

Short thesis for the degree of Doctor of Philosophy (PhD)

**Investigation of waste forms, engineered barriers, and
the geological environment for the final disposal of
radioactive waste**

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Abbreviations

ASTM	American Society for Testing and Materials
BCF	Boda Claystone Formation
BVI	Bulk Volume Irreducible
CFL	Cumulative Fraction Leached
CPMG	Carr–Purcell–Meiboom–Gill pulse sequence
CSH	Calcium silicate hydrate
EDTA	Ethylenediaminetetraacetic acid
FFC NMR	Fast Field Cycling NMR
FFI	Free-Fluid Index
HF-NMR	High- field Nuclear Magnetic Resonance
ICP- MS	Inductively coupled plasma mass spectrometry
ILW	Intermediate- level waste
IR	Inversion recovery pulse sequence
LF-NMR	Low- field Nuclear Magnetic Resonance
LLW	Low-level waste
NPP	Nuclear Power Plant
NRWR	National Radioactive Waste Repository
MIP	Mercury Intrusion Porosimetry
PURAM	Public Limited Company for Radioactive Waste Management
SEM	Scanning Electron Microscopy

I. Introduction and research objectives

The application of multi-barrier systems in radioactive waste repositories is crucial, as a single containment layer cannot ensure complete containment of radionuclides over the required long period of time. By the combination of engineered barriers with the natural environment, the system provides multiple layers of protection. From the viewpoint of the potential migration of radionuclides from the repository, the comprehensive characterization of each level of the multi-barrier system is required. The typical components of the engineered barrier system are the solidified waste form, the waste container, and other buffer or backfilling materials. One of the most crucial parts of the engineered barrier system is the solidified waste, since the solid matrix is the primary barrier to the migration of radionuclides. Cementation is one of the main solidification techniques; however, in several cases, the improvement of the cement matrix is necessary, like in the form of blended cement. Regarding the applicability of such materials, the comprehensive characterization of the solid matrix and its interaction with the waste itself is essential.

In this thesis, the structure and aqueous behavior of the different levels of a multi-barrier system are investigated from a materials science perspective to estimate their long-term stability. Special attention is paid to the examination of the structure influencing effect of the components of cemented waste packages. The diversity and complexity of the examined samples necessitated a multidisciplinary approach and the combined application of various techniques, mainly low-field NMR methods with the aim of showing how these can be applied in the characterization steps of radioactive waste management.

My PhD research can be divided into three main parts:

- I)* characterization of binders for radioactive waste immobilization
- II)* investigation of the impact of real waste management conditions
- III)* examination of the repository's multi-barrier system.

The aim of the topic *I)* was to characterize the micro- and mesostructure of Ordinary Portland Cement, a base binding material, and to show the applicability and sensitivity of NMR relaxometry for this purpose through comparison with other techniques. The second aim was to study the effect of metakaolin and fly ash, as pozzolanic additives for the improvement of cement, with the goal of finding a favorable additive and its ratio regarding the aimed application of the cement matrix.

The aim of the topic *II)* was to study the real waste management conditions. On one hand, it meant to describe the leaching behavior, porosity, and permeability of model cemented waste packages prepared according to the actual cementing recipe of liquid radioactive waste (condensation residue). On the other hand, the long-term behavior of model waste packages was monitored under real disposal conditions in the NRWR.

The aim of the topic *III)* was to investigate the aqueous behavior of two levels of the multi-barrier system of waste repositories: *a)* the swelling properties of Na- and Ca- bentonite as engineered barriers; and *b)* the $T_{2\text{-cutoff}}$ value, characterizing the effective porosity, of Boda Claystone Formation, the geological environment suitable for the disposal of high-level waste in Hungary.

Furthermore, our aim was also to comprehensively describe the diffusivity of water within the individual levels (waste package, bentonite, geological environment) of a repository to predict the mobility of ground water.

II. Methods

- **Sample preparation:** Pure Portland cement samples were prepared by mixing Portland cement (CEM I 42.5 N, Duna-Dráva Cement Ltd) with deionized water in 0.4- 0.6 water-cement (w/c) ratios. After homogenization, the cement paste was poured into cylindrical PVC molds ($h \sim 2$ cm, $d = 0.6$ cm) and cured for 28 days at 298 ± 0.1 K, 100%RH. To study the effect of pozzolans, two sample series were prepared using Portland cement mixed with metakaolin (KM60, Keramost Plc) and fly ash (Microsit®10, NEWCHEM GmbH) separately in 0, 10, 20 and 30 m/m% mass ratios. The water-solid (w/s) ratio was 0.5 for each sample. The curing process of the cement composite paste is the same as described for pure Portland cement. For studying the effect of the complexing agent content in the model cemented waste packages, samples were prepared based on the recipe for the cementation of LLW and ILW at Paks NPP in Hungary, with the permission of PURAM. Accordingly, 80 m/m% Portland cement and 20 m/m% metakaolin were mixed with a model solution, containing H_3BO_3 , NaOH, KOH and HNO_3 , in $w/s=0.5$ ratio. Radioactive isotopes (^{135}Cs , ^{59}Ni , ^{129}I , ^{36}Cl) were replaced by their inactive forms or substituted: technetium (^{99}Tc) was replaced with rhenium, while americium (^{241}Am) was modeled with neodymium. Complexing agents in different concentrations (0 – 20 g/l) were added to the solution in 1:1:1 mass ratio: citric acid, oxalic acid, Na_2 -EDTA. Samples for testing the long-term effect of the waste storage conditions were prepared in the same way. Ca- and Na-bentonite were used without any pretreatment, as received. From the two borehole samples of Boda Claystone Formation (BCF) cylinders ($d \sim 7$ mm) were drilled out using a rose-drill under water cooling. To mimic the pore liquid of BCF, a model solution was prepared.

I. Characterization of binders for radioactive waste immobilization

- **Structural characterization of Portland cement:** The porous structure of the cement samples was studied by 1D LF-NMR relaxometry, which gave insight into the size and quantity of liquid- filled pores through T_2 relaxation

decays of water confined in the porous materials. The different samples were studied either in quasi-dry, dry or water saturated states in 10 mm wide glass NMR tubes by a 20 MHz NMR instrument (Minispec mq20, Bruker, Germany) at room temperature (298 K) using the CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence. The size and geometry of the pores in the hardened Portland cement paste were studied by NMR cryoporometry; for which the sample was saturated with cyclohexane and the signal intensity of the proton spectra of the molten liquid was recorded between 276 – 280 K with a Bruker Avance II 360 MHz NMR instrument. In the framework of collaborations nitrogen porosimetry (Prof. Dr. Krisztina László, Budapest University of Technology and Economics) and mercury intrusion porosimetry (Dr. Cedric Gommès and Dr. Léonard Alexandre, University of Liege) measurements were also performed on the cement sample. The nitrogen adsorption isotherms were recorded by a NOVA 2000 (Quantachrome) automatic analyzer at 77 K. The MIP measurement was carried out on a Quantachrome Poremaster 60 in a pressure range of 0.009 MPa – 400 MPa.

- ***Monitoring the effect of pozzolans:*** The curing process of Portland cement and the pozzolan composites was in-situ followed by LF-NMR relaxometry (CPMG measurements, 298 K, Minispec mq20) and FFC-NMR relaxometry (IR measurements, 298 K, SMARtracer, Stelar SRL). The pore structure of the hardened materials was investigated in both dry and wet states: SEM imaging and nitrogen porosimetry were used for dry samples, while various liquid-phase NMR techniques were applied to wet samples. The nitrogen porosimetry measurements were performed as detailed previously, while the SEM imaging (Thermo Fisher Scientific-Scios 2) was carried out at the HUN-REN Institute for Nuclear Research within the framework of a collaboration with Dr. Attila Csík. Additionally, 2D T_1 - T_2 correlation NMR relaxometry and H_2O - D_2O exchange diffusion measurements (FID measurements) were performed on a Minispec mq20 instrument at 298 K, to assess the permeability of the pore network.

II. Investigation of the impact of real waste management conditions

- **Monitoring the effect of complexing agents:** The effect of the complexing agent content on the leachability of the model cemented waste packages, as well as their effect on the structure of the cement matrices were studied. To examine the leaching behavior of Cs, Ni and Re from the waste packages, accelerated leaching tests were performed on 298 K according to ASTM C 1308-08 Standard, and the model ion content of the leachates were analyzed by ICP MS (Agilent 7500 ICP-MS, Isotoptech Ltd). The organic carbon content of the leachates in case of the 5 and 20 g/l complexing agent containing samples were studied by 1D and 2D ^1H and ^{13}C NMR methods (^1H , ^{13}C , DOSY, COSY, HSQC). To investigate the structure and permeability of the model waste packages, the above-mentioned techniques were used (SEM, NMR relaxometry, 2D T_1 - T_2 correlation NMR relaxometry, H_2O - D_2O exchange diffusion measurements).

- **Long-term effect of the waste storage conditions:** Model waste packages with 5 g/l and 20 g/l complexing agent concentrations were set in the western ditch of the NRWR at three different locations (dry, stagnant water, flowing water area). Their structural change and degradation were followed for 10 months by LF-NMR relaxometry.

III. Examination of the repository's multi-barrier system

- **Aqueous behavior of Na- and Ca-bentonites- engineered barriers:** To investigate the structure and to identify the water types, present in the layered structure of Na- and Ca-bentonite, samples with various water content were prepared and studied by LF- NMR relaxometry. The swelling process of the two bentonite samples was followed in- situ by repetitive CPMG measurements at 298 K. The diffusion of water in the water saturated samples at equilibrium state was studied by PGSE NMR at 298 K, on a Bruker Avance II 500 NMR spectrometer.

- **Characterization of Boda Claystone Formation- natural geological barrier:** The two borehole samples of BCF were studied in water saturated

(model solution) and oven-dried states by NMR relaxometry to determine the so-called $T_{2\text{cutt-off}}$ value of the bound water content within the samples. The porosity of the borehole samples was determined after a water calibration. The diffusion of water in one of the BCF samples was followed by H_2O - D_2O exchange diffusion.

III. New scientific results

I. We have described the pore structure of Portland cement with the novel combination of NMR methods and traditional structural characterization techniques; and have gained a detailed understanding of how two pozzolans (metakaolin and fly ash) influenced the pore structure of the cement composites and their interaction with water.

I.1. Through the comparison of various structural characterization methods (see in **Figure 1a**) and the Powers' empirical model, we demonstrated that NMR relaxometry is a well applicable technique for comprehensive characterization and quantification of the micro- and mesoporous structure of the main cement hydrate phase (CSH gel), for the separation of different pores according to the T_2 relaxation times, and is a sufficiently sensitive method to test the drying induced changes of cement (see in **Figure 1b**).

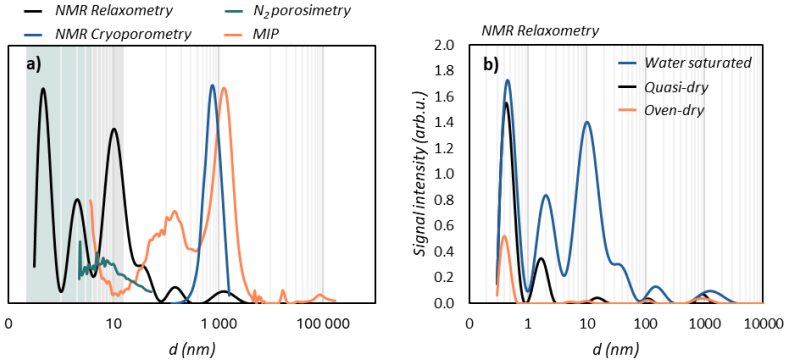


Figure 1. a) Comparison of pore size distributions of Portland cement resulted from different characterization methods. The intervals with different colors indicate the different pore types in cement: intra CSH sheet pores (blue), inter CSH gel pores (gray) and capillary pores (no color). **b)** Pore size distributions of Portland cement at various levels of water saturation.

1.2. Through the evolution of the T_2 relaxation of water over the early hydration of pozzolan containing cement composites, we found that metakaolin and coal fly ash, as pozzolan additives, similarly increased the amount of CSH gel and aluminum-containing hydrate phases, however, they did it at different stages of the cement hydration process (see in **Figure 2**). While metakaolin accelerated the precipitation of the main hydration product mainly in the declaration stage of cement hydration (10-24 h, shown in **Figure 2b**), fly ash slowed down all stages of the process (see in **Figure 2c**). These deviations from pure cement become more noticeable with increasing additive concentration.

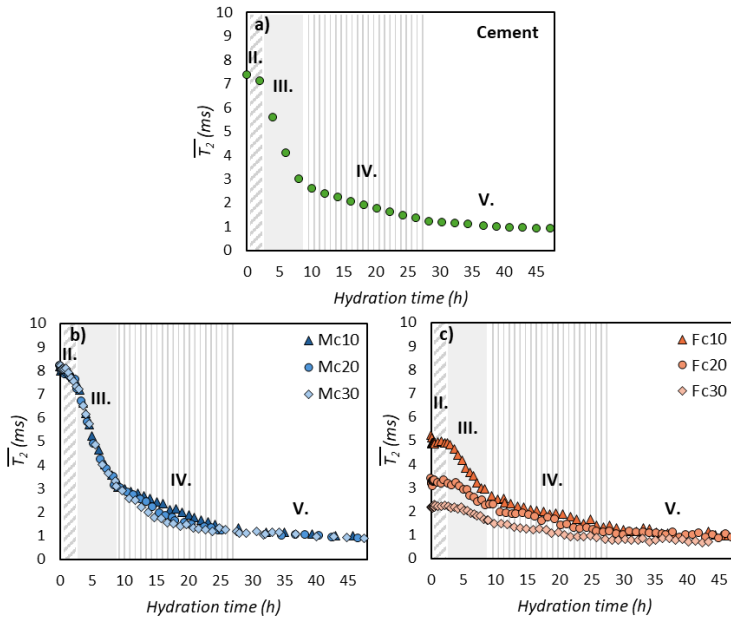


Figure 2. Change of the weighted T_2 relaxation time ($\bar{T}_2$) over the early hydration process for **a)** pure Portland cement, **b)** 10 - 30% metakaolin containing and **c)** 10 - 30% fly ash containing cement composites. The stages of cement hydration are marked according to pure Portland cement.

1.3. The comprehensive structural investigation of the composites showed that the metakaolin composites possessed a more contiguous solid matrix with few macroscopic voids, where the porous structure is dominated by the presence of micro- and mesopores (see in **Figure 3a** and **3c**). In the fly ash composites, the remaining spherical fly ash particles enhanced the heterogeneity of the structure and increased the macro- and microporous features of the solid (see in **Figure 3b** and **3d**).

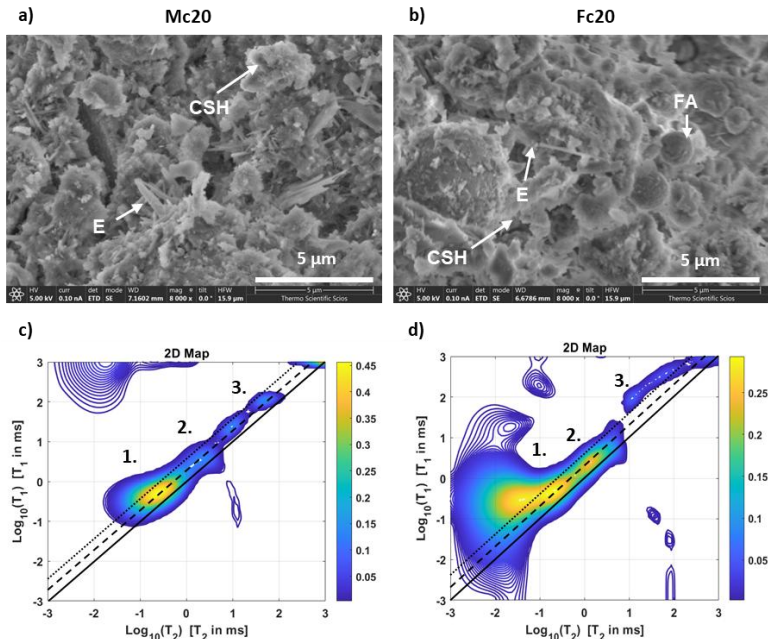


Figure 3. Scanning electron microscopy images of **a)** 20% metakaolin (Mc20) and **b)** fly ash (Fc20) containing cement composites showing the characteristic hydration products and the remaining pozzolanic additives. (CSH- calcium silicate hydrate, E- ettringite, FA- fly ash). The 2D T_1 - T_2 relaxation correlation maps of **c)** Mc20 and **d)** Fc20 cement composites with the characteristic pore types in the diagonal (1 - intra CSH sheet pore, 2- inter CSH gel pore, 3- capillary pore). The dashed ($T_1=2T_2$) and dotted ($T_1=4T_2$) lines show the shifted principal diagonal.

I.4. We demonstrated that the H_2O - D_2O exchange diffusion technique is a sufficiently sensitive method to follow the diffusion of water within modified cement composites. The presence of pozzolans also affected the diffusion of water within the solid, causing a more restricted diffusion process in the metakaolin composite (see in **Figure 4a**) and a significant amount of remaining water in the micropores for the fly ash composites (see in **Figure 4b**). Regarding the aimed application of the cement matrix, the substitution of cement with 20% metakaolin resulted in the most promising binder for the long-term safe disposal of radioactive waste (**Figure 4c**).

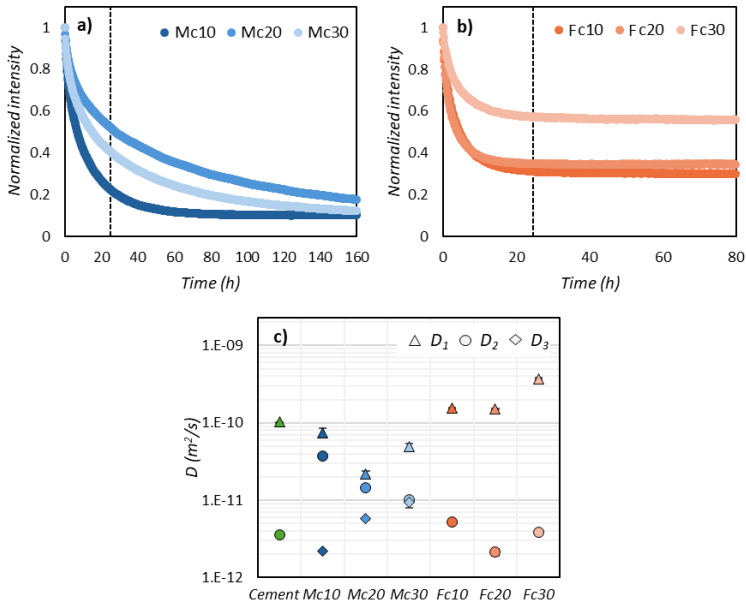


Figure 4. The normalized intensity of the proton signal over time in **a)** 10-30% metakaolin and **b)** 10-30% fly ash containing cement composites. **c)** The self- diffusion coefficients (D_{1-3}) of water in 10-30% metakaolin (blue) and 10-30% fly ash (orange) containing composites. The errors of the fitted D values are also indicated.

1.5. We were the first to apply the *3-Tau* model for the evaluation of FFC NMR measurements, with the aim to investigate the effect of additives on cement hydration. The *3-Tau* model shed light on stronger water- solid interactions (see the variation of τ_l in **Figure 5**) in the fly ash composite, which was also supported by 2D T_1 - T_2 correlation NMR measurements.

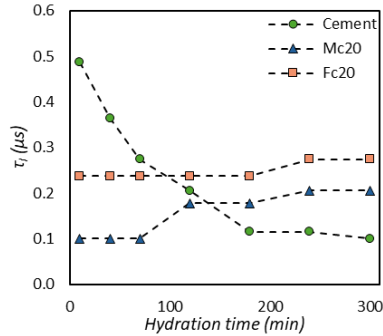


Figure 5. The surface diffusion time(τ_l) of water during the early hydration of Portland cement (green circle), Mc20 (blue triangle) and Fc20 (orange cube).

II. The complexing agent content of model cemented waste packages affected the quantity and quality of the leached metal complexes, caused the formation of new hydration products, altering the porous structure of cement, and influenced the resistance to real disposal conditions. These effects were described in detail by the joint use of accelerated leaching studies, LF- and HF-NMR methods, paying special attention to the effect of real-disposal conditions.

II.1. The complexing agent content ($\text{Na}_2\text{-EDTA}$, citric acid, oxalic acid) of the modeled cemented waste packages influenced the leachability of cesium, nickel and rhenium from the cement matrix according to the following trend: 0 and 20 g/l < 10 g/l < 5 and 15 g/l, which means that at certain concentrations the leaching process was facilitated. The effective diffusion coefficient of the model ions quasi decreased with increasing the concentration of the complexing agents.

II.2. Regarding the complexing agent content of the leachates, it was found that at 5 g/l concentration, the complexing agents leached out in the form of various metal complexes as well as transformed into compounds containing double bonds and rings, enhancing the mobilization of the model ions (see in **Figure 6a**). At 20 g/l concentration, the large-scale leaching of calcium complexes, in addition to other metal complexes, was observed (see in **Figure 6b**).

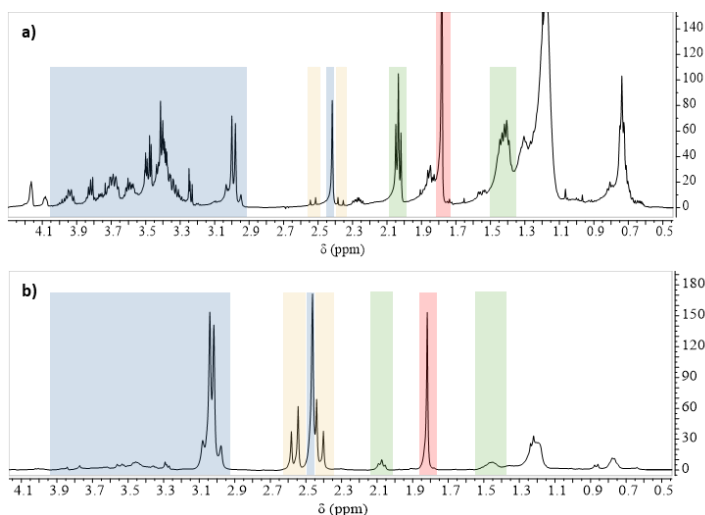


Figure 6. The aliphatic part of the ¹H-NMR spectrum of the organic compounds leached out of **a)** the 5 g/l and **b)** the 20 g/l complexing agent containing model cemented waste packages (500 MHz, 298 K, *ns*=64). The different colors indicate the identified compounds: metal-EDTA complexes (blue), metal- citrate complexes (yellow), acetate (red).

II.3. In the case of the 5 g/l sample, an one-order-of-magnitude slower, anomalous water diffusion process was observed, compared to the 20 g/l sample, caused by the lower permeability of the cement matrix (see in **Figure 7**). We demonstrated that the H₂O-D₂O exchange diffusion technique can be suitable for monitoring water diffusion in such complex systems, where the

dissolution and diffusion of some proton containing components (e.g. complexing agents/ metal complexes) could be also detected.

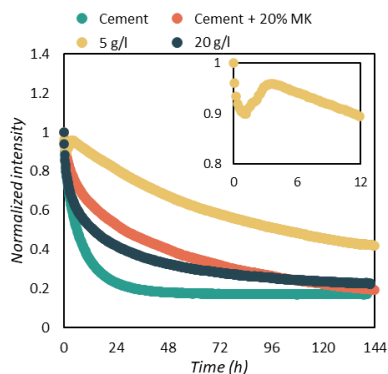


Figure 7. The normalized intensity of the proton signal over time in cemented model waste packages with 5 g/l (yellow) and 20 g/l (dark blue) complexing agent content. For comparison, the curves of pure cement (green) and the 20% metakaolin containing composite (orange) are also presented. The inserted figure is a magnification of the initial section of the curve obtained for the 5 g/l complexing agent content sample.

II.4. Under the influence of complexing agents and model ions, a few new cement hydrate phases were formed (e.g.: NiAl-LDH, calcite, see in **Figure 8**), which increased the contribution of the smaller pores and slightly reduced the volume of larger pores.

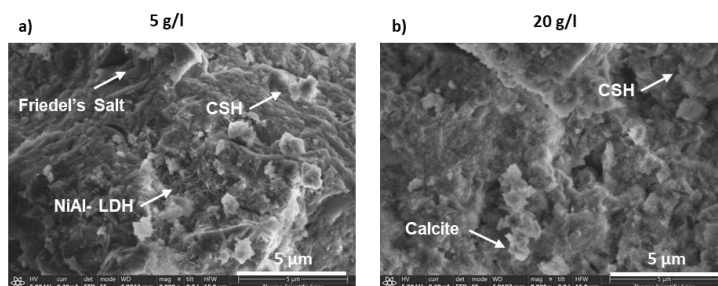


Figure 8. Scanning electron microscopy images of a) 5 and b) 20 g/l complexing agent containing cement specimens showing the precipitated hydration products (CSH- calcium silicate hydrate, NiAl-LDH- nickel-aluminum layered double hydroxides, calcite and Friedel's salt).

II.5. By monitoring the structural changes of modeled cemented waste packages placed at three different points (dry, flowing water, stagnant water; see in **Figure 9**) of the NRWR, it was shown that flowing water had a significant structural shaping effect, while in the case of dry samples, drying of the CSH gel was detectable. The aqueous environments had a slightly greater impact on the 20 g/l samples compared to the 5 g/l, since it had a more permeable porous structure, which resulted in a less restricted water diffusion process. It was shown that NMR relaxometry may be a favorable method for industrial applications as well, since it could be reproducibly used to investigate the structure of wet and dry samples, as well as to monitor the formation/change of the structure in situ.

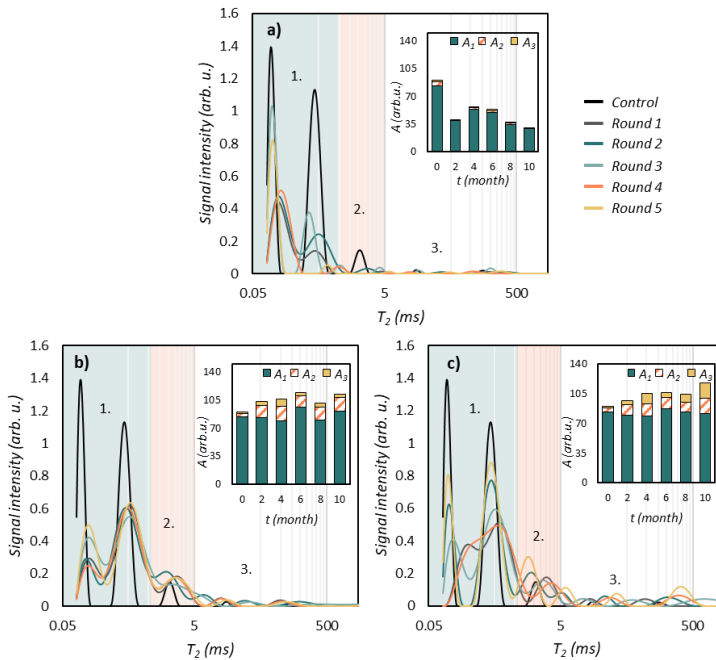


Figure 9. The effect of real conditions on the T_2 relaxation time distributions of the cemented model waste packages with 20 g/l complexing agent content. The three distinct placement points were: **a)** dry, **b)** stagnant water and **c)** flowing water. The inserted graphs show the change of the amplitudes assigned to the water types over time.

III. The mobility of water within the porous solid, swelling kinetics and bound water content were determined within two levels of the multi-barrier system by NMR relaxometry: the engineering barrier (Na-, Ca-bentonite) and the geological environment suitable for the disposal of high-level waste (BCF).

III. 1. The structural changes of bentonite samples with increasing water content indicated the greater swelling ability of Na-bentonite. The swelling of Na-bentonite was monitored in situ and the modeling of the time dependence of the measured T_2 relaxation times indicated second-order kinetics swelling mechanism. In the swollen Na-bentonite sample, two restricted water diffusion processes were distinguished during HF-NMR measurements.

III.3.2. In the case of the BCF borehole samples, the $T_{2-cut-off}$ value characterizing the porosity and bound water content was determined using NMR relaxometry (see in **Figure 10**). Based on these parameters the permeability of the rock, important geophysical parameter, was determined. With the H_2O - D_2O exchange diffusion technique, two different water diffusion processes were distinguished in the reservoir rock.

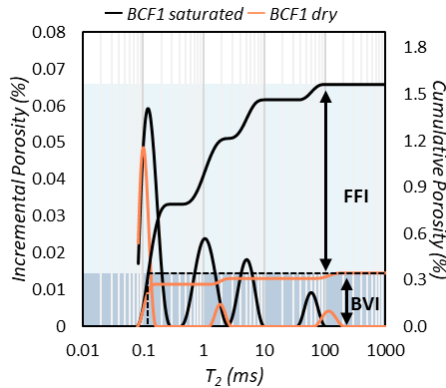


Figure 10. T_2 relaxation time distribution and the derived cumulative pore volume distributions of BCF1 in water saturated (black curves) and dry (orange curves) states. The vertical dashed line shows the $T_{2cut-off}$ value, which separates the movable (FFI) pore filling water from the non-movable (BVI) bound water in the rock.

IV. It was proven that each single level of the multi-barrier system can retrain the diffusion of water, thus the migration of radionuclides. The apparent diffusion coefficients (D) of water were determined at different levels of the radioactive waste repository.

IV.1. The determined D values are summarized in **Figure 11**, where a quasi-enhanced, but still restricted water diffusion can be observed by moving from the cemented waste form towards the host rock.

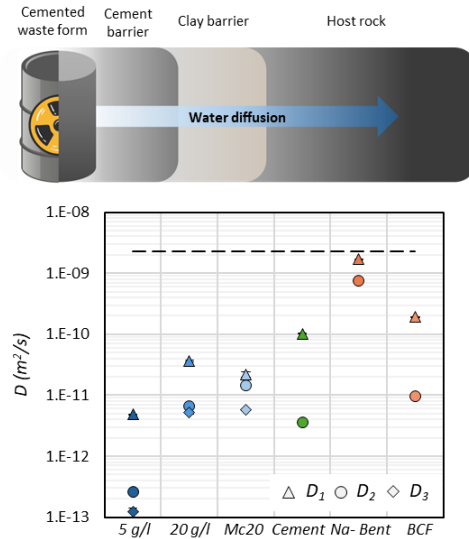


Figure 11. The alteration of the self-diffusion coefficient of water from the cemented model waste packages, through the engineered barriers (cement, bentonite), towards the geological barrier (host rock). The dashed line shows the self-diffusion coefficient of bulk water.

IV. Potential applications of the results

The objective of this PhD research was the characterization of the different levels of the multiple barrier system of radioactive waste repositories from a materials science perspective, paying special attention to the examination of waste packages. The multidisciplinary approach and the combined application of various examination methods led to key pieces of information (e.g.: porosity, permeability, leachability, water diffusion) that are useful not only for the basic knowledge of the studied porous material, but also for the safety analysis of radioactive waste repositories and the development of matrix materials for waste packages.

In the case of new binders for radioactive waste conditioning, the solid matrix must meet several criteria, including the knowledge of the binder's structure, hardening process, interactions with water and sorption properties. Based on our results so far, the aforementioned properties can be investigated in a complex manner using various NMR techniques. Testing the influence of additives (e.g.: pozzolans) by this novel methodology can contribute to the development of such matrix materials the structure of which is less permeable and have higher sorption capacity for radionuclides. The determined parameters (e.g.: porosity, water content) may also serve as input data for modelling the properties of the matrix material. For example, in the case of cement, the stochastic modeling of the drying induced structural changes of cement are in progress in the framework of a collaboration, which is of great importance for understanding the behavior of waste packages under real-disposal conditions.

The porosity and the self-diffusion coefficients of water (e.g. in the BCF host rock, bentonite) can also be used for the safety analysis of radioactive waste repositories, where the mobility of water within the barrier system fundamentally affects the migration of the radionuclides.

With the combination of HF- NMR and elemental analysis methods one can gain insight not only into the concentration of the leached model ions from the

waste forms, but also into their leached, complex forms and the possible degradation processes of the complexing agents.

Overall, LF-NMR methods have great potential for industrial applications as well, since they can be reproducibly used to investigate the structure of wet and dry samples, as well as to monitor the formation/change of the structure in situ.

Publications

Publications related to the dissertation

1. **V. Papp**, I. Ardelean, A. Bulátkó, K. László, A. Csík, R. Janovics, M. Kéri: *Effect of metakaolin and fly ash on the early hydration and pore structure of Portland cement*, Cement and Concrete Research **2025**, Volume 196, 107928. <https://doi.org/10.1016/j.cemconres.2025.107928>
2. **V. Papp**, B. Vadkerti, I. Bányai, S. Kéki, M. Kéri: *Structure and Swelling Properties of Biodegradable Cross-Linked Polyurethanes by Means of Nuclear Magnetic Resonance*, The Journal of Physical Chemistry B **2025**, 129 (22), 5607-5620. <https://doi.org/10.1021/acs.jpcc.5c01046>
3. **V. Papp**, R. Janovics, M. Kéri: *NMR characterization of the permeability and structure of Boda Claystone Formation (BCF)*, Scientia et Securitas **2024**, 4(4), 285-293. <https://doi.org/10.1556/112.2023.00187>
4. **Papp V.**, Papp I., Janovics R., Nemes Z., Kéri M.: *Radioaktív hulladékok komplexképző tartalmának hatása a kötőanyag szerkezetére és kioldhatóságára*, Sugárvédelem **2024**, XVII. évf. 1. szám 1-14.
5. **V. Papp**, R. Janovics, T. P. Kertész, Z. Nemes, T. Fodor, I. Bányai, M. Kéri: *State and role of water confined in cement and composites modified with metakaolin and additives*, Journal of Molecular Liquids **2023**, 388, 122716. <https://doi.org/10.1016/j.molliq.2023.122716>
6. **Papp V.**, Janovics R., Nemes Z., Kéri M.: *Cementkő mátrixok rehidratációjának NMR spektroszkópiás vizsgálata*, XXIV. Tavaszi Szél Konferencia kiadvány **2021**, 536-550. ISBN 978-615-81991-1-7

Other publications

7. A. Forgács, **V. Papp**, G. Paul, L. Marchese, A. Len, Z. Dudás, I. Fábíán, P. Gurikov, J. Kalmár: *Mechanism of Hydration and Hydration Induced Structural Changes of Calcium Alginate Aerogel*, ACS

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<https://doi.org/10.1021/acsami.0c17012>
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<https://doi.org/10.1016/j.actbio.2020.01.016>
 9. I. Lázár, A. Forgács, A. Horváth, G. Király, G. Nagy, A. Len, Z. Dudás, **V. Papp**, Z. Balogh, K. Moldován, L. Juhász, Cs. Cserhádi, Zs. Szántó, I. Fábián, J. Kalmár: *Mechanism of Hydration of Biocompatible Silica-Casein Aerogels Probed by NMR and SANS Reveal Backbone Rigidity*, Applied Surface Science **2020**, 531. 147232.
<https://doi.org/10.1016/j.apsusc.2020.147232>
 10. **Papp V.**, Kéri M., Forgács A., Len A., Dudás Z., P. Gurikov, Kalmár J.: *Kalandozás a nanovilágban, pórusos anyagok vizsgálata különleges módszerekkel*, A Debreceni Egyetem Szakkollégiumainak I. Tudományos Konferenciájának Tanulmánykötete **2020**, 93-105. ISBN 978-963-490-223-2
 11. **Papp V.**, Kéri M., Forgács M., Len A., Dudás Z., Kalmár J.: *Szilika-zselatin aerogélek szerkezete és nedvesedési tulajdonságai*, I. FKF Szimpózium Konferencia Kiadvány **2019**, 178-183. ISBN 978-615-6018-00-7

Conference presentations related to the dissertation

1. **Papp V.**, Janovics R., Nemes Z., Kéri M.
Cementkő mátrixok rehidratációjának NMR spektroszkópiás vizsgálata (lecture presentation)
XXIV. Tavaszi Szél Konferencia, Kémiai és környezettudományi szekció, Gyógyszerészeti, analitikai, ipari és szintetikus kémiai alszekció
2021.05.29-30. Online
2. **Papp V.**, Janovics R., Nemes Z., Kéri M.
Víz a hulladéktárolóban? Avagy a rehidratáció hatása a cementkő mátrixok szerkezetére (poster presentation)
II. FKF Szimpózium
2021.06.16-18. Online

3. **Papp V.**, Janovics R., Nemes Z., Kéri M.
Radioaktív hulladékok végleges elhelyezéséhez kapcsolódó cementkő mátrixok szerkezetének vizsgálata (lecture presentation)
XLVI. Sugárvédelmi Továbbképző Tanfolyam
2021.09.14-16. Zalakaros, Hungary
4. **Papp V.**, Vadkerti B., Kéri M.
Biodegradálós keresztkötött polimerek viselkedése vizes közegben (lecture presentation)
XLIV. Kémiai Előadói Napok
2021.10.26-27. Online
5. **V. Papp**, V. Nagy, B. Vadkerti, M. Kéri
Study of swelling biodegradable crosslinked polymers by NMR (poster presentation)
10th Jubilee Interdisciplinary Doctoral Conference (2021IDK)
2021.11.12-13., Pécs, Hungary
6. **V. Papp**, R. Janovics, Z. Nemes, M. Kéri
Investigation of the structure of binders related to the final disposal of radioactive waste (lecture presentation)
2021 évi ELFTSV Online Sugárvédelmi Mikulás
2021.12.06. Online
7. **Papp V.**, Janovics R., Nemes Z., Kéri M.
Radioaktív hulladékok végleges elhelyezéséhez kapcsolódó cementkövek szerkezetének vizsgálata (lecture presentation)
HISZ Tavaszi Tudományos Hallgatói Konferencia
2022.05.06. Debrecen, Hungary
8. **V. Papp**, R. Janovics, Z. Nemes, I. Bányai, M. Kéri
Investigation of the structure of binders related to the final disposal of radioactive waste (lecture presentation)
ATOMKI Seminar
2022.05.24. Debrecen, Hungary
9. **V. Papp**, R. Janovics, Z. Nemes, I. Bányai, M. Kéri
Investigation of the structure of binders related to the final disposal of radioactive waste (lecture presentation)
6th European Congress on Radiation Protection
2022.05.30.-06.03. Budapest, Hungary

10. **V. Papp**, R. Janovics, Z. Nemes, I. Bányai, M. Kéri
NMR characterization of cement binders related to the radioactive waste conditioning (poster presentation)
Chemistry Physics and Biology of Colloids and Interfaces
2022.06.06-10. Eger, Hungary
11. **Papp V.**, Vadkerti B., Kéri M.,
Biodegradálható keresztkötött polimerek NMR spektroszkópiás vizsgálata (lecture presentation)
DE Intézményi ÜNKP Konferencia
2022.06.13. Debrecen, Hungary
12. **V. Papp**, R. Janovics, Z. Nemes, I. Bányai, M. Kéri
Role of water in the curing process and structure formation of cement and metakaolin-based binders (lecture presentation)
International Symposium on recent advances in NMR applications to materials
2022.09.16-19. Hirschegg, Austria
13. **Papp V.**, Janovics R., Nemes Z., Bányai I., Kéri M.
Geopolimerek, mint potenciális kötőanyagok a radioaktív hulladék kondicionálásban (lecture presentation)
Meeting with PURAM
2022.09.28. Paks, Hungary
14. **Papp V.**, Janovics R., Nemes Z., Bányai I., Kéri M.
A metakaolin szerepe a radioaktív hulladékok kondicionálása során (lecture presentation)
10. Környezetkémiai Szimpózium
2022.09.29-30. Siófok, Hungary
15. **Papp V.**, Janovics R., Kéri M.
Geopolimerek szerepe a radioaktív hulladékok kondicionálásában (lecture presentation)
Hatvani István Szakkollégium, Őszi Tudományos Hallgatói Konferencia
2022.12.08. Debrecen, Hungary
16. **V. Papp**, D. Nyul, L. Novák, I. Bányai, M. Kéri
What can liquid-phase NMR tell us about porous materials? (poster presentation)
Workshop on Aerogels Characterization and Modelling
2023.03.29-31. Debrecen, Hungary

17. **Papp V.**, Kertész T. P., Nyul D., Janovics R., Bányai I., Kéri M.
Mit ad a kötőanyagok megismeréséhez a folyékony fázisú NMR?
(poster presentation)
MKE 4. Nemzeti Konferencia
2023.07.10-12. Eger, Hungary
18. **V. Papp**, R. Janovics, I. Papp, T. P. Kertész, Z. Nemes, M. Kéri
What can leach out of the cements that bind radioactive waste? (lecture presentation)
Alpine NMR Workshop on recent advances in NMR methods
2023.09.14-17. Mátrafüred, Hungary
19. **Papp V.**, Papp I., Janovics R., Nemes Z., Kéri M.
Radioaktív hulladékok komplexképző tartalmának hatása a kötőanyag szerkezetére és kioldhatóságára (lecture presentation)
HISZK 2024. évi Tavaszi Tudományos Hallgatói Konferencia
2024.05.10. Debrecen, Hungary
20. **Papp V.**, Janovics R., Kéri M.
Kisterű NMR módszerek cement alapú kötőanyagok megismerésére
(lecture presentation)
NMR Munkabizottság 2024. évi Előadóülése
2024.05.23-24. Balatonszemes, Hungary
21. **V. Papp**, R. Janovics, I. Papp, Z. Nemes, M. Kéri
Applicability of Liquid- phase NMR to characterize the structure and leachability of cement- based binders (lecture presentation)
International Atomic Energy Agency, Technical Meeting on Achievements and Challenges in Radioactive Waste Characterization
2024. 08. 26-30 Vienna, Austria
22. **V. Papp**, R. Janovics, I. Ardelean, K. László, A. Csík, M. Kéri
Effect of pozzolans on the early hydration and structure of Portland cement by means of NMR (lecture presentation)
Alpine NMR Workshop
2024.09.20-22. Cluj-Napoca, Romania



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PhD Publication List

Candidate: Vanda Papp

Doctoral School: Doctoral School of Chemistry

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List of publications related to the dissertation

Hungarian scientific articles in Hungarian journals (1)

1. **Papp, V.**, Papp, I., Janovics, R., Nemes, Z., Kéri, M.: Radioaktív hulladékok komplexképző tartalmának hatása a kötőanyag szerkezetére és kioldhatóságára. *Sugárvédelem*. 17 (1), 1-14, 2024. ISSN: 2060-2391.

Foreign language scientific articles in Hungarian journals (1)

2. **Papp, V.**, Janovics, R., Kéri, M.: NMR characterization of the permeability and structure of Boda Claystone Formation (BCF). *ScientSec*. 4 (4), 285-293, 2024. EISSN: 2732-2688.
DOI: <http://dx.doi.org/10.1556/112.2023.00187>

Foreign language scientific articles in international journals (3)

3. **Papp, V.**, Ardelean, I., Bulátkó, A., László, K., Csik, A., Janovics, R., Kéri, M.: Effect of metakaolin and fly ash on the early hydration and pore structure of Portland cement. *Cem. Concr. Res*. 196, 1-15, 2025. ISSN: 0008-8846.
DOI: <http://dx.doi.org/10.1016/j.cemconres.2025.107928>
IF: 13.1 (2024)
4. **Papp, V.**, Vadkerti, B., Bányai, I., Kéki, S., Kéri, M.: Structure and Swelling Properties of Biodegradable Cross-Linked Polyurethanes by Means of Nuclear Magnetic Resonance. *J. Phys. Chem. B*. 129 (22), 5607-5620, 2025. ISSN: 1520-6106.
DOI: <http://dx.doi.org/10.1021/acs.jpcc.5c01046>
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5. **Papp, V.**, Janovics, R., Kertész, T. P., Nemes, Z., Fodor, T., Bányai, I., Kéri, M.: State and role of water confined in cement and composites modified with metakaolin and additives. *J. Mol. Liq*. 388, 1-10, 2023. ISSN: 0167-7322.
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6. **Papp, V.**, Janovics, R., Nemes, Z., Kéri, M.: Cementkő mátrixok rehidratációjának NMR spektroszkópiás vizsgálata.
In: XXIV. Tavaszi Szél Konferencia 2021 : Tanulmánykötet I.. Szerk.: Molnár Dániel; Molnár Dóra, Doktoranduszok Országos Szövetsége, Budapest, 536-550, 2021. ISBN: 9786158199117

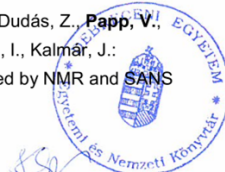
List of other publications

Hungarian book chapters (1)

7. **Papp, V.**, Kéri, M., Forgács, A., Len, A., Dudás, Z., Gurikov, P., Kalmár, J.: Kalandozás a nanovilágban, porusos anyagok vizsgálata különleges módszerekkel.
In: A Debreceni Egyetem Szakkollégiumainak I. Tudományos Konferenciája konferenciakötet. Szerk.: Dajnoki Krisztina, Felföldi János, Debreceni Egyetem Gazdaságtudományi Kar, Debrecen, 93-105, 2020. ISBN: 9789634902225

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8. Forgács, A., **Papp, V.**, Paul, G., Marchese, L., Len, A., Dudás, Z., Fábíán, I., Gurikov, P., Kalmár, J.: Mechanism of Hydration and Hydration Induced Structural Changes of Calcium Alginate Aerogel.
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9. Kéri, M., Forgács, A., **Papp, V.**, Bányai, I., Veres, P., Len, A., Dudás, Z., Fábíán, I., Kalmár, J.: Gelatin content governs hydration induced structural changes in silica-gelatin hybrid aerogels: implications in drug delivery.
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DOI: <http://dx.doi.org/10.1016/j.actbio.2020.01.016>
IF: 8.947
10. Lázár, I., Forgács, A., Horváth, A., Király, G., Szemán-Nagy, G., Len, A., Dudás, Z., **Papp, V.**, Balogh, Z., Moldován, K., Juhász, L., Cserhádi, C., Szántó, Z., Fábíán, I., Kalmár, J.: Mechanism of hydration of biocompatible silica-casein aerogels probed by NMR and SANS reveal backbone rigidity.
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11. **Papp, V.**, Kéri, M., Forgács, A., Len, A., Dudás, Z., Kalmár, J.: Szilika- zselatin aerogélek szerkezete és nedvesedési tulajdonságai.

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április 3-5.. Szerk.: Ádám Anna Adél, Ziegenheim Szilveszter, Fiatal kémikusok Fóruma, Debrecen, 178-183, 2019. ISBN: 9786156018007

Total IF of journals (all publications): 47,337

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The Candidate's publication data submitted to the Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

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