value from 5 entries was calculated to be 54.9 ± 3.5 Bq/g (2σ). The analysis of H-3 can be affected by the efficiency of its release from the matrix and capture in the absorption solution. However, the results show excellent consistency e.g. low robust standard deviation of the assigned value (6.3%) and all the results were in acceptable range. Therefore, it can be concluded that the thermal oxidation methods utilised in this project were powerful tools for H-3 analysis in activated concrete.

The effectiveness of thermal oxidation in C-14 analysis was not exhibited due to its low activity concentration. Only utilisation of traditional acid digestion in a closed system was able to produce measurable results. However, discrepancies were observed with the submitted results since up to 5 g samples with 100% yields were not able to produce results above LOD whereas traditional acid digestion produced results for only 0.5 g sample. Therefore, further studies should be carried out in order to verify that the thermal oxidation methods release 100% of C-14 from the activated concrete. The C-14 yields in the sorption solutions are determined using spiked samples and as such, the speciation is different compared to activated concrete and can have an effect on the release. On the other hand, the result produced with traditional acid digestion may have been affected by memory effect, for example, due to very low activity. As a conclusion, more studies should be carried out, since uncertainties in C-14 analysis arise from effective release of the analyte from the solid matrix, oxidation of carbon to CO_2, effective trapping of CO_2 in absorption solution, and yield determination. Preparation of in-house spiked concretes can be a way to investigate the C-14 yield better.

The analysis of optional DTM Cl-36 was carried out by 2 laboratories. Cl-36 is one of the main volatile DTMs in decommissioning waste in addition to H-3 and C-14, and therefore its analysis has similar difficulties as mentioned in previous paragraph. In addition to release and trapping, the radiochemical procedures included also precipitation and ion exchange purifications making the Cl-36 analysis lengthy and prone to yield loss. However, the results show that high yields are possible when routine capabilities have been obtained and down to mBq/g activity concentrations are measurable.

The analysis of optional DTM Ca-41 was carried out by 3 laboratories. The analyses were affected by either spectral interferences or significant quenching. As such, further studies would be needed in assessment of the results.

The main gamma emitters Eu-152 and Co-60, which were optional, were analysed by all laboratories. The results showed good consistency for Eu-152 analysis based on the low robust standard deviations of the assigned values which were 8.3% whereas there was more variation in the Co-60 results with 18.4% robust standard deviation of the assigned value. The difference is most likely caused by orders of magnitude difference in activity concentrations of Eu-152 and Co-60.

As a conclusion, the DTM Decom II project further strengthened the collaboration between the participating laboratories and increased their capabilities in DTM determinations. Discussions

were carried out during the project analysis phase and collective information sharing was carried out in the preliminary meeting, which was held a month before the final meeting. The discussions in the preliminary meeting focused on the overview of the radioanalytical methods, difficulties in the analysis and recommendations. Therefore, the participants were able to carry out final adjustments prior to the final meeting. Additionally, against all odds, some laboratories were able to recruit students. Similarly to DTM Decom I, DTM Decom II produced interesting set of results and they will be further analysed and discussed in a peer reviewed publication together with modelling results.

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11. References

Currie, L. A., (1968). Limits for qualitative detection and quantitative determination. Application to radiochemistry. Anal Chem 40(3): 586-593

Eichrom Method (2014) Nickel-63/59 in water, No NIW01 analytical procedure revision 1.3

Ervanne, H., Hakanen, M., Lehto, J., (2009) Determination of 45Ca and γ-emitting radionuclides in concrete from a nuclear power plant. Radiochim Acta 97:631-636

Gautier, C., Laporte, E., Lambrot, G., Giuliani, M., Colin, C., Bubendorff, J., Crozet, M., Mougel, C., (2020) Accurate measurement of ^{55}Fe in radioactive waste. J. Radioanal. Nucl Chem 326:591-601

Gautier, C., Colin, C., Garcia, C., (2015) A comparative study using liquid scintillation counting to determine ^{63}Ni in low and intermediate level radioactive waste, J. Radioanal. Nucl. Chem., 308:261-270

Hou X.L., (2005) Determination of ^{14}C and ^{3}H in Reactor Graphite and Concrete for Decommission, Appl Radiat Isotop, 2005, 62:871-882

Hou X.L., (2005b) Radiochemical determination of ^{41}Ca in reactor concrete for decommissioning, Radiochim Acta, 93:611-617

Hou, X., (2018) NKS-B RadWorkshop Risø October, Analytical procedure for simultaneous determination of ^{63}Ni and ^{55}Fe

Hou, X., Østergaard L.F., Nielsen S.P., (2005a) Determination of ^{63}Ni and ^{55}Fe in nuclear waste samples using radiochemical separation and liquid scintillation counting, Anal Chim Acta 535(1-2): 297-307.

Hou, X.L., Østergaard L.F., Nielsen S.P., (2005b) Determination of ^{63}Ni and ^{55}Fe in nuclear waste and environmental samples, Anal Chim Acta, 535:297-307

Hou, X.L., Østergaard L.F., Nielsen S.P., (2007). Determination of ^{36}Cl in Nuclear Waste from Reactor Decommissioning, Anal Chem, 79:3126-3134

Itoh, M., Watanabe, K., Hatakeyama, M., Tachibana, M., (2002) Determination of ^{41}Ca in biological-shield concrete by low-energy X-ray spectrometry, Anal Bioanal Chem 372:532-536

International Standard ISO 11929-1:2019, Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation – Fundamentals and application – Part 1: Elementary applications

International Standard ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison.

Leskinen, A., Salminen-Paatero, S., Räty, A., Tanhua-Tyrkkö, M., Iso-Markku, T., Puukko, E., (2020a) Determination of ^{14}C, ^{55}Fe, ^{63}Ni and gamma emitters in activated RPV steel samples - a comparison between calculations and experimental analysis, J Radioanal Nucl Chem 323:399-413

Leskinen, A., Tanhua-Tyrkkö, M., Kekki, T., Salminen-Paatero, S., Zhang, W., Hou, X., Stenberg Bruzell, F., Suutari, T., Kangas, S., Rautio, S., Wendel, C., Bourgeaux-Goget, M., Stordal, S., Fichet, P., Gautier, C., (2020b) NKS-429 report ISBN 978-87-7893-519-9

Leskinen, A., Salminen-Paatero, S., Gautier, C., Räty, A., Tanhua-Tyrkkö, M., Fichet, P., Kekki, T., Zhang, W., Bubendorff, J., Laporte, E., Lambrot, G., Brennetot, R., (2020c) Intercomparison exercise on difficult to measure radionuclides in activated steel: statistical analysis of radiocanalytical results and activation calculations, J Radioanal Nucl Chem, 324:1303-1316

Nottoli, E., Bourles, D., Bienvenu, P., Labet, A., Arnold, M., Bertaux, M., (2013) Accurate determination of ^{41}Ca concentrations in spent resins from the nuclear industry by accelerator Mass spectrometry, Appl Rad Isot 82:340-346

Triskem International method, (2013) Cl-36/I-129 separation, TKI – CL01 – V-1.4_EN.

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Abstract max. 2000 characters	An intercomparison exercise was carried out for difficult to measure radionuclides in activated concrete samples. The results were analysed according to the ISO 13528 standard. The performance assessment was carried out using z score. Report includes an overview of the radioanalytical procedures, preliminary and final results, and performance assessments.