



Development of ^3H , ^{14}C , ^{41}Ca , ^{55}Fe , ^{63}Ni radiochemical analysis methods in activated concrete samples

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Received: 15 March 2021 / Accepted: 21 October 2021 / Published online: 21 November 2021
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Abstract

Development of ^3H , ^{14}C , ^{41}Ca , ^{55}Fe and ^{63}Ni radiochemical analysis methods were carried out independently by two laboratories using both inactivate and activated concrete samples. Two preliminary radioanalytical procedures for the non-volatile radionuclides (^{41}Ca , ^{55}Fe , ^{63}Ni) and one Thermal oxidation method for the volatile radionuclides (^3H , ^{14}C) were developed. The difficulties in the method development and analysis of results are discussed.

Keywords Characterisation of decommissioning waste · Activated concrete · Biological shield · Difficult to measure

Introduction

Radiochemical analysis of Difficult To Measure radionuclides (herein referenced as DTM) in decommissioning waste has been a challenge for decades. DTMs are a general term for alpha and beta emitters, which require their quantitative extraction from the matrix and purification from other radionuclides. Destructive analysis techniques are needed for the determination of DTMs such as ^3H , ^{14}C , ^{41}Ca , ^{55}Fe and ^{63}Ni in solid decommissioning waste. In general, the radionuclides of interest are first separated from the matrix, then separated and purified from other radionuclides and, finally, measured using liquid scintillation counting (LSC). Other measurement techniques (e.g., X-ray, proportional counters, and mass spectrometry) are available but not as often utilised [1]. Due to the long separation and purification processes, the yields of the analytes of interest are corrected in the end of the procedure by using analytical measurement techniques. Also, standard addition method, in which radioactive standard is added and analysed, can be used. ^3H and ^{14}C yields are determined experimentally using standard solutions, because utilisation of corresponding stable

elements (e.g., stable ^{56}Fe for ^{55}Fe) is not viable due to the difficulties of ^1H and ^{12}C analysis.

One of the most important material in decommissioning projects is concrete, because contaminated and activated concretes are a major source of radioactive waste volume. These two types of concretes differ in their nuclide vector due to the source of radionuclides. The contaminated concretes can contain variety of radionuclides depending on the origin. For example, the contaminated concrete can originate from a waste silo, into which laboratories working on variety of radionuclides have collected their contaminated wastewaters or from a floor of a dedicated radiochemistry laboratory, in which only specific radionuclides have been handled. In the first case, continuous contamination can be expected whereas in the second case, the contamination can be unevenly distributed. In activated concrete, the radionuclide vector depends on the original chemical composition of the concrete, irradiation history and distance from the irradiation source. Additionally, the activated concrete can be divided to heavy and normal concrete. Heavy concrete mainly consists of BaSO_4 and silicates giving the material high absorption capacity for gamma radiation i.e., shielding properties are increased compared to normal concrete [2]. In this case, the heavy concrete contains higher amounts of Ba, which activates to gamma emitting ^{133}Ba whereas in normal concrete, there is relatively more Ca, which activates to ^{41}Ca decaying with electron capture. Therefore, complete separation of ^{133}Ba from the ^{41}Ca fraction is especially important when activated heavy concrete is analysed. Additionally, acid digestion even with HF cannot completely decompose

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heavy concrete [2]. The concrete can be also a mixture of contaminated and activated concrete and as such, the different types of concretes can require different approaches in the sample collection and analysis. For example, tritiated water (HTO) contaminated structures require special consideration regarding the volatility of ^3H during sampling whereas high temperatures are needed in ^3H analysis of activated concrete, in which ^3H is partly strongly bound in the lattice structures [3, 4].

One challenge in determining DTMs from concrete is sample digestion, which depends on the particular concrete composition and scope of the study, i.e., whether acid digestion gives adequately dissolved sample releasing the isotopes of interest into solution, or if total dissolution of the sample, including silicates, is required. Both acid digestion and alkaline fusion have benefits and drawbacks and therefore, it is not always clear, which one is the better option for the particular purpose [5]. Sometimes the choice of dissolution method is based on familiarity, safety, easiness, availability and time resources. Additionally, almost quantitative dissolution can be enough, even though some more efficient method would exist. A variety of alkaline fusion methods exist for a complete dissolution of, e.g., geological, environmental and nuclear decommissioning samples. These methods utilise sodium hydroxide [6, 7], lithium borate [8, 9], sodium peroxide [10, 11] and similar alkaline compounds in different mixtures together with high temperature (most often over 600 °C) for complete destruction of even resistant silica minerals. In traditional methods, alkaline fusion is carried out in crucibles which are manually placed in and out of the oven. Manual operation of the extremely hot and alkaline sample vessels causes a health and safety concern for the workers. However, sophisticated and safe instruments have been developed for this purpose during the last decades, which minimise the safety hazards of sample treatment. Modern fusion techniques also enable automated fusion processes [9]. In this study, preliminary tests were carried out according to Ref. [2] using 3 g of NaOH and 1 g of Na_2CO_3 mixed with up to 5 g of concrete and fusing them in a crucible at 500–550 °C for 3–4 h. Dissolving of the fused cake was attempted with hot solution of 0.2 M Na_2CO_3 [2]. However, the tests were not successful resulting in dissolving of the porcelain crucible and therefore, different acid digestion methods were tested and their efficiency in dissolving Fe, Ni and Ca from the concrete is reported.

Second challenge in determination of DTMs is related to the above mentioned alkali fusion tests in which repeating of published method was not successful. In this case, fairly simple method was repeated several times, but the results were not satisfactory. The difficulties in repeating of published methods is also discussed in the experimental section of this paper as the two laboratories produced different results with utilisation on *aqua regia* in dissolving of the concrete.

Third challenge is the presence of interfering elements (i.e., radioactive and stable) depending on the matrix, contaminants and activated radionuclides. In the case of matrix, for example large amounts of stable Fe has been shown to cause difficulties in the analysis of activated steel samples due to the need of large amount of ion exchange resin in Fe and Ni separation [12]. The challenge has been addressed by carrying out the analysis with aliquots and preparatory precipitations and by increasing the necessary amount of ion exchange resin [12]. In the case of contaminants and activated radionuclides, the challenge is caused by the similar behaviour of the interfering radionuclides with the analyte of interest. In the case of steel, one of the main interfering radionuclides is ^{60}Co in ^{63}Ni analysis as Co easily follows Ni [13]. This challenge was addressed by utilisation of method by Hazan and Korkisch [13, 14] or with two Ni-resin separations [13]. In this study, the studied concrete was known to contain high amounts of Fe whereas its activity concentrations were known to be low according to activation calculations.

The third challenge can be encountered in the measurement phase. Especially low energy DTMs, such as ^{55}Fe and ^{41}Ca , which decay with electron capture, suffer from quenching in the LSC measurement. Quenching can be lowered with selection of the chemical composition of the purified fractions, e.g., 1 M H_3PO_4 for ^{55}Fe [13]. Additionally, low activity concentration requiring large amount of sample can cause quenching due to large amounts of stable elements in the ^{41}Ca fraction as shown in this study with analysis of 10 g of activated concrete.

In a nutshell, this paper presents the development of three preliminary radiochemical analysis methods for the determination of ^3H , ^{14}C , ^{41}Ca , ^{55}Fe , and ^{63}Ni in activated concrete. The activated concrete originated from the biological shield concrete of FiR1 TRIGA Mark II type research reactor in Finland. The radiochemical analysis methods were first tested with inactive FiR1 biological shield concrete and then modified for activated FiR1 biological shield concrete analysis. Acid digestion of the concrete followed by precipitations, ion exchange and extraction chromatography column separations were utilised for the measurement of ^{41}Ca , ^{55}Fe and ^{63}Ni . The volatile ^3H and ^{14}C were analysed using the thermal oxidation method. The encountered difficulties in the DTM analyses (e.g., solubility, interfering radionuclides, quenching) are discussed in the experimental section and the problem solving were carried out independently by the two laboratories. The consequences of the made decisions are also discussed.

FiR 1 biological shield concrete

The on-going characterisation efforts of FiR1 TRIGA Mark II type research reactor have been published previously [15–17]. The characterisation of the biological shield

concrete began with drilling of core samples from the non-activated part of the biological shield concrete in order to determine the chemical composition of major activating elements for activation calculations. The summary of relevant elements, which produced DTMs analysed in this study in FiR1 biological shield concrete, are presented in Table 1. The analysis results are an average of three replicate measurements with standard deviation. The second sampling campaign was carried out in a few years later order to collect activated core samples.

Experimental

Two radiochemical method developments (Method 1 and 2) for the analysis of ^{41}Ca , ^{55}Fe and ^{63}Ni were carried out independently by two laboratories, using inactive concrete samples and analysis of the purified fractions using elemental analysis. Method 3 was developed using inactive concrete samples spiked with liquid ^3H and ^{14}C standards. All the methods were different combinations of published articles [2–4, 12–14, 19–29]. The Methods 1 and 2 were both based on acid digestion, precipitations, ion exchange and extraction chromatography whereas the Method 3 was based on thermal oxidation using a combustion furnace. In all cases, the initial tested methods with inactive concrete required further developments for the radiochemical analysis of activated concrete. The procedures and actions taken are discussed in the subsections.

Sample preparation

A dedicated drilling configuration was developed for the sampling of the inactive and activated concrete cores. In brief, the sample was drilled with a hollow drill and the powdered concrete was collected. The powdered concrete had a small particle size, which was foreseen to enable more efficient complete destruction of the material in acid digestion due to larger surface area and also better release of volatile DTMs in the thermal oxidation technique as suggested in Ref [12].

Chemicals and equipment used in Method 1

All chemicals and reagents (Na_2CO_3 , NaOH , NH_4Citr i.e., ammonium citrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, CoCl_2) were of analytical grade or purer. Solutions were prepared into deionised water. Bases and acids were of analytical grade with concentration of 85 w-% H_3PO_4 , 25 w-% NH_4OH , 65 w-% HNO_3 , 36–38 w-% HCl , 72 w-% HClO_4 . Ion exchange columns were prepared using AG 1×4 50–100 mesh anion exchange resin (Bio-Rad) and extraction chromatography columns using Ni-Resin B 100–150 μm (Triskem International).

Orion 2 Star pH Benchtop pH meter combined with Ross combination pH electrode (Thermo Scientific) was calibrated with pH 4, 7 and 10 AVS TITRINORM buffer solutions.

^{41}Ca , ^{55}Fe and ^{63}Ni were analysed using HIDEX 300 SL liquid scintillation counter (later referred as Hidex) with TDCR (triple to double coincidence ratio) technology for the counting efficiency determinations. Samples were mixed with OptiPhase HiSafe 3 (later referred as HiSafe) liquid scintillation cocktail purchased from Perkin Elmer and let to stabilise at least 12 h before measurement in order to minimise luminescence. 1 ml or more of ^{41}Ca , ^{55}Fe and ^{63}Ni sample solutions were mixed with 10–20 ml of HiSafe.

Elemental analysis of the acid digested solution and radiochemical yield analyses were carried out using Agilent SVDV 5100 ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). The samples were diluted into 1% suprapur HNO_3 solution. Ca, Fe and Ni measurements were carried out using radial view with four different wavelengths in order to detect interference. Since all four wavelengths gave consistent results, the reported results were taken from the first selected line, namely 315.887 nm for Ca, 234.350 nm for Fe, and 216.555 nm for Ni. Ca, Fe, and Ni standard solutions were prepared using IV-Stock-4 (Inorganic Venture, USA) 1000 ppm multielement standard.

Table 1 ^3H , ^{14}C , ^{41}Ca , ^{55}Fe , and ^{63}Ni producing stable elements, their averaged concentrations (internal data), activation reactions and thermal cross sections [18] in inactive FiR1 biological shield concrete. The chemical analyses were carried out using ICP-MS, ICP-OES and CHN gas analyser technologies

Element	Averaged concentrations of inactive concrete subsamples (mg kg^{-1})	Activation reaction	Thermal activation cross section (barns)
Li	34 ± 6	$^6\text{Li}(n,\alpha)^3\text{H}$	936 ± 6
C	1910 ± 230	$^{13}\text{C}(n,\gamma)^{14}\text{C}$	$(0.9 \pm 0.05) \times 10^{-3}$
N	< 200	$^{14}\text{N}(n,p)^{14}\text{C}$	1.75 ± 0.05
Ca	$88,300 \pm 8300$	$^{40}\text{Ca}(n,\gamma)^{41}\text{Ca}$	0.22 ± 0.04
Fe	$22,300 \pm 1200$	$^{54}\text{Fe}(n,\gamma)^{55}\text{Fe}$	2.7 ± 0.4
Ni	< 50	$^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}$	15 ± 2

Chemicals and equipment used in Method 2

All used reagents were of analytical grade and reagent solutions were prepared in Milli-Q-water. Acid and base stock solutions were 85 w-% H_3PO_4 , 65 w-% HNO_3 , 36–38 w-% HCl , 25 w-% NH_4OH , and 48 w-% HF . Ion exchange chromatography resin Dowex 1 \times 4, 50–100 mesh (Sigma-Aldrich) and extraction chromatography resins TRU, 100–150 μm (Triskem International) and Ni resin, 100–150 μm (Triskem International) were used in radiochemical column separations.

The activity concentration of ^{41}Ca , ^{55}Fe , and ^{63}Ni in the final separated fractions was determined with Quantulus 1220 Ultra Low Level Liquid Scintillation Counter (Perkin-Elmer, previously Wallac). 18–19 ml of LSC cocktail Ultima Gold uLLT (Perkin-Elmer) was added to each sample (1–2 ml of sample solution), always having 20 ml of the total LSC sample volume. The sample mixture was shaken and kept 24 h inside the LSC counter before starting the measurement, to avoid interference from chemiluminescence. Counting efficiency of Quantulus 1220 for ^{55}Fe ($E_\beta = 231$ keV, $E_{x\text{-ray}} = 5.89$ keV), ^{63}Ni ($E_\beta = 66.95$ keV) and ^{41}Ca ($E_{x\text{-ray}} = 3.31$ keV) was determined by measuring quench series samples, prepared from ^3H ($E_\beta = 18.6$ keV), ^{63}Ni and ^{41}Ca standard solutions, respectively. The obtained efficiency/SQP plots were used for quench correction in activity calculation of the real samples.

Chemical yield of Ca, Fe, and Ni in the separated Fe and Ni fractions was determined with Agilent 4100 MP-AES (microwave plasma-atomic emission spectrometer). The selected emission wavelengths were 393.366 nm for Ca, 371.993 nm for Fe, and 345.846 nm for Ni. Calibration standard series for MP-AES were prepared from 1000 ppm Fe and Ni reference solutions (Romil) and from ERM-AE701 Ca standard solution (JRC, Geel, Belgium). All measurement samples were prepared by diluting the samples with 5% suprapur HNO_3 (v/v).

Chemicals and equipment used in Method 3

0.1 M HNO_3 trapping solution for ^3H was prepared into deionised water and 65 w-% HNO_3 (analytical grade). Carbo-Sorb® E (later referred as Carbosorb) CO_2 absorber for ^{14}C was purchased from Perkin Elmer. Expired ^3H and ^{14}C standards were dissolved into deionised water obtaining 70 000 dpm/ml and 42 000 dpm/ml solutions, respectively. These standards were considered to be fit for purpose as the calculated yield results were produced with comparison to original solutions.

The combustion furnace was a Pyrolyser-2 Trio (RAD-DEC International), which enabled simultaneous analysis of two samples. The Pyrolyser had three furnaces and the samples were placed in the first furnace. The temperature in first

furnace was controlled by the operator. The second furnace had been set by the manufacturer to heat to 500 °C as soon as the first furnace reached 500 °C. The second furnace ensured that volatile organic species were efficiently transferred into the catalyst zone, i.e., third furnace. The third furnace was pre-heated to 800 °C as set by the manufacturer. The catalyst (0.5% Pt-alumina) was placed in the third furnace in order to maximise the ^3H conversion to tritiated water (HTO) and ^{14}C to CO_2 . The HTO and CO_2 were trapped into 20 ml trapping solutions. In this study, 0.1 M HNO_3 and Carbosorb trapping solutions were used even though also 0.4 M NaOH for ^{14}C trapping was tested. Some evaporation occurred and therefore it was controlled with weighing the solutions before and after the heating cycle. The airflow (compressed air) was adjusted to 0.2–0.25 l min^{-1} and O_2 (industrial grade) 50:50 flow was added when the first furnace reached 500 °C while keeping the same flow rate as previously.

The same LSC and scintillation cocktail were used as in Method 1. 5 ml of ^3H and ^{14}C sample solutions were mixed with the liquid scintillation cocktail and let to stabilise at least 12 h. The recommended liquid scintillation cocktail for Carbosorb is Permafluor E+ by Perkin Elmer. However, HiSafe gave consistent results even though it occasionally formed a gel with Carbosorb.

Testing of Method 1 in inactive concrete and the radiochemical analysis of ^{41}Ca , ^{55}Fe and ^{63}Ni in activated concrete

The initial radiochemical Method 1 for the determination of ^{41}Ca , ^{55}Fe and ^{63}Ni was a combination of published articles [2, 12, 25, 26]. The procedure was based on 4 h acid leaching of the solid subsample (0.5 g) using 30 ml of conc. HCl and 10 ml of conc. HNO_3 , removal of the undissolved solid via filtering through a glass filter, and separation of Ca from metals (e.g., Fe and Ni) and transuranics using hydroxide precipitation [2]. Hold back carriers (4 mg Co) and carriers (Ca to 200 mg, Fe to 4 mg, Ni to 2 mg depending on the original content in the acid digested solution i.e., approximately 175 mg Ca, 2 mg Ni and no Fe) were added after acid digestion. Ca in the supernatant was further purified from other interfering radionuclides (e.g., Ba, Cs, Sr and Ra) using sequential precipitations and dissolving of the precipitate [2]. Fe and Ni were separated from each other and purified similarly to the Radioanalytical Method 1 in Ref [12] using AG ion exchange and Ni-resin.

The Method 1 was tested with three 0.5 g subsamples of the inactive concrete. The efficiency of the acid leaching to release the Ca, Fe and Ni from the solid matrix was determined by analysing the Ca, Fe and Ni concentrations in the acid leached solutions and comparing the results with the previously determined concentrations in Table 1. The results (M1a-c) in Table 2 show that the acid leaching

was able to release 50–60% of the original Ca content and 60–80% of the original Fe content. The Ni concentrations were below limit of the detection. Even though the solubility of the concrete was foreseen to be a major challenge, several references indicated that in the case of normal concrete (e.g., not heavy concrete), complete destruction of the matrix was not necessary since leaching in *aqua regia* was able to release more than 98% of the Ca [2]. As the measured results were contrary to this statement, Method 1 was modified in order to achieve complete destruction of the matrix using HNO₃, HF and HClO₄ acid mixture [25]. The change of acid digestion mixture from HNO₃ and HCl mixture to 5 ml conc. HNO₃, 5 ml conc. HF and 3 ml conc. HClO₄ and subsequent treatment with 5 ml conc. HNO₃ and 3 ml conc. HClO₄ mixture was successful as the yields in the acid digestion of 0.6 g activated concrete subsamples M1d-f was increased from 50 to 60% and 60–80% to 80–82% and 82–86% for Ca and Fe, respectively. The destruction of the matrix was considered to be complete even though small amount of solid silicates remained as the acid mixture was evaporated.

The yields in the purified Ca, Fe, and Ni fractions in the inactive (M1a-c) and activated (M1d-f) concrete subsamples are presented in Table 3. As the Ca yield results show, the sequential precipitations and dissolving of the Ca fraction ended up in low yields of less than 18% in the inactive concrete samples. Due to the easiness of sequential precipitations, almost the same method was continued also in the analysis of the activated concrete subsamples, the difference being longer reaction times in the precipitation steps. Even though the results in Table 2 show that Ca yields in the purified fractions of activated concrete were increased compared to the corresponding results using in

Table 3 Ca, Fe, and Ni yields in purified fractions of inactive and activated concrete samples using different methods. Uncertainties with coverage factor $k=2$ have been calculated with propagation of uncertainties taking into account uncertainty sources such as weighing, pipetting, and measurement technology

Concrete	Sample #	Ca yield \pm uncertainty (%)	Fe yield \pm uncertainty (%)	Ni yield \pm uncertainty (%)
Inactive	M1a	18 \pm 4	49 \pm 10	91 \pm 26
	M1b	16 \pm 4	48 \pm 10	89 \pm 26
	M1c	16 \pm 4	80 \pm 36	92 \pm 26
Activated	M1d	34 \pm 6	13 \pm 2	114 \pm 32
	M1e	24 \pm 4	18 \pm 4	102 \pm 30
	M1f	24 \pm 4	19 \pm 4	101 \pm 28
Inactive	M2a	61 \pm 4	29 \pm 2	104 \pm 5
	M2b	43 \pm 3	36 \pm 3	97 \pm 5
	M2c	56 \pm 4	34 \pm 3	92 \pm 5
Activated	M2e	90 \pm 5	57 \pm 6	82 \pm 7
	M2f	48 \pm 3	57 \pm 6	72 \pm 6

inactive concrete, the yields were still relatively low i.e., 24–34%.

The Fe yield results in the purified Fe fractions of inactive concrete were also relatively low (48–80%) most likely due to the high Fe content i.e., AG resin capacity for Fe had been breached. Therefore, the amount of AG resin was increased from two 10 g AG resin columns to one 30 g AG resin column in the analysis of the activated concrete. However, the change of two subsequent 10 g AG resins to one 30 g AG resin was not successful to increase the Fe yield in the purified fractions as the yields lowered from 48 to 80% to 13–19%.

Table 2 Fe and Ca yields in all acid digested solutions of inactive and activated concrete samples by different dissolution methods compared with Table 1. Uncertainties with coverage factor $k=2$ have been calculated with propagation of uncertainties taking into account uncertainty sources such as weighing, pipetting, and measurement technology

Concrete	Sample #	Mass (g)	Dissolution method	Fe yield \pm uncertainty (%)	Ca yield \pm uncertainty (%)
Inactive	M1a	0.5	40 ml of <i>aqua regia</i> , heating for 3 h	79 \pm 14	60 \pm 14
	M1b			62 \pm 12	47 \pm 12
	M1c			74 \pm 32	55 \pm 12
Activated	M1d	0.6	Heating with 5 ml HNO ₃ + 5 ml HF + 3 ml HClO ₄ \rightarrow 5 ml HNO ₃ + 3 ml HClO ₄ for ~ 1.5 h	86 \pm 13	80 \pm 11
	M1e			82 \pm 12	80 \pm 11
	M1f			86 \pm 13	82 \pm 12
Inactive	M2a	0.5	20 ml of <i>aqua regia</i> , heating for 4 h	106 \pm 9	85 \pm 6
	M2b			97 \pm 9	89 \pm 6
	M2c			104 \pm 10	94 \pm 7
Activated	M2d	10	Heating with 20 ml 9 M HCl for 30 min \rightarrow 15 \times 10 ml series of HF treatments \rightarrow 80 ml of mixture HNO ₃ :HCl:HF (10:8:2) for 3 h	54 \pm 6	60 \pm 6
	M2e			80 \pm 8	41 \pm 2

As discussed in previous publications [12, 14, 22, 27], purification of Ni from Co can be challenging. The yield results for Ni in inactive concrete subsamples show that about 90% of the Ni was carried over to the final purified Ni fraction. The above mentioned modifications (i.e., acids in acid digestion, longer reaction times in Ca precipitations, and amount of AG resin in Fe and Ni separation) were not targeted for Ni. However, the Ni yield was increased to near 100% in the activated concrete samples with the modifications. The final Method 1 utilised in the radiochemical analysis of the activated concrete samples is presented in Fig. 1.

In all the cases, the ^{41}Ca , ^{55}Fe , and ^{63}Ni activity concentrations in the active concrete subsamples M1d-f were below limits of detection (Table 4). The limits of detections were calculated using the Currie method [30]. In the Finnish regulations by the Radiation and Nuclear Safety Authority

[31], the free release limits for ^{55}Fe and ^{63}Ni are 1000 Bq g^{-1} and 10 Bq g^{-1} , respectively whereas there is no release limit given for ^{41}Ca . On the other hand, the free release limits for ^{45}Ca and ^{47}Ca are 100 Bq g^{-1} and 10 Bq g^{-1} , respectively. Therefore, it can be concluded that the provided results are well below the free release limits whereas scientifically speaking, the method could be tested further in order to increase the yield or larger sample size could be used in order to overcome the low yields. Larger sample size, however, can introduce further problems such as significantly higher amount of stable Fe in the samples complicating the AG resin separation as discussed in next sub-section.

LSC counting efficiencies for ^{41}Ca , ^{55}Fe , and ^{63}Ni by TDCR with CoreF correction (Hidex) are presented in Table 4. CoreF correction is a mathematical corrective function for deviations of TDCR at higher quench levels.

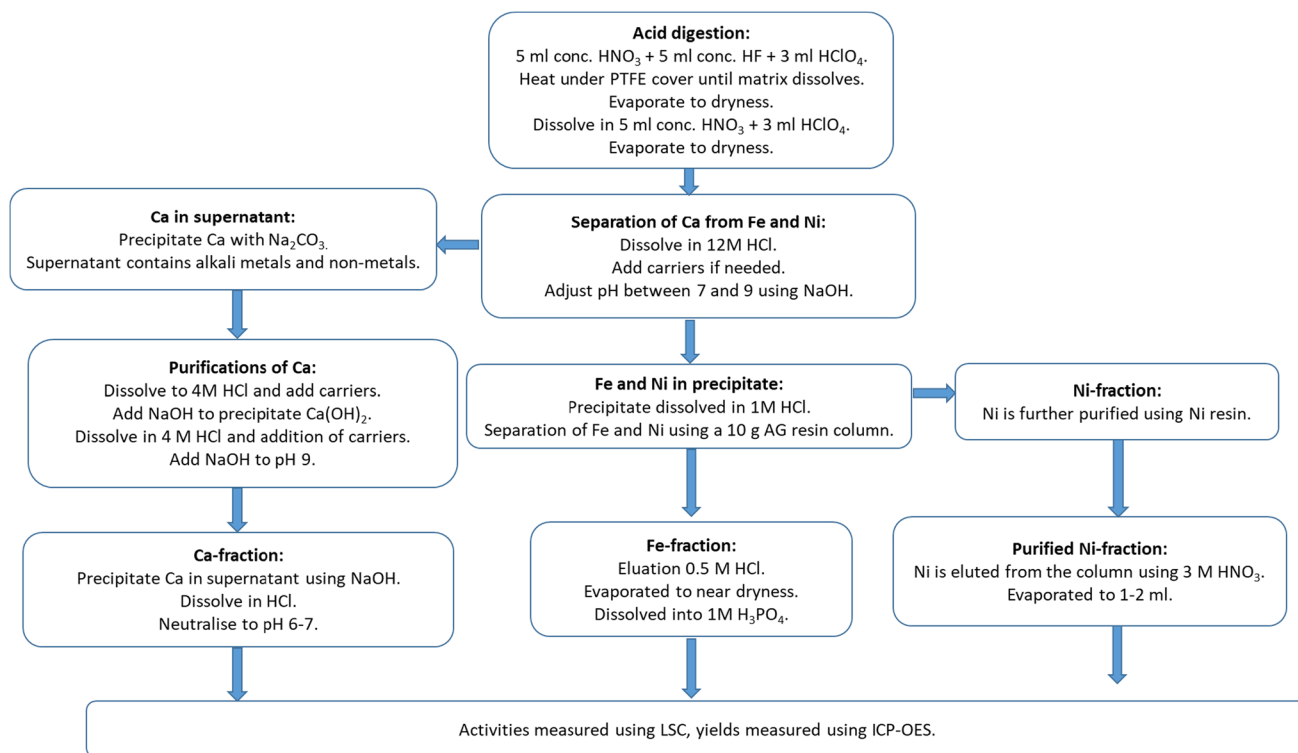


Fig. 1 Radioanalytical Method 1 for determination of ^{14}C , ^{55}Fe and ^{63}Ni in activated concrete

Table 4 Radiochemical analysis of ^{41}Ca , ^{55}Fe and ^{63}Ni in activated FiR1 concrete using different methods

Sample #	Mass (g)	^{41}Ca LSC efficiency	^{41}Ca (Bq g^{-1})	^{55}Fe LSC efficiency	^{55}Fe (Bq g^{-1})	^{63}Ni LSC efficiency	^{63}Ni (Bq g^{-1})	Efficiency determination
M1d	0.6	0.505	<0.3	0.649	<0.5	0.410	<0.06	TDCR with CoreF correction
M1e	0.6	0.513	<0.4	0.628	<0.4	0.384	<0.06	
M1f	0.6	0.317	<0.4	0.536	<0.4	0.441	<0.06	
M2e	10	0.021	<0.3	0.080	2.3 ± 3.7	0.68	<0.5	Eff/SQP
M2f	10	0.024	<0.3	0.066	2.9 ± 4.6	0.68	<0.4	

The CoreF corrections for ^{55}Fe and ^{63}Ni were provided by the manufacturer whereas lack of corresponding correction for ^{41}Ca resulted in use of CoreF correction of ^{55}Fe which similarly decays with electron capture. The obtained values had some variation among subsamples, from 0.317 to 0.649, and there was no clear difference between efficiency values for different radionuclides.

Testing of Method 2 in inactive concrete and the radiochemical analysis of ^{41}Ca , ^{55}Fe and ^{63}Ni in activated concrete

Method 2 was modified from previously published methods for separating Ca, Fe and Ni from each other and from disturbing elements by hydroxide and carbonate precipitations and extraction chromatography [2, 22–24, 28]. Three parallel subsamples of 0.5 g inactive concrete were used for experimenting the initial Method 2. 20 mL of *aqua regia* was added to each concrete sample and the samples were digested on a hot plate for four hours. The sample solutions were filtered and solution parts were evaporated to dryness. After treatment with 2 ml of conc. HCl, the evaporation residues were dissolved to 1 M HCl and Ni carrier (2 mg) was added to each sample. Small fractions were taken from the sample solution before and after addition of Ni carrier for MP-AES measurements. The results in Table 2 show that the sample dissolution procedure with *aqua regia* released 85–94% of Ca and >97% of Fe from the inactive concrete subsamples to the solution. The percentages were calculated similarly with Method 1, i.e., from the ratio of the determined concentrations in digestion solution to the previously determined reference values in Table 1. Concentration of Ni was below the detection limit in the subsamples of 0.5 g. Visually estimating, approximately half of the concrete was dissolved to acids during leaching. Although the dissolved amounts of Ca and Fe were satisfactorily high and the residual concrete contained probably mainly silicates, for the next tests with much higher sample masses of active concrete, a more efficient digestion method was sought. Therefore, sample dissolution method was changed from a single *aqua regia* digestion to a more extensive procedure. As discussed with Method 1, the activated concrete contained only low amounts of investigated radionuclides and for obtaining results exceeding detection limits, a large subsample mass was needed for the radiochemical analysis. The main reason for adjustments was much higher subsample amount (10 g) required for activated concrete, compared to small subsamples (0.5 g) used with inactive concrete. The concrete samples were first treated with 9 M HCl heating on a hot plate for 30 min, evaporated to dryness and a series of HF attacks (milliliters of HF was added to samples, heated and evaporated to dryness) was followed. The use of HF was expected to improve dissolution of residual silicates in

the concrete samples. Finally, the samples were digested with a mixture of $\text{HNO}_3\text{:HCl:HF}$ (10:8:2) for three hours on a hot plate and evaporated to dryness. Despite extensive leaching procedure, only ~60% of concrete was dissolved, the remaining 40% being chemically resistant silicates. The dissolved fraction might have been increased with even more HF treatment steps.

In the inactive concrete subsamples, Ca was separated from Fe and Ni in hydroxide precipitation and Ca fraction was further purified with carbonate co-precipitation and two different anion exchanges. Fe and Ni were separated from each other with TRU column separation and Ni fraction was further purified with Ni resin column. For later tests and analyses of the activated concrete, efficient purification cycles were planned in order to remove interfering radionuclides from the final purified fractions. In a previous study [24], Ca fractions were treated with (at least) three carbonate precipitations and 2–3 anion exchange column pairs in order to efficiently purify ^{41}Ca fraction. Additionally, based on previous experiences with activated steel containing higher concentration of ^{60}Co compared to concrete [13], Ni fractions of activated concrete would require at least two Ni resin column separations for decreasing the concentration of ^{60}Co to a tolerable level, concerning LSC measurement. Furthermore, the residual activity of ^{60}Co in LSC spectrum of ^{63}Ni (and ^{60}Co) could be taken into account by measuring exact activity of ^{60}Co from the LSC sample by gamma spectrometry [13].

The yields of Ca, Fe and Ni after chemical purification of inactive concrete samples M2a-c were 43–61% for Ca, 29–36% for Fe and 92–104% for Ni (Table 3). For Ni, the separation method can be considered successful, whereas for Fe and Ca did not work as well. Explanation for low Fe yield is the loss of Fe in TRU separation: part of Fe in the sample load solution did not bind to TRU resin and it was eluted within the Ni fraction. Fe content of the subsamples exceeded 3 mg of Fe which is considered being the upper tolerance limit of a regular (0.7 g of resin) TRU column for Fe [27]. Therefore, working with even larger sample masses, two options existed for maintaining efficient separation of Fe, Ni and Co from each other, and not exceeding the binding capacity of the resin i.e., (1) it would be possible to use significantly higher amount of TRU resin, or alternatively (2) use ion exchange instead of extraction chromatography for separating Fe, Ni and Co from each other.

The radiochemical separation procedure for analysis of the activated concrete was a combination of methods published by Eichrom [28] and Hou [32] for Fe and Ni and by Ervanne et al. [24] for Ca. For Ca, the analysis method was almost the same as with inactive concrete, but the carbonate precipitation was replaced with an oxalate precipitation, because for some reason carbonate precipitate did not form in the solutions of the activated concrete. Only one anion

exchange column cycle (first column purification in 8 M HCl and the second in 8 M HNO₃) was performed for Ca fractions, because based on gamma measurements, there was no ⁶⁰Co or other gamma emitters left in the Ca solutions after the first anion exchange cycle. For Fe and Ni analysis in activated concrete, it was decided to replace TRU column separation with Dowex 1×4 anion exchange column separation. Although it would have been possible to perform Fe/Ni/Co separation with a higher amount of TRU resin, it was more economical and less sensitive to column load capacity to use anion exchange resin instead.

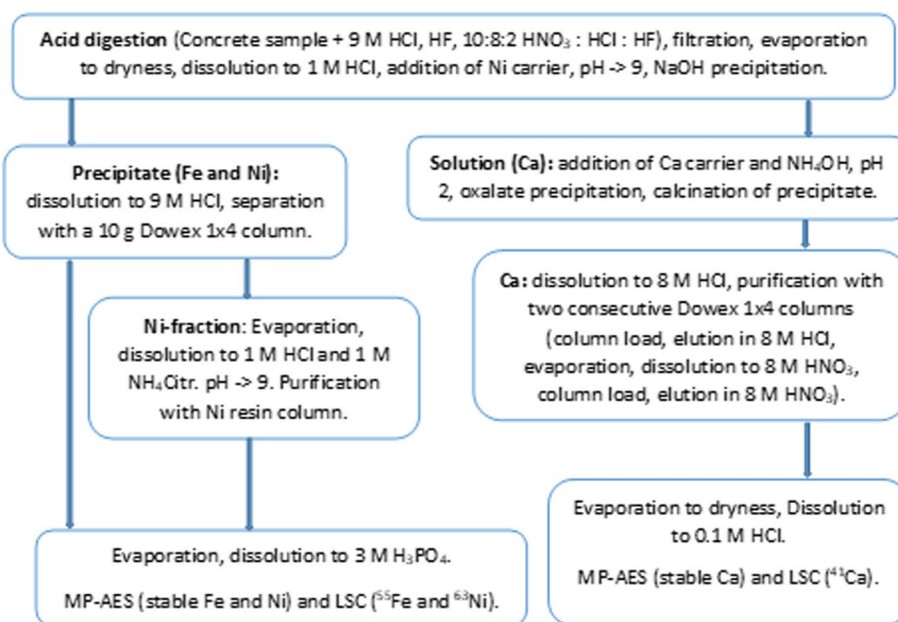
The yields of purified fractions in the activated concrete subsamples were 48 and 90% for Ca, 57% for Fe, 72 and 82% for Ni (Table 3). Compared with corresponding yields in inactive concrete, the yields for Ca and Fe were higher, and for Ni the yield was lower in activated concrete. The increase in the yield of Fe was due to replacement of TRU separation with inadequate resin amount with anion exchange separation. Based on testing of Method 2 with inactive concrete and its modification, few hours leaching with *aqua regia* produced adequate dissolution of concrete, concerning determination of ⁴¹Ca, ⁵⁵Fe, and ⁶³Ni. The final Method 2 utilised in the radiochemical analysis of the activated concrete samples is presented in Fig. 2.

The activity concentrations of ⁴¹Ca and ⁶³Ni in the activated concrete were below limit of the detection and the activity concentrations of ⁵⁵Fe were 2.3 ± 3.7 and 2.9 ± 4.6 Bq g⁻¹ (two sigma uncertainty) in the two subsamples (Table 4). Uncertainties of the activity concentration values for ⁵⁵Fe were high, due to low activity

concentration in the concrete (high statistical counting error of radioactivity) and quenching in LSC measurement, leading to decreased counting efficiency.

The LSC counting efficiencies for ⁴¹Ca, ⁵⁵Fe, and ⁶³Ni by E/SQP plotting (Quantulus) are presented in Table 4. The relationship between beta particle energy and detection efficiency of Quantulus is clearly seen as decreasing efficiency values with decreasing decay energy, from ⁶³Ni via ⁵⁵Fe to ⁴¹Ca. The counting efficiency for ⁵⁵Fe in two concrete samples containing 15 and 22 mg of stable Fe was 7 and 8%, respectively, whereas it was 32% in an unquenched standard sample. Even though the subsample mass was maximized in order to obtain radioactivity concentrations over detection limit, high concrete amount led to matrix-related quenching with all determined beta emitters, due to precipitation or colour in the samples. This was crucial in detecting ⁵⁵Fe and especially ⁴¹Ca, which decay by electron capture, having very weak Auger or x-ray emissions, 5.9 keV and 0.3–3.6 keV, respectively. The difference in counting efficiencies for these low energy betas obtained by Hidex (three photomultiplier tubes) and Quantulus (two photomultiplier tubes) is remarkable: Hidex had roughly tenfold efficiency for ⁵⁵Fe and ⁴¹Ca, compared to Quantulus. For ⁶³Ni having higher decay energy, the counting efficiencies of the two LSCs were at the same level. This observation indicates Hidex as an attractive option in determination of low energy beta emitters. On the other hand, for samples having very low activity content, Quantulus may be the only choice due to its generally lower background count rate.

Fig. 2 Radioanalytical Method 2 for determination of ¹⁴C, ⁵⁵Fe and ⁶³Ni in the activated concrete



Testing of Method 3 in inactive concrete and radiochemical analysis of ^3H and ^{14}C in activated concrete

The Method 3 tests using thermal oxidation were carried out using 100 mg of inactive concrete spiked with 100 μl of ^3H and ^{14}C standard solutions. Since some of the ^3H in activated concrete originates from Li, which can be tightly bound in the lattice, the temperature in the first furnace needed to reach high temperature of 900 $^\circ\text{C}$ [3, 4]. Therefore, a heating profile recommended in the manufacturer's additional training material was adjusted and the heating profile of the first furnace was set to increase 10 $^\circ\text{C min}^{-1}$ until 900 $^\circ\text{C}$ and stay at 900 $^\circ\text{C}$ for 90 min. 20 ml of 0.1 M HNO_3 trapping solution was used for the HTO trapping. Initial tests were carried out with 20 ml of 0.4 M NaOH and 20 ml of Carbosorb solutions for trapping of ^{14}C . The results showed that only 50% of the released ^{14}C was trapped by the 0.4 M NaOH whereas 100% was trapped with Carbosorb. Therefore, Carbosorb was used as the ^{14}C trapping solution. The trapping solutions were cooled with an ice block in order to lower evaporation. Evaporation was determined by measuring the initial and final weights. 5 ml of each trapping solutions were mixed with 10 ml of HiSafe and measured using LSC after stabilisation inside of Hidex at least for 12 h.

The Method 3 was able to provide consistent results for several spiked inactive concrete samples giving an approximate yield of 92% for ^3H and 115% for ^{14}C after evaporation correction. The evaporation rates for 0.1 M HNO_3 and Carbosorb trapping solutions were approximately 0.2 ml h^{-1} and 0.6 ml h^{-1} , respectively. Analysis time in the pyrolyser was approximately 3.5 h. The results suggested that some ^3H was carried either in or through the Carbosorb absorption solution. Additionally, the over 100% yield of ^{14}C suggested that either ^3H was absorbed into the Carbosorb or evaporation of Carbosorb did not cause decrease of ^{14}C . The ^{14}C spectra did not support the theory of ^3H absorption and additionally Carbosorb is specific for carbon. Therefore, an additional study was carried out in order to see if evaporation of Carbosorb also released ^{14}C . Four samples with 25 μl of ^{14}C standard solution were mixed with 5 ml of Carbosorb. First sample was closed with a cap in order to minimise evaporation whereas nitrogen gas flow was subjected into the 3 remaining samples in order to evaporate increasing amount of Carbosorb from the vials. In the end of the experiment approximately 8, 17 and 33% of solutions were evaporated. Afterwards 10 ml of HiSafe was added into all the samples and they were measured using LSC after at least 12 h stabilisation. The results showed that 100% of ^{14}C remained in the evaporation vials i.e., even though the Carbosorb evaporates, ^{14}C remains in the solution. Therefore, it was concluded that experimental yield for ^3H was 92% (with

evaporation correction) and for ^{14}C 100% (without evaporation correction). The ^{14}C activity concentration in the FiR1 activated concrete was below LOD whereas ^3H activity concentration was $43 \pm 13 \text{ Bq g}^{-1}$ calculated from 10 replicate measurements.

Since spiked samples have different ^3H and ^{14}C speciations compared to activated concrete, Method 3 was further studied with increasing amount of FiR1 activated concrete in order to establish linearity range. A linear relation with increasing amount of sample was expected until a plateau. The plateau was expected to represent a situation in which the volume of the sample blocks efficient release of the analytes or a situation in which the absorption solutions are saturated. The studied sample sizes varied from 100 mg to 5 g and the results showed linear correlation between yield corrected DPM and sample mass with R^2 0.9935. Linear range may be even higher but larger sample sizes were not studied due to the limited amount of sample.

In general, the radiochemical analysis of ^3H and ^{14}C using a pyrolyser was a straight forward process, but several parameters need to work optimally in order to produce reliable results. Firstly, the amount of sample needs to be tested. In case when consistent results are obtained using different amounts of sample, the results are more reliable. Secondly, the heating profile needs to be tested for the sample type. Especially high organic matter content in the sample requires slow increase of temperature in order to avoid uncontrolled combustion of the organic matter i.e., soot. Additionally, in cases when high temperatures are used, cooling time can be long limiting the analysis frequency to be only two samples per day. Thirdly, the flow rate should be constantly in the optimal flow rate range. Especially addition of O_2 as the first furnace reaches 500 $^\circ\text{C}$ requires good flow in order to oxidise ^3H and ^{14}C efficiently. Additionally, too low flow rate can lower the HTO and CO_2 to reach the trapping solutions and too high can push them through the solutions too quickly lowering the trapping percentage. Fourthly, the oxidative power of the catalyst is limited and change of the catalyst is recommended after every 15th analysis. However, the oxidative power is affected by the analysed samples and can be decreased towards last analysis. All these above mentioned parameters can occur separately or in different combinations making the radiochemical analysis of ^3H and ^{14}C challenging. The effects of these parameters would be detected if tracers could be used for the yield determination. However, use of tracers for ^3H and ^{14}C determinations is not possible and determination of an estimated yield needs to be carried out separately. Most often, such as in this study, spiked samples were used even though it was clear that the speciations of ^3H and ^{14}C in standard solutions are different to the speciations in activated concrete. Contaminated concrete would be more similar to spiked concrete.

Conclusions

Three radioanalytical methods were tested for determining volatile (^3H and ^{14}C) and non-volatile (^{41}Ca , ^{55}Fe and ^{63}Ni) beta emitters from activated concrete samples. Based on the first results with inactive concrete, the methods were further modified for improving their forthcoming performance with activated concrete samples. Comparison of Method 1 inactive and activated subsamples' yields for both Fe and Ca increased when complete destruction of the matrix was obtained. On the other hand, in comparison of Method 2, inactive and activated subsamples show significant decrease in Fe and Ca yields, which are most likely caused by the significantly higher amount of sample under digestion. Formation of CaF_2 from Ca in concrete and F in added HF is also possible in some extent, this would have decreased effect on Ca yield. Comparison of Method 1 and 2 in inactive concrete subsamples shows significantly different results even though both methods used same amount of sample, but different volumes of *aqua regia* and digestion time. On the other hand, digestion temperatures were not recorded. As the utilised Methods 1 and 2 did not significantly differ, the reason for better yields using Method 2 remained unknown emphasizing that even published methods can produce different results depending on the laboratory.

The radiochemical analyses of activated concrete suffered from low activities and color quenching in LSC. Both ^{41}Ca and ^{63}Ni activity concentrations were below limit of detection even in cases in which 10 g subsamples were analysed. ^{55}Fe activity concentrations were below limit of detection with 0.6 g subsamples and suffered from high uncertainties with 10 g subsamples. Out of the volatile DTMs, ^{14}C activity concentration was below limit of detection whereas consistent results were obtained for ^3H .

Later the same activated concrete material was analysed among wider group of laboratories and the obtained experiences and results are summarised in Refs. [33, 34]. Comparison of the results presented in this paper are well comparable with the results of the wider group of laboratories as no major difficulties were observed for ^3H analysis, thermal oxidation method was not able to provide ^{14}C results, major difficulties were encountered for ^{41}Ca (spectral interference and quenching) and ^{55}Fe (incomplete dissolution of matrix and yield correction) analyses, and ^{63}Ni analyses would have required minimum of 5 g subsamples and an LSC sample as colorless as possible, for obtaining results above limit of detection.

As a conclusion, all methods are potential starting points for analysing activated concrete, but further development is needed, e.g., for improving especially radiochemical yield of ^{41}Ca and overcome quenching problems

in LSC. The main problems originated from low solubility and low activity concentration of the activated concrete, then high sample mass was required for analysis, which in turn resulted in high amount of stable interfering elements. More results exceeding detection limit are needed in order to fully compare the methods with each other.

Acknowledgements The research was funded by KYT 2022 (Finnish Research Programme on Nuclear Waste Management 2019–2022). The authors would also like to thank VTT personnel and FiR1 decommissioning task force for their collaborative actions and provision of the studied material.

Funding Open Access funding provided by Technical Research Centre of Finland (VTT).

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