Annual Report 2024
RACEMAT / WP2

Radionuclides' transport in cementitious materials

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1. Research topic, background and motivation

1.1 Background and state-of-the-art

Low- and Intermediate Level Waste (LILW) from Finnish nuclear power plants (NPPs) operated by Fortum and TVO will be disposed in geological on-site repositories. LILW to be disposed of includes radioactive waste generated during operation and decommissioning phases. According to the Loviisa LILW Repository Safety Case Main Report (Nummi, 2018), the various radioactive wastes produced at the Loviisa NPP can be divided into operational waste, decommissioning waste and to spent nuclear fuel. Spent nuclear fuel is disposed in Olkiluoto repository but operational and decommissioning wastes are deposited in Loviisa LILW waste repository. The radioactivity originates from neutron activation (either directly or as fission products) in the reactor core and in the structures surrounding the core. The operational wastes are classified as liquid wastes or (solid) maintenance waste. The liquid wastes often include ion exchange resins from different filtering where they are used to remove impurities. They can also be boron and salt-containing evaporator condensates from processing drainage waters, or sludge and sediments from drainage waters as a result of precipitation and sedimentation of large particles. All the liquid wastes accumulated are stored at the liquid waste storage. Liquid waste that cannot be cleared from regulatory control needs to be immobilized for safe handling and deposition. The intermediate level wastes are solidified into concrete containers at the solidification plant prior to their disposal in order to produce a stable waste product that limits the radionuclide release. Low level liquid wastes are solidified into concrete in steel drums. In Olkiluoto NPP, wet or intermediate level waste in cast into bitumen but TVO is considering the change to cement as the immobilization medium (Kumpula, et al, 2022).

Besides the LILW material itself, the disposal concept includes various materials in the constructed structures and waste packages. LILW containers are often made of concrete and the waste caverns containing the solidified waste are lined with concrete, forming a concrete basin as in Loviisa, or a silo, as in Olkiluoto. The waste caverns are also planned to be backfilled with concrete upon closure. These engineered barrier systems are surrounded by bedrock, which acts as a natural barrier hindering radionuclide release. It is important to understand the evolution and potential interactions of these materials during the repository timescale. After the repository closure, the structure and evolution of waste material itself may affect the performance of the repository over long time scale. Concrete structures experience degradation over time due exposure to surrounding pore waters and the waste material can also degrade over time.

Concretes with different types of compositions are used depending on the specific purpose of the concrete structure. The different purposes might be the forming the concrete basin or silo structure of the waste cavern, acting as a waste container or part of it, as the waste immobilization material or as the cavern backfill material. Different recipes might be needed to build a sound structure lining the waste cavern or to contain for example ion exchange resin waste (Kotatkova, et al, 2017). Superplasticicers are used to improve workability of concrete and they are especially useful when the concrete is planned to be used as a backfill material and achieving even spreading and mixing is difficult due to cramped conditions or other limitations. A topic of considerable research interest is effect of organic compounds, such as superplasticicers, on the mobility of radionuclides (Young, 2012; Isaacs, et al, 2013). This change in mobility would manifest itself by changes in the diffusion coefficients and distribution coefficients of the concrete material. The transport and retention properties of cementitious materials can vary between different compositions and the values forming the basis for calculations should be preferably based on the similar compositions as used in the LILW repository setting to minimise uncertainty. Especially any changes in radionuclide mobility due to differing material compositions should be known in order to lessen conservatism in safety case calculations.

The radionuclide inventory of LILW is commonly composed of activation products, such as C-14, Cl-36, Ni-59 and Ni-63 and also uranium wastes. Other activation and fission products may also present, as well as the actinides and their progeny. Other nuclides however have a lower contribution to dose and release rates and hence their inventory estimates contain more margin with respect to long-term safety criteria. All these different elements have specific chemical interactions with the barrier systems. Bedrock retards significantly the transport of many radionuclides originating from uranium wastes, but has little known retarding effect for C-14 and Cl-36, and only slight effect for Ni-59 and Ni-63. For these radionuclides the retardation of transport is mainly based on the engineered barriers, such as concretes.

The transport of the radionuclides present in LILW in cementitious materials have been studied with batch sorption experiments to investigate the sorption processes and with diffusion experiments to study the diffusion behaviour. Batch sorption experiments have shown that the retention properties of C-14 depend strongly on whether it is in an organic or inorganic form. Inorganic species of C-14 can adsorb to positive sites or precipitate as carbonates but organic C-14-species tend to often only weakly adsorb on surfaces (Evans, 2008). There are however differences between organic compounds, ranging from very weak bonding to a small amount of selective binding for formate, presumably into ettringite (Wieland, et al, 2016). Differing cement matrices were also shown to have very different diffusion coefficients for C-14-acetate species. Cl-36 sorbs into cement by forming chloride and oxychloride compounds. In some conditions it can form Friedel's and Kuzel's salts. Sorption, or secondary phase formation, depends on the type of binder and the nature of the cations in the pore solution (Evans, 2008). The retention of Cl-36 by cementitious backfill has been studied by (Van Es, et al., 2015). They

found out that the breakthrough of Cl-36 is dependent of chloride concentration and sorption like process takes place. The spatial distribution of the Cl-36 has been in NVRB cement paste (Van Es, et al., 2015) and in CEMV-based concrete (Macé et al, 2019) by storage phosphor screen autoradiography (SPA). Nickel has been found to sorb considerably into cement phases, especially into hydroxides, with coprecipation or surface complexation as a possible mechanism. Nickel species also tend to have low solubility at high pH. This together with sorption leads to immobilisation in cement (Evans, 2008). This feature retards the diffusion of nickel isotopes until the concrete barrier degrades (Nummi, 2018).

Our research group has long been involved in studies of the interactions of cementitious materials with the repository environment especially in co-operation with the French Nuclear Safety Institute (IRSN). The mineralogical and microstructural evolution Portland cement paste in contact with argillite was studied especially with regard to diffusion and porosity properties (Lalan, et al, 2019). The changes brought by exposure of Low-pH cement to calcareous and argillite pore water were also a focus of another study (Neji, et al, 2022). Our work also contributed to reactive transport modelling of cement model system under degradation (Seigneur, et al, 2017). Our research group has also pioneered the use of novel autoradiographic techniques to study the diffusion of radionuclides and porous space where the diffusion takes place. C-14-PMMA autoradiography was originally developed to study the porosity of low porosity crystalline rock (Siitari-Kauppi, 2002) but has since been successfully used to study high porosity materials such sedimentary rock and cementitious materials (Sammaljärvi, 2017; Lalan, et al, 2019; Neji, et al, 2022). During KYT2022-funded RASK project we developed methods to study and image the transport of radionuclides in concretes and their interfaces with crystalline rock.

1.2 Objectives and expected results

In this study we investigated the diffusion and retention behaviour of long-term safety relevant radionuclides in cementitious materials found specifically in LILW repository. We focus on the main concrete structures found in LILW repository: the concrete-based source term, the waste cavern concrete and the backfill concrete that will be found around the waste packages in considerable volume. The results from this study will then increase the robustness of the safety case calculations for LILW repositories and build confidence. This study will build on the existing know-how and experience in our research group. These methods can be applied in the scope of this work and would constitute a validation of those techniques for LILW repository-relevant concrete types and safety case-important radionuclides. Some of the radionuclides planned to be studied in this project, such as Ni-63, haven't been studied extensively with autoradiography in the context of cementitious materials in a repository environment.

The experiments performed in the scope this research project produce several concrete results. The diffusion experiments will produce apparent and effective diffusion coefficients, and distribution coefficients for HTO, Cl-36 and Ni-63 in realistic concrete material environments. The coefficients produced for Ni-63 are also valid for another important isotope, Ni-59, as the isotopes have similar chemistry. This brings more certainty into estimating the retarding effect of the concrete on the diffusion of these radionuclides. The studies of the in situ solidification concrete samples will produce information on the spatial distributions and speciation of the radionuclide waste species. This information can be used to estimate the long-term behaviour of the waste and how the release happens into the next level of the engineered barrier system.

Overall the results from this research project will promote the safe use of nuclear energy by decreasing uncertainties associated with LILW disposal. Two article manuscripts can be produced based on this work; The first focusing on the through-diffusion experiments and the second focusing on the in situ material characterisation. In terms of human resources, the research project will produce new experts for the nuclear waste management field and helps to update and expand the expertise of senior researchers.

1.3 Exploitation of the results

The results can be applied in the LILW repository safety case calculations. While this study focuses on the behaviour of radionuclides' in pristine materials, the results can be used as a basis for studying the evolution of the concrete structures, considering the combined impact of various processes (see section 1.4) contributing to the concrete degradation over time scale of repository use. The study focuses on radionuclides identified as most important to the long-term safety. For the studied radionuclides, we can estimate the radionuclide release from solidification product, activated concrete, contaminated concrete. The results can be used as basis for estimating the long-term durability of the solidification product in relation to durability of concrete structures.

Radiation safety authorities will especially benefit from these results and can use them to evaluate LILW repository scheme. Additional end users are the power companies Fortum and TVO. They too will benefit from increased know-how of LILW repository-relevant radionuclide behaviour. The results can be applied as soon as the results are published in articles and annual reports and can be of use to international waste management organisations too.

Work package 2 (WP2), In situ waste material characterisation

1.4 Overall work plan

Samples containing immobilised ion exchange resin waste are studied to ascertain the distribution of activity in the immobilised waste material. The waste effluent is heterogeneous in composition, containing both anion and cation exchange resins in different amounts. We will therefore study samples from different immobilization batches to account for this heterogeneity, if possible. The 3D-structure of the immobilized waste material, or suitable mock-up, will be studied with XCT. Autoradiography will be used to characterise the spatial distribution of activity on centimetre scale. This characterisation will be complemented by XAS analysis to ascertain the chemical speciation of the immobilized radionuclides. Micrometre scale structural and elementary analysis could be with SEM/EDS, while nanometre scale structural analysis could be done with TEM/EDS at VTT.

1.5 Sample preparation

Samples of solidified waste products were prepared at Fortum during 2023 and arrived in August 2024. The sample weighs 5-6 kg and have diameter of 20 cm and height of 19 cm. The dose rate from sample surface is 100 µSv/h, while at 30 cm distance it is 5 µSv/h. The sample material contains the waste material (mostly spent ion exchange resins) and cement clinker without any rock aggregate. This causes the sample to be rather soft, requiring lengthy settling time. The sample was let to settle at least 28 days to attain compressive strength of at least 5 MPa, with the most common compressive strength value being around 15 MPa.

Inactive mock-up samples have also been prepared to develop safe methods for handling active waste material. Different cementitious materials and mock-up waste ratios were tested to produce suitable test samples for method development. Two cementitious based material were used; CEMII B-M (S-LL) cement and S100 Plus CEMI concrete mix (20 % CEMI by weight), with Dowex Marathon MSA anion exchange resin as the waste simulant. The compositions of the inactive mock-up samples are shown in Table 1.

Table 1 Inactive mock-up sample compositions.

	Component Ratios				
Sample code	**Cement/Concrete**	**Water**	**Waste**	**Water-Cement-ratio**	**Water-Solid-ratio**
CEMII cement (01)	0.72	0.28	0	0.39	0.39
CEMII cement (02)	0.67	0.20	0.13	0.25	0.30
CEMII cement (03)	0.66	0.25	0.09	0.37	0.33
CEMI concrete (01)	0.94	0.05		0.31	0.06
CEMI concrete (02)	0.82	0.09	0.09	0.54	0.09
CEMI concrete (03)	0.78	0.06	0.16	0.36	0.06

Following preparation of inactive mock-ups samples, we prepared also active mock-up waste samples containing only a single radioactive nuclide in preparation for investigating multi-nuclide samples.

1.6 Experimental methods and Results

As the work planned in WP2 involves multi-nuclide open source radioactive samples, it as decided to start with method development for sample handling and measurement methods. The overall workflow is detailed in Figure 1.

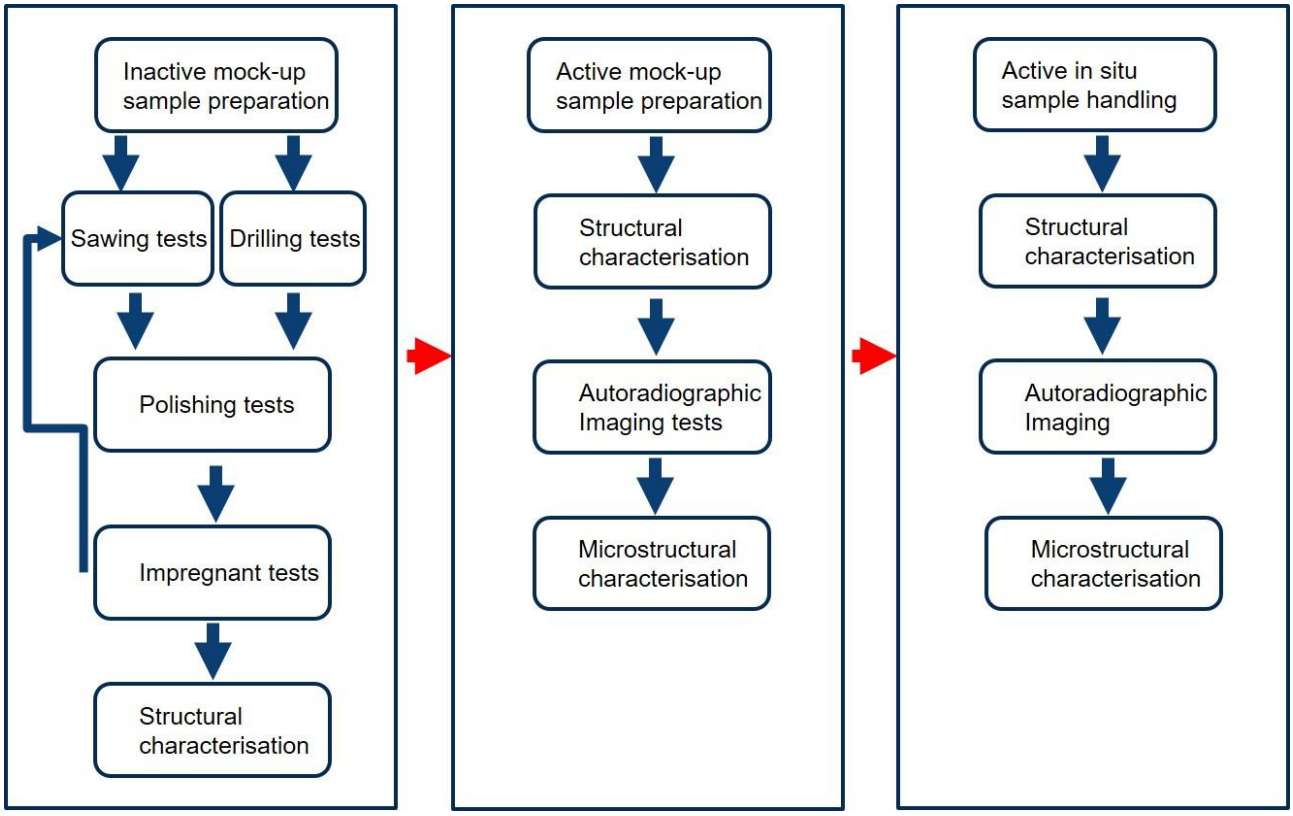

Figure 1 WP2 Workflow plan

1.6.1 Task 1 (T2.1), Structural analysis of solidified concrete waste

1.6.1.1 Summary of 2023

Concretes have been studied extensively with x-ray computed tomography (XCT). Concrete is an optimal sample material for XCT and the method has been used to study the structure and porosity of concrete and concrete-like materials (Solismaa et al., 2021, Niu et al., 2022). XCT analysis will be performed to obtain a 3D structure of the solidified concrete waste. 3D structural analysis will show whether the waste material is homogeneous and how the different structural features are distributed throughout the samples. A novel deep learning method will be used to more effectively combine the different methods to obtain 3D structural maps. This will guide the subsequent sample handling for autoradiography, microscopic techniques and X-ray-based analyses.

Different inactive mock-up samples were cast from both a CEMII-cement clinker and a CEMI-based concrete mix. Different waste loading ratios were tested, ranging from 0 to 16 % by weight. For 0 % waste loading the samples become solid to touch with 1 day of setting, while with higher waste loading the setting time had to be increased to 2 days. After setting, the samples were cured under a synthetic cement pore water solution for at least 28 days before further work. The sample integrity was checked during the curing time to see any signs of slow-setting structural changes. In all cases, the samples stayed intact throughout the curing period. After the curing period, sample handling tests were performed to evaluate material behaviour in sawing, drilling and polishing steps necessary for sample production for further analyses.

Drilling tests showed that the mock-up waste sample was pliable to drilling but care needs to be taken to prevent the sample material from spreading. The sample material flaked and chipped fairly easily during the drill core removal. The resin beads were found to be distributed quite evenly about the sample. In all stages of the handling it was noted that the resin beads could quite easily be dislodged from the material.

Sawing and polishing tests were performed on the different inactive mock-up samples to characterise possible differences in behaviour. The samples proved to be easy to saw but polishing easiness varied. Surface scans from different are shown in Figure 2. In comparison between 0% waste CEMII sample (Figure 2 A) and 9-13 % waste loading CEMII samples (Figure 2 B-C) the waste material contribution is easily visible. All of the CEMII-cement samples were easy to polish. It was noted that resin beads could become dislodged both during sawing and polishing. In the CEMI-based concrete samples the change in mechanical strength was considerable between 0 % loading (Figure 2 D) and 9-16 % loading (Figure 2 E-F). The increasing waste loading causes the material to be increasingly crumbly, causing a more uneven sawed surface. This in turn makes the polishing process more time-consuming as more time is needed to smooth out the surface. Similar pattern of resin bead dislodging was noted with CEMI-based concrete samples as well.

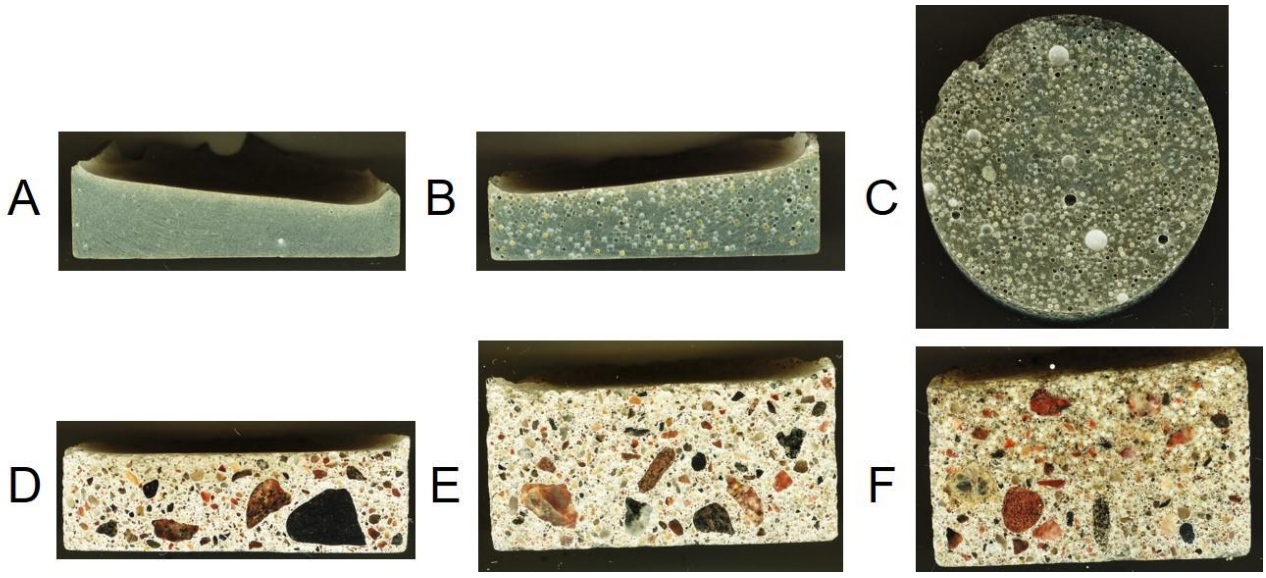

Figure 2 Sawing&Polishing tests. A: CEMII-cement sample with 0 % waste loading. B: CEMII-cement sample with 13 % waste loading. C: CEMII-cement sample from drill core with 9% waste loading. D: CEMI-based concrete sample with 0 % waste loading. E: CEMI-based concrete sample with 9 % waste loading. F: CEMI-based concrete sample with 16 % waste loading.

All in all, the drilling, sawing and polishing tests proved that the solidified waste material can be handled with available laboratory equipment. However the sample material is fairly fragile which can lead to generation of dust, chips, flakes and waste water. In active samples, these could cause the spread of activity, which must be prevented. In all parts of the sampled handling, it is important to use suitable amount of coolant water to stop the generation of dust. The preventive measures for the drilling process could be setting a transparent plastic cover over the drilling apparatus to prevent the spread of activity. The drilling cooling waters must also be collected and their activity measured before possible release. In sawing some amount of the sample will be loosened from the whole, resin beads can become dislodged and active coolant water will be generated. The solid parts of the sample will be washed off together with the coolant water. These same contamination sources are possible for the polishing as well. Out of these two, polishing tends to be more time-consuming and therefore generate more waste. Waste water should be collected and monitored for activity before release. The release of resin beads could perhaps be mitigated by casting the samples in an impregnant solution which fills the porosity and imparts further mechanical strength.

1.6.1.2 Work in 2024

In 2024 the inactive mock-up samples were characterized in terms of their 3D structure and porosity distribution. In preparation for the porosity characterisation by C-14-PMMA autoradiography, the samples were impregnated with C-14-MMA.

This acted as an impregnant test (Figure 1) and provided parallel method of porosity determination. The 3D structural analysis was performed with X-ray tomography (Figure 3). Based on these results it could be concluded that the anion exchange resin beads can be easily distinguished from the surrounding cement paste. The sample preparation method seemed to produce isotropic samples, with evenly distributed beads.

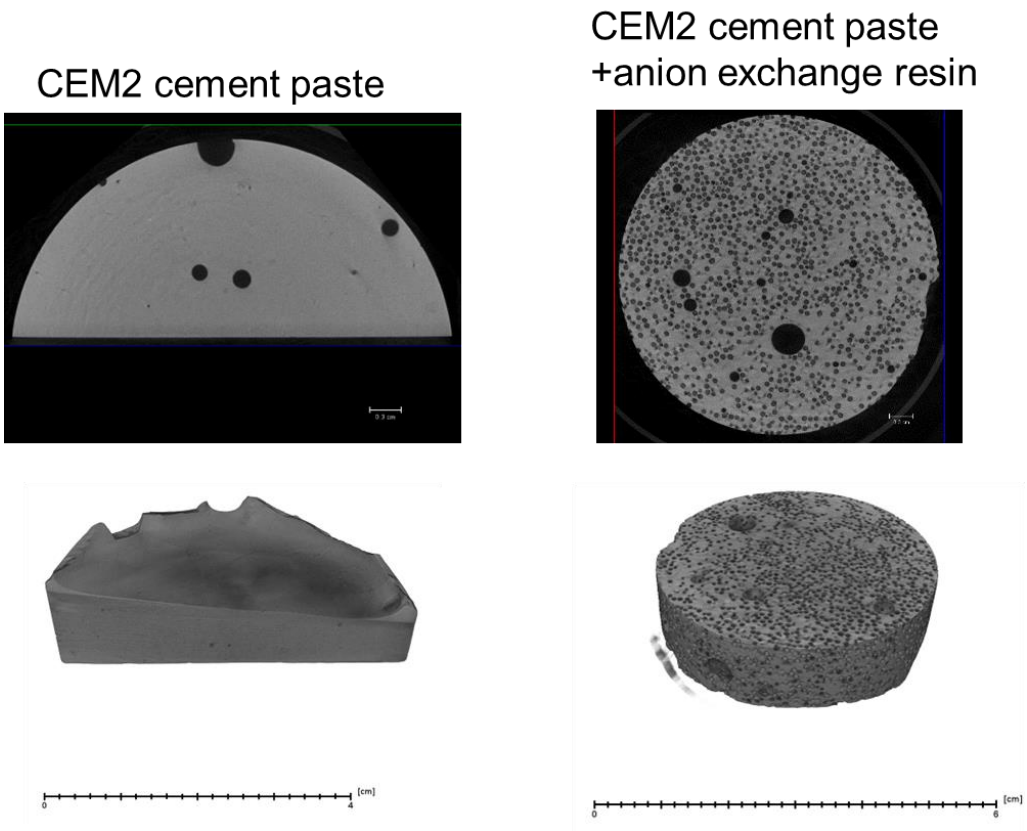

Figure 3 Left: XCT imaging of CEM2 cement paste sample. Right: XCT imaging of CEM2 cement paste including immobilized anion exchange resin beads.

The porosities of the inactive mock-up samples were studied in water gravimetry and C-14-PMMA autoradiography. Water provided bulk porosity values while C-14-PMMA provides also spatial distributions of porosity. Examples of the porosity distributions for inactive mock-up sample with and without resin beads are shown in Figure 4. The results for the cement paste sample without beads shows a typical homogeneous porosity distribution and bulk porosity of 32.2 % by water gravimetry and 28.0 % by C-14-PMMA autoradiography. These values are fairly close to each other.

In preparation for the C-14-PMMA autoradiography the samples were sawn and polished as previously. It was noted that the resin beads tend to flake of the sampled in a fairly similar manner as without impregnants. It seemed therefore that the impregnant doesn't improve upon this aspect of sample mechanical stability. However the overall mechanical stability of the surrounding cement was slightly improved, making the polishing work easier.

The results for cement paste with resin beads (Figure 4) showed that resin beads can also be distinguished in porosity distributions. The porosity distribution is therefore considerably more heterogeneous when there are immobilized resin beads present. The resin beads appears as areas of higher porosity compared to the surrounding cement paste. The overall bulk porosity appears to be higher as well. The bulk porosity was determined to be 42.1 % by water gravimetry and 55.0 % by C-14-PMMA autoradiography. This considerable increase is likely due to the resin beads being highly porous for increased reaction surface area. The results by C-14-PMMA autoradiography is considerably higher than the results by water gravimetry. This could be due to the beads swelling by soaking the C-14-MMA tracer. The resin beads themselves are crosslinked polystyrene that can be swell in the presence of organic solvents, such as MMA. The issue should be further investigated.

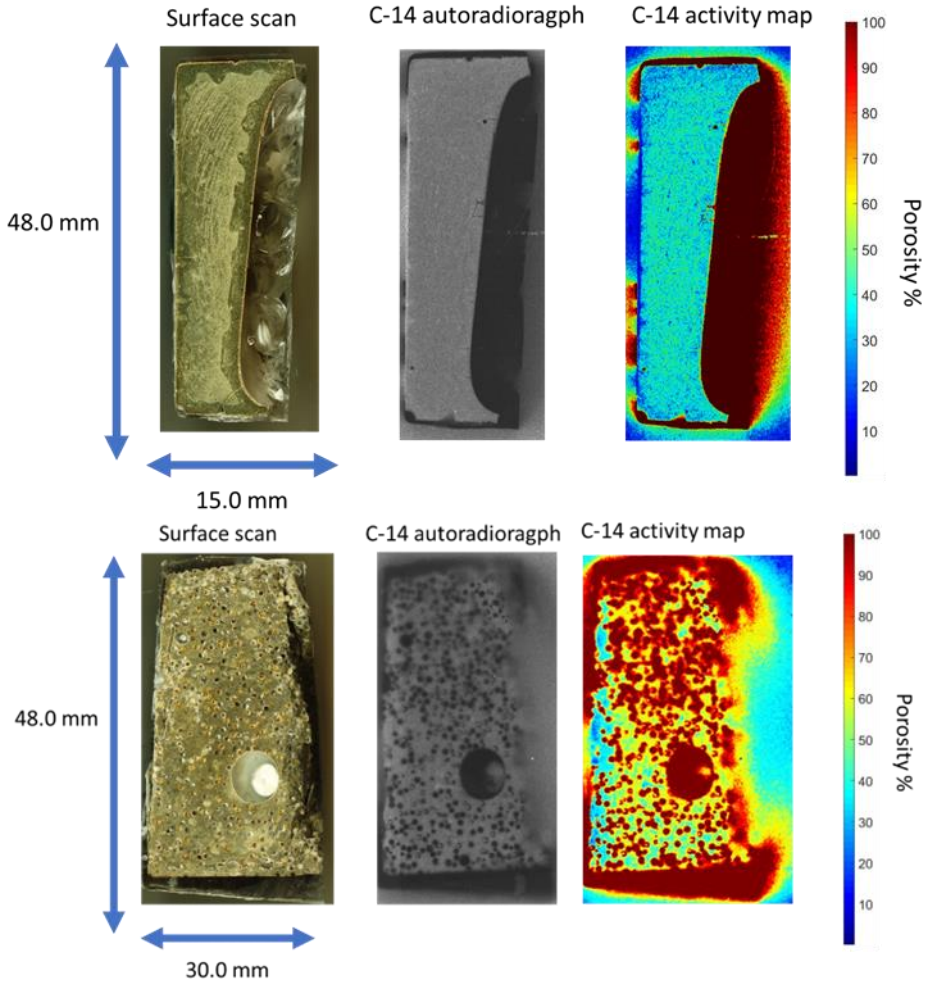

Figure 4 Up: Surface scan, corresponding autoradiograph and porosity map CEM2 cement paste sample. Down: Surface scan, corresponding autoradiograph and porosity map CEM2 cement paste containing anion exchange resin beads sample.

1.6.2 Task 2 (T2.2), Spatial distributions of activity in solidified concrete waste

1.6.2.1 Summary of 2023

The distribution of activity and chemical speciation in the source term influences the release rate of radionuclides. Contamination on the surface of the source term will be released more quickly than the activity deeper in the source, possibly requiring further degradation of the cementitious waste matrix. In such as case, the chemical speciation still affect how quickly the release would happen. The autoradiographic techniques developed by our research group can characterise the distribution of activity in centimetre-scale samples and together with electron microscopic and X-ray-based techniques we can correlate their presence with different phases of the concrete waste matrix, such as the cement phases, rock aggregate and the resin waste. This comprehensive study is best performed on actual samples obtained in situ from a LILW repository to obtain realistic results.

Autoradiography will be used to characterise the spatial distributions of radio activity in the solidified waste following XCT analysis. These results will show whether the radionuclides are distributed homogeneously or if there is preferential distribution into some specific phase of the material. Alpha and gamma spectrometry will be used to characterise the radioactivity content quantitatively and determine the radionuclides present in the heterogeneous waste material. New advances in autoradiography, such as Beaquant, can then be used to provide nuclide-specific spatial distributions as has been done

for geomaterials (Sardini, et al, 2016; Lefeuvre, et al, 2022). Once microstructural and chemical speciation data is available, the information can be combined to see in what kind of phases the radionuclides are found in.

Spatial distributions of radionuclide activities on the cementitious waste samples are to be measured by storage phosphor screen autoradiography with imaging plates (SPA) scanned with a Fuji FLA-5100 scanner, and the micro-pattern gas detector-based autoradiography (MPGDA) performed with the BeaQuant imaging system (Donnard, et al, 2009). Both of these autoradiography techniques have complementary strengths and weaknesses (Delayre, et al, 2020). SPA has good sensitivity and a wide linear range and it is quite tolerant of artefacts caused by imperfections in the samples. SPA however doesn't allow nuclide- or radiation-specific imaging. The exposure times needed with SPA are also usually found via trial and error, and in any case, after about 1 week the signal fade will start to affect the results (L'Annuziata, 2003). MPGDA has even better sensitivity and a wide linear range. MPGDA also allows for radiation-type, and in some cases, nuclide-specific imaging based on different radiation energies (Delayre, et al, 2020). The measurement is performed straight from the sample and it detects in real-time pulses coming from the radioactive elements in the sample. There are no imaging plates or films that could be overexposed, allowing the measurement can be continued as long as necessary. The high sensitivity of MPGDA is however a disadvantage in some cases. The technique is sensitive to artefacts resulting from imperfect sample preparations and discontinuities, such as cavities (Billon, et al, 2019). Therefore, it is sensible to use two techniques of autoradiography to obtain a comprehensive characterization of the spatial distributions of activity.

1.6.2.2 Work in 2024

The work of studying the spatial distributions of activity was started by preparing active mock-up samples containing only a single radionuclide. The idea being here that active mock-up samples provide a test case by autoradiographic imaging that is easy to interpret before moving to more complex and realistic samples. In this case, the radionuclide used was Ra-226. Several samples containing crushed rock from Ra-226 sorption experiments and a sample containing spent Ra-226 exchange resin were prepared. The solid phase containing the activity was mixed into cement paste in the similar manner as with inactive mock-up sample preparation. The samples solidified in about 2 days and they were let to stay 1 month before further experimental steps. Following the 1 month waiting time, the samples were cut open and polished using the previously tested methods. The samples were then imaged with autoradiography to produce activity maps.

Results from representative examples of the active mock-up samples prepared with Ra-226 doped biotite grains are shown in Figure 5. In these cases, the activity was distributed quite heterogeneously. It is possible that the mixing was not vigorous enough to mix the biotite grains evenly into the sample matrix, although it might also be possible that the grains settled near the bottom of the vessel while the cement was not hardened yet. In both of cases presented here the Ra-226 activity has stayed mostly in the biotite grains, especially in the sample presented in the upper part of Figure 5.The activity distribution of the sample on the lower part of Figure 5 however shows a more spread out distribution of activity. Perhaps in this case some of the activity was then moved into the cement phase.

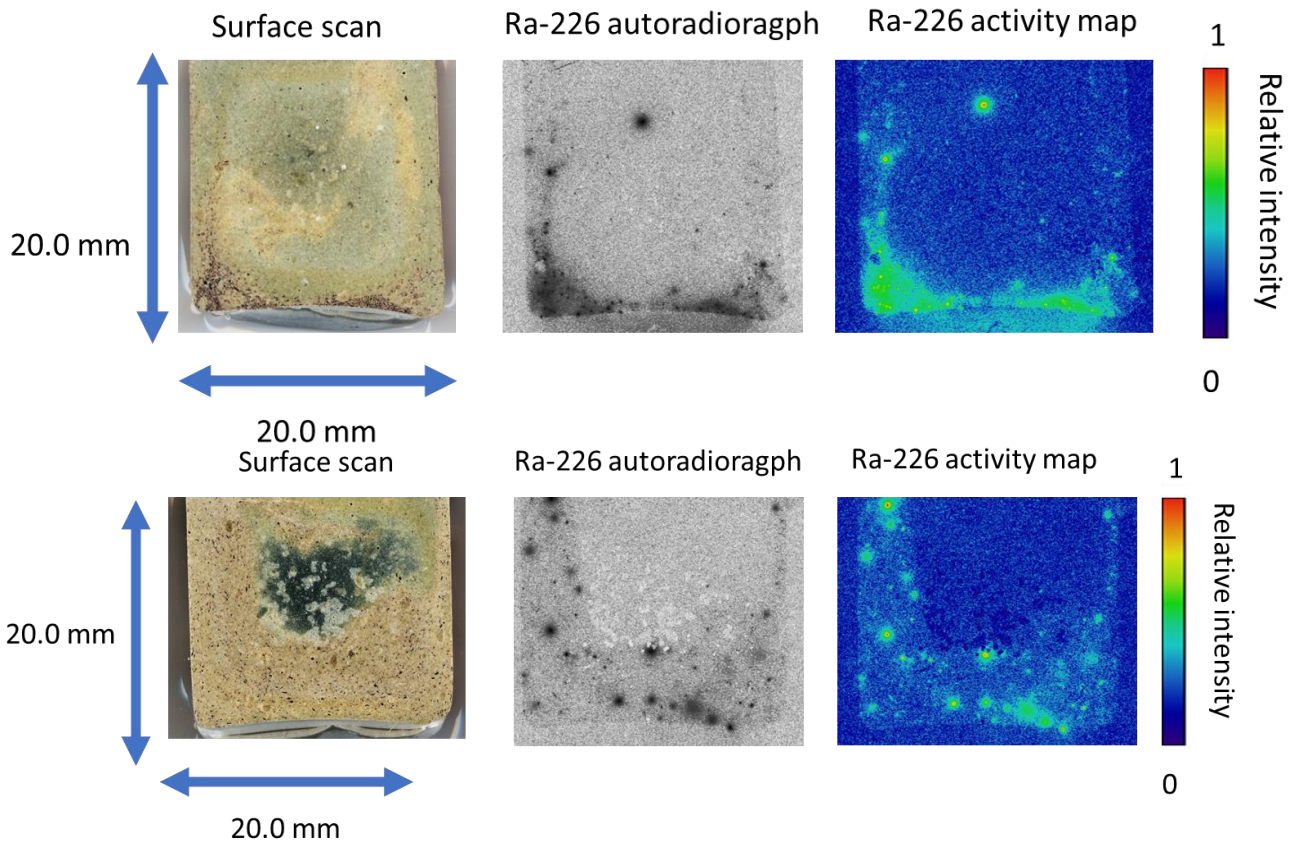

Figure 5 Surface scans (left), corresponding autoradiographs (center) and Ra-226 activity maps of two parallel active mock-up samples made with Ra-226 doped biotite.

Example of the results from active mock-up sample prepared with Ra-226 resin is shown in Figure 6. Here the distribution of activity appears quite uniform, although some low-activity areas are found. Here perhaps the mixing worked better, resulting in a more uniform distribution. Another possibility is that the activity from the spent resin was redistributed into the cement matrix. This should be investigated in further microstructural studies.

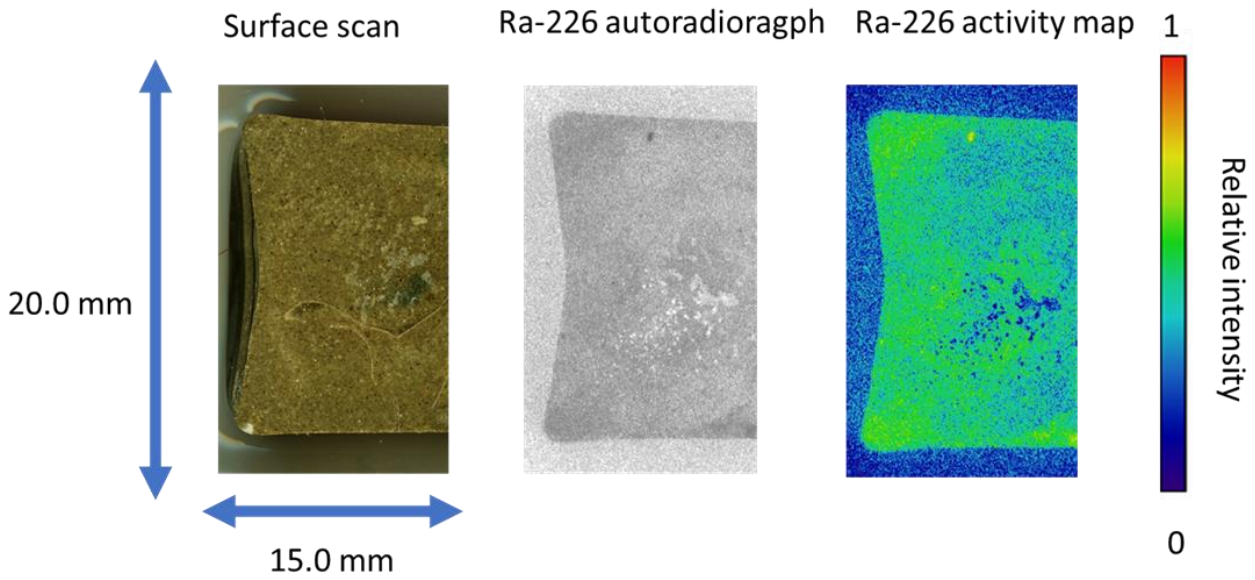

Figure 6 Surface scan (left), corresponding autoradiograph (center) and Ra-226 activity map of an active mock-up samples made with spent Ra-226 resin.

All in all, the tests with active mock-up were used to develop methods for imaging activity distributions in cementitious samples containing immobilized activity sources. The method development proved successful and good quality imaging of activity distributions were obtained. Therefore, the method development was at stage were active in situ samples could be handled. In situ sample containing mostly spent ion exchange resin embedded in cement matrix was obtained from Loviisa Power Plant. This sample was known from background information to contain mostly Cs-137 with smaller contributions from Ni-63, Co-60, and minor contributions from host of other radionuclides. This sample was then sawed to produce surfaces for autoradiographic imaging.

The results from the imaging of the in situ sample are shown in Figure 7. It can be seen that the activity is distributed into both the cement phase and hotspots, which are likely associated with the spent ion exchange resin beads. As the large majority of the sample's activity comes from Cs-137, ít can be deduced that Cs-137 must also be present in both resin beads and the cement matrix. This means that the Cs-137 would diffuse from the cement matrix and from the resin beads, perhaps at different rates. The activity from the resin beads would still have diffuse through the cement matrix before transport to any further waste barriers. The activity distribution seems fairly isotropic and the distribution of the resin beads resembles the distribution present in inactive mock-up samples. The in situ sample's activity distribution resembles quite closely that of the active mock-up sample shown in the lower part of Figure 5. These points prove that the mock-up tests contributed to successful analysis of the in situ sample.

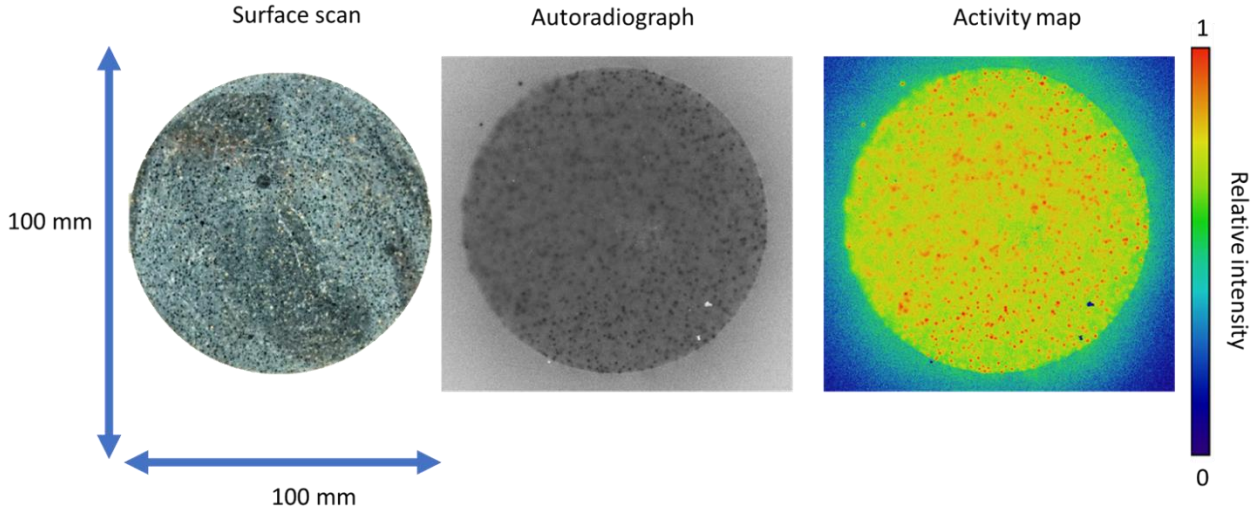

Figure 7 Surface scan (left), corresponding autoradiograph (center) and activity map of an active in situ sample containing mostly spent ion exchange resin immobilized into cement.

1.6.3 Task 3 (T2.3), Microstructural analysis and chemical speciation in solidified concrete waste

In 2025 we will perform microstructural analysis of the solidified waste. SEM-EDS analysis at UH will be done to compare distributions of activity to microstructural features. TEM-EDS at VTT will be done to what kind of nanoscale structures are found in the material. µ-XRF will be used to obtain chemical mapping on larger hand specimen scale. XAS analyses at UH will be done to ascertain the chemical environment and speciation of the radionuclides on atom and molecular scale.

1.7 Conclusion

Inactive mock-up samples have been cast for drilling, sawing polishing tests in 2023. These tests were performed and they provided valuable insight into the waste material behaviour. The sample material proved to be mechanically somewhat weak but could still be handled with the laboratory equipment available. Based on these tests, the sampling handling procedures were developed to safely handle active samples, both mock-up and in situ during 2024. The 3D structure and porosity distribution of inactive mock-up samples were determined. Concurrently with porosity distribution study, the use of impregnants for increasing mechanical strength was studied. the impregnant use improved slightly the overall mechanical strength but the flaking behaviour remained. This still needs to be taken into account as a possible source of contamination during sample preparation and storage. Active mock-up samples containing Ra-226 were cast and prepared for autoradiographic and structural analyses. Methods were developed to handle the active cementitious samples. The analysis results showed different possible scenarios for radionuclide distribution; mainly connected to mock-up waste, mainly in in cement phase and activity found in both mock-up waste and cement phase. An in situ sample containing multiple radionuclides was prepared and measured based on the methods developed during the mock-up tests. The activity in the in situ sample was mainly Cs-137, with Co-60 and Ni-63 as other minor components and several other in considerably smaller amounts. Activity was found to be distributed to both cement phase and hotspots corresponding to resin beads.

1.8 Outlook for year 2025

Project year 2025 will focus on microstructural analyses. The active mcok-up samples and the in situ sample will be characterised first with by SEM-EDS. Autoradiographic imaging will be developed to account for multiple nuclide sources. Further autoradiographic analyses will be done on the in situ sample and supporting alpha and gamma-analyses. Chemical speciation in active in situ samples is also planned to be studied.

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