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DOCTORAL SCHOOL OF ENERGY ENGINEERING

PhD THESIS SUMMARY

CONTRIBUTIONS TO THE ASSESSMENT OF RADIONUCLIDE TRANSPORT AND BEHAVIOR THROUGH ENGINEERED BARRIERS OF RADIOACTIVE WASTE DISPOSAL FACILITIES

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CONTEXT AND MOTIVATION

During the period 2019-2024, at the level of the European Union, the first European Joint Programme on Radioactive Waste Management, EURAD, was implemented. As a result of several decades of research, development, and demonstration in the field of safe radioactive waste management and disposal, EURAD's mission was to coordinate research activities of common interest for European Waste Management Organisations (WMO), Technical Support Organisations (TSO), and research institutes. This joint programme aimed to complement national research, development, and demonstration programmes and to strengthen collaboration among European stakeholders involved in radioactive waste management.

The aforementioned programme generated and managed technical knowledge that supports the implementation of Directive 2011/70/Euratom (the Waste Directive), taking into account the different stages of development and progress of the national programmes of the Member States. EURAD's objectives included the development, maintenance, and strengthening of the scientific and technical basis for radioactive waste management, addressing important and complex issues, facilitating interaction among experts, improving knowledge management, encouraging knowledge transfer between organisations, Member States, and generations, involving also civil society.

Within the EURAD programme, CORI (Cement-Organic-Radionuclide Interactions) was one of the work packages dedicated to research, development, and demonstration activities. In this work package, Technologies for Nuclear Energy State Owned Company – Institute for Nuclear Research, RATEN ICN Pitești, participated as a partner. Through its chosen research topics, CORI aimed to improve the level of knowledge and understanding regarding the sorption properties of organic molecules and their influence on radionuclide mobility in the post-closure phase context of geological disposal facilities for long-lived intermediate-level radioactive waste, including surface disposal facilities.

In this context, the research topic addressed in the current thesis was identified, the selection of investigated and studied systems beeing based on the priorities considered by the international scientific community, while also taking into account the main national research directions.

In light of the research topic addressed, the scientific activities focus in the following main directions: the quantification and evaluation of interactions occurring within the cement–organics/radionuclides system, and the improvement of knowledge regarding the solubility and sorption phenomena of radionuclides in cementitious systems, both in the absence and presence of organic molecules and iron. The studies carried out within this work propose an experimental approach that enables the quantitative description of the interactions between radionuclides and cement-based materials, by selecting the following systems for investigation: First, the interactions between pure phases of calcium–silicate–hydrate (C–S–H) at different calcium-to-silicon ratios and uranium were studied. Uranium was selected both as a representative element of the actinide series and due to the fact that, under oxic conditions, it is commonly present in the U(VI) oxidation state, which is considered highly mobile in aqueous environments. Second, the interactions were investigated between CEM I and CEM V hardened cement pastes in various

degradation stages, as these materials represent the main solid matrices used in the design and construction of engineered barrier systems in most disposal concepts. For the investigation of sorption processes occurring in these systems, the organic molecules selected for study were chosen based on the results obtained by RATEN ICN Pitești in CAST project - specifically, ^{14}C-labeled organic compounds generated by the degradation of spent ion-exchange resins from the CANDU reactor. Their presence may influence the performance of the disposal system. The potential effect is related to the formation of complexes in solution with certain radionuclides, which can lead to increased solubility and decreased sorption of radionuclides. The potential competitive effect of iron on sorption sites was also investigated in the studied systems. To evaluate the effect of organic molecules on the mobility of radionuclides within the ternary cement–organics–radionuclides system, ^{63}Ni was selected as the radionuclide of interest. This radionuclide is representative of divalent radionuclides and is considered to be safety relevant in performance assessment of radioactive waste disposal facilities. There is limited information in the scientific literature regarding the effect of organic molecules on nickel sorption in cementitious systems, and no data exist concerning the effect of ^{14}C-labeled formic acid on its mobility.

Therefore, the research objectives of this doctoral thesis are consistent with the current research trends in the field of radioactive waste management. This study complements the current state of knowledge by addressing critical open issues and providing the necessary data set for the evaluation and quantification of interactions occurring within the complex cement–organics–radionuclides systems.

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1. Introduction

The implementation of appropriate solutions to ensure the permanent and safe disposal of radioactive waste represents a major concern for all countries harnessing the benefits of nuclear energy. Radioactive waste generated from various types of activities is classified into distinct categories based on their radioactivity level and/or physical and chemical form, range of management options and alternatives beeing available for their safe disposal [1].

Romania has a comprehensive strategy for radioactive waste management, aligned with the requirements of the International Atomic Energy Agency (IAEA) and the European Union [2]. According to the National Medium - Long-Term Strategy for the Safe Management of Spent Nuclear Fuel and Radioactive Waste, Romania must address the challenge of disposing low- and intermediate-level radioactive waste. Permanent surface disposal is suitable for very low-level waste, requiring less complex arrangements, while low- intermediate-level short-lived waste is planned to be disposed of in near-surface or surface disposal facilities. For long-lived radioactive waste and spent nuclear fuel, the selected option according to the National Strategy is deep geological disposal in stable rock formations at considerable depth, within disposal facilities based on the concept of defense-in-depth, with an implementation target year of 2055.

In all disposal concepts, whether surface or geological disposal of radioactive waste, it is essential to ensure the isolation of waste from the environment and humans, the retention of radioactivity, and the limitation of radionuclide release into the biosphere. To achieve this, disposal facilities rely on a multi-barrier system, which has two main components: the natural barrier (geosphere) and the engineered barrier system. Each component of this in-depth defense strategy fulfills specific safety functions, either individually or in synergy, to ensure the confinement of radioactive waste and its constituents for sufficiently long periods, allowing the decay of radionuclides contained in the disposed waste [3] [4]. The importance of the engineered barrier system relies on its ability to compensate for uncertainties, being designed to provide redundant safety functions and to contribute to the overall robustness of the disposal system [5].

Understanding the sorption mechanisms of radionuclides on the engineered barriers of a disposal system is of fundamental importance when these data are used in repository performance assessment.

This study contributes to the continuously evolving scientific and technical database necessary for selecting robust disposal strategies, by exploring the interactions between radionuclides and cement-based materials under conditions as close as possible to those prevailing in the near-field environment of a disposal facility. By addressing this topic, the aim is to reduce uncertainties associated with performance assessment and to improve the scientific and technical basis for future decisions regarding policies and engineering solutions in the field of radioactive waste management.

Despite the fact that it is widely recognized that organic molecules play a significant role in the mobility and behavior of radionuclides in disposal environments, their cumulative effects on radionuclide transport and on the durability of the cement matrix are still insufficiently

understood and investigated, especially under conditions that closely replicate those present in the disposal environment.

The experimental research carried out addresses this field, focusing on the sorption of radionuclides and evaluating the influence of low molecular weight organic compounds on radionuclide mobility and the performance of the cement barrier used in radioactive waste disposal systems.

The scientific content of the present doctoral thesis corresponds to the ongoing research focus area in radioactive waste management.

2. Materials and Methods

Synthesis of C-S-H Phases in Laboratory Conditions

Under laboratory conditions, the synthesis of C-S-H phases can be carried out using the following methods:

- ✓ The direct reaction method, through which appropriate amounts of reactants (CaO and SiO_2) are brought into contact with the liquid phase in order to form a specific Ca/Si ratio;
- ✓ The hydration of alite or belite.

In this study, for the preparation of the C-S-H suspensions used in the experimental sorption tests, the direct reaction method has been selected, which involves the following reagents addition into the testing tubes: CaO, SiO_2, and double-distilled water or simulated cement pore water (ACW).

The C-S-H phases were synthesized in water that simulates cement pore water, and at the end of the equilibration stage, the suspensions investigated in sorption kinetics tests and in the determination of uranium sorption isotherms have been directly obtained.

Through this method, C-S-H phases corresponding to three different calcium/silicon ratios were synthesized, with a solid-to-liquid (S/L) ratio of ~50 g/L:

- ✓ C/S ratio = 1,8;
- ✓ C/S ratio = 1,6;
- ✓ C/S ratio = 1.

In general, the atomic Ca/Si ratio of the C-S-H phases ranges between 1,7 and 2,0 in hydrated cement pastes corresponding to Stage I, and decreases as the cement undergoes degradation. These pure phases obtained in laboratory correspond to a wide range of degradation stages associated with hardened cement pastes.

Hardened Cement Pastes

Radionuclides sorption tests were carried out on two different types of CEM I hardened cement pastes (Hardened Cement Paste – HCP) and also on CEM V hardened cement pastes, in different degradation stages, covering the entire range of the main degradation stages of cement:

- ✓ CEM I cement paste, Cemex Prachovice prepared at a water-to-cement ratio (w/c) = 0,45
  - Stage I
- ✓ CEM I 52,5 Ordinary Portland Cement (LAFARGE, Val d'Azergues plant), prepared with a w/c = 0,38
  - Stage II
  - Carbonated samples (Stage IV)
- ✓ CEM V/A 32,5 (Portland cement blended with blast furnace slag and fly ash, HOLCIM, Heming plant), ratio w/c = 0,38
  - Stage II
  - Stage III

Analysis of the Composition of Cement Pastes by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The experimental sorption studies, carried out to obtain specific data required for assessing the mobility of radionuclides through the materials in the disposal zone, as well as for understanding the sorption processes, must be correlated with the composition of the studied materials, mainly their major elements content (Ca, Si) and also minor elements (Na, K, Mg, Fe).

The content of major and minor elements in the cement pastes and in the pore water of the cement pastes was determined by inductively coupled plasma - optical emission spectrometry (ICP-OES), a versatile method that allows the simultaneous determination of a large number of elements.

In order to determine, by emission spectrometry, the concentration of various elements of interest in a solid or powdered sample, the elements must first be brought into liquid phase. For this reason, the decomposition and dissolution of the matrix represent an important step in emission spectrometry analysis.

The composition of the cement pastes used in the laboratory experiments was determined from a series of liquid samples obtained by acid dissolution of the hardened cement paste samples based on CEM I and CEM V, in a closed microwave digestion system.

The composition of the mineralized cement paste samples analyzed according to the described experimental protocol is presented în

Table *2-1*.

Table 2-1 The concentration of major oxides in the cement pastes, determined by ICP-OES

	CaO	**Al_2O_3**	**Fe_2O_3**	**MgO**	**K_2O**	**Na_2O**	**SiO_2**
CEM I 52,5	613,64	36,20	49,56	6,02	7,21	2,47	200,87
CEM V/A 32,5	450,48	98,75	33,45	28,84	15,43	3,08	250,63

The optical spectrometry analysis of the solutions obtained from the acid dissolution tests of the CEM I 52.5 and CEM V/A 32.5 cement paste samples shows a lower calcium content determined for the composite cement paste samples (CEM V/A).

Composition of Cement Pore Water

The composition of the major cations in the solution simulated in equilibrium with the CEM I cement paste (ACW – Artificial Cement Pore Water), corresponding to the initial stage of cement degradation at pH = 13.3, is reported in Table 2-2.

Table 2-2 Composition of the ACW stock solution in equilibrium with CEM I HCP

[K]t	**[Na]t**	**[Ca]t**	**[Al]t**	**[S]t**	**[Si]t**
0.18 M	0.114 M	1.6 x E-03 M	5 x E-05 M	2 x E-03 M	5 x E-05 M

The stock solution simulating the composition of pore water in CEM V/A 32.5 cement paste, representative of non-degraded pastes, is presented in Table 2-3.

Table 2-3 Composition of ACW stock solution in equilibrium with CEM V/A HCP

[K]t	**[Na]t**	**[Ca]t**	**[SO_4^{2-}]t**	**[Cl^-]t**
291 mM/L	77 mM/L	2,1 mM/L	0,96 mM/L	0,56 mM/L

Composition of Pore Water in Degraded Cement Pastes

In order to obtain the degradation stages of CEM I 52.5 and CEM V/A 32.5 cement pastes samples by applying the static leaching protocol, the cement paste samples were maintained in the corresponding volumes of degassed double-distilled water. The pH of the suspensions was monitored and used as a reference parameter to indicate the degradation stage. The solutions resulting from the degradation tests were analyzed by ICP-OES spectrometry to determine the concentrations of Al, Ca, K, Na, and Si (Table 2-4).

Table 2-4 Composition of the solutions obtained from the degradation tests of CEM I 52.5 cement pastes determined by ICP-OES

pH	**[K]t**	**[Na]t**	**[Ca]t**	**[Al]t**	**[Si]t**

11,3	5,11E-06 M	1,29E-06 M	4,48E-04M	1,07E-05 M	4,63E-04M

The degradation protocol adopted for CEM V/A cement pastes involves contacting the cement paste samples with a volume of distilled water (DDW). A solid–liquid ratio of 12.5 g/L was selected to achieve a degradation stage free of portlandite, while still hydrated calcium silicate and ettringite phases are present [6]**.** The phases were separated by filtration, after an equilibration period of 15 days.

The solutions resulting from the degradation test were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the concentrations of Al, Ca, K, Na, and Si, and the composition is shown in Table 2-5.

Table 2-5 Composition of the solutions obtained from the degradation test of CEM V/A cement pastes

[K]t	**[Na]t**	**[Ca]t**	**[Al]t**	**[Si]t**
4,32E-04 M	6,09E-08 M	2,15E-04 M	1,05E-04 M	1,72E-04 M

The solutions obtained from the degradation tests were used in the sorption experiments to prepare the stock solutions in which the radionuclides, whose sorption behavior in the cement-based material system was investigated, were dissolved.

Solubility Experiments

The retention or sorption of radionuclides in cementitious systems results from interactions between the radionuclide species dissolved in the solution and the solid matrix surface associated with the cement-based material. The added concentration of the radionuclide must be chosen so that it is well below the solubility limit (precipitation and sorption are often impossible to separate and distinguish in the absence of sorption isotherms).

To avoid the occurrence of precipitation processes, prior to conducting sorption kinetics experiments and sorption isotherms, preliminary experimental tests were carried out to evaluate the operational solubility limit. The values obtained vary significantly within the pH range [11.3 – 13.3], being approximately one order of magnitude higher at pH 11.3 in the cement pore water obtained in the degradation tests.

The results obtained highlight the following:

- ✓ In cement pore water, at pH 13.3, the total and dissolved nickel concentrations are consistent up to a total nickel concentration of approximately 2×10^{-7} M. Beyond this limit, the formation of a precipitate or a colloidal nickel fraction may occur, resulting in

lower Ni concentrations in ACW after the centrifugation and filtration steps, although visually no precipitate was observed in the test tubes.

- ✓ In cement pore water at pH 13.3, when organic molecules (formic acid - HCOOH) are added to the system, the total and dissolved nickel concentrations are not significantly affected compared to the test without HCOOH addition.
- ✓ The average concentration value was calculated, resulting in a nickel concentration of $(1.2 \pm 0.3) \times 10^{-7}$ M. Based on this operational solubility limit of nickel in cement pore water, the test concentrations for the sorption kinetics experiments and the generation of Ni-63 sorption isotherms on non-degraded cement pastes were selected.
- ✓ In the cement pore water resulting from the degradation tests of the cement pastes, at pH 11.3, the total and dissolved nickel concentrations are consistent up to a total nickel concentration of approximately 5×10^{-6} M. Thus, the composition of the pore water from the degraded cement and the pH have a significant influence on the nickel solubility limit at pH 11.3, concentrations in solution beeing one order of magnitude higher compared to those obtained at pH 13.3.
- ✓ The average nickel concentration corresponding to DCW was calculated, resulting in a value of $(2.3 \pm 0.46) \times 10^{-6}$ M. Based on this operational nickel solubility limit in cement pore water at pH 11.3, the test concentrations for sorption kinetics experiments and the Ni-63 sorption isotherms were selected.

3. Experimental Contributions to the Investigation of Radionuclide Sorption

Quantification of U(VI) Sorption on C-S-H Phases

To avoid the precipitation of uranium as calcium or sodium uranate, the uranium concentrations in the sorption kinetics tests and sorption isotherms were selected in the range 10^{-7} M – 10^{-6} M.

Sorption kinetics studies investigate the time required to reach equilibrium or a steady state. In general, short reaction times indicate fast sorption processes, such as ion exchange or surface complexation.

At the established sampling intervals, the solutions were centrifuged and analyzed by fluorimetry to determine the dissolved uranium concentration in the liquid phase. This allows the determination of concentrations in solution and the calculation of the amount of uranium retained on the C-S-H phases, with the results expressed as the percentage uptake (Ati, %) and the distribution ratio (Rd):

$$R_d\ (L/kg) = \frac{[U_{initial}] - [U_{solution}]}{[U_{solution}]} \times \frac{solution\ volume\ (L)}{solid\ mass\ (kg)} \quad (0\text{-}1)$$

The sorption kinetics of uranium on C-S-H phases with C/S ratios of 1.8, 1.6, and 1.0 are graphically represented in Figure 0-1.

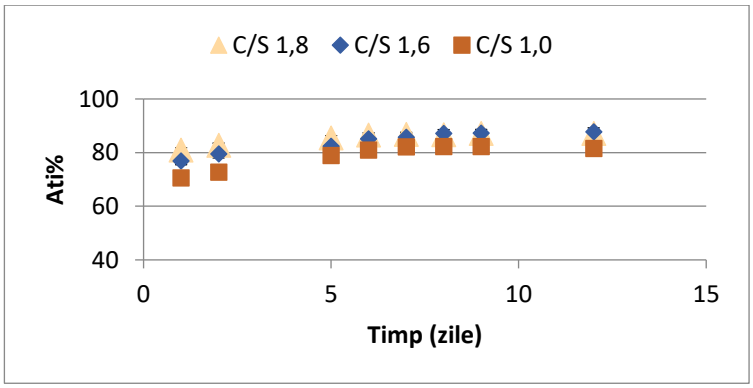


Figure 0-1 Percentage uptake of uranium on C-S-H phases with C/S ratios of 1.8, 1.6, and 1.0

The uranium sorption kinetics experiments on C-S-H phases with a C/S ratio of 1.8 in artificial cement pore water, at pH = 13.3 and a solid-to-liquid ratio of 5×10^{-2} kg/L, show distribution ratio (Rd) values ranging from 9.27×10^{1} to 1.38×10^{2} L/kg. These results are consistent with the values obtained by Tits et al. (2018) [7] for U(VI) sorption on C-S-H phases synthesized in simulated cement pore water, at a solid-to-liquid ratio of 5×10^{-3} kg/L.

In all systems, the sorption kinetics occurs in two stages: after an initial very rapid uranium uptake kinetic, which takes place within approximately one day of suspension contact, the Rd values continue to increase slowly until a steady state is reached after about 12 days of suspension equilibration. A similar sorption kinetics behavior was also reported by Pointeau et al. (2004) [6].

Such a result may suggest that the initial mechanism involves a surface sorption process, followed by the slow incorporation into the structure of the C-S-H phase.

The sorption isotherms of uranium on C-S-H phases with C/S ratios corresponding to different degradation stages of hydrated cement pastes are illustrated in Figure 0-3 și 3-4.

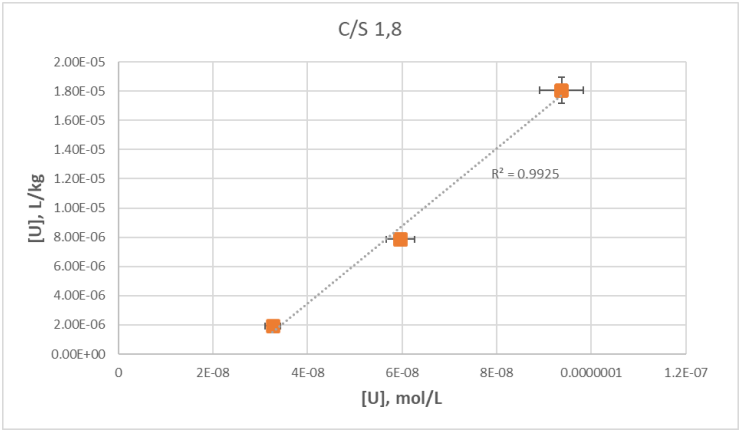


Figure 0-2 Uranium sorption isotherm on C-S-H phases with C/S ratio of 1,8

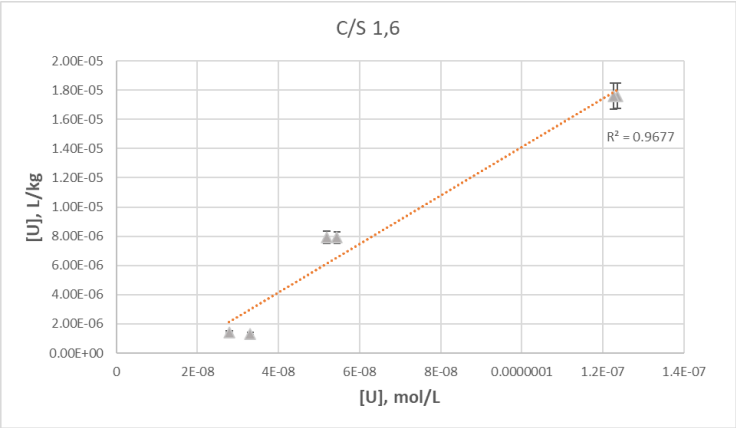


Figure 0-3 Uranium sorption isotherm on C-S-H phases with C/S ratio of 1,6

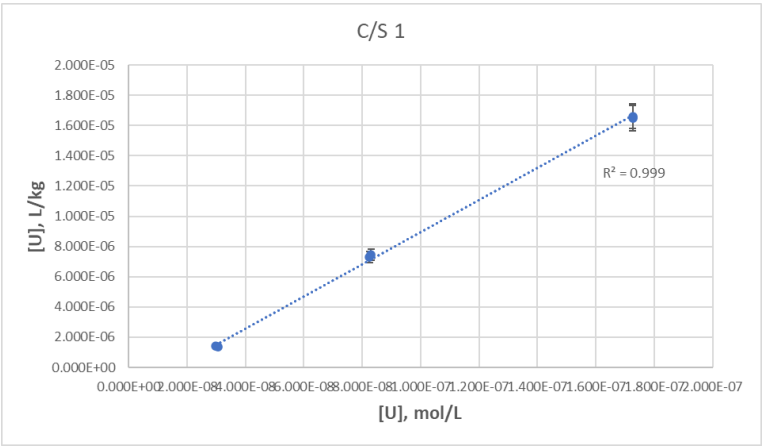


Figure 0-4 Uranium sorption isotherm on C-S-H phases with C/S ratio of 1,0

The correlation coefficients for the linear sorption model were 0.9925 for the data corresponding to uranium sorption on C-S-H phases with a C/S ratio of 1.8, 0.9677 for phases with a C/S ratio of 1.6, and 0.999 for a C/S ratio of 1.0.

The presence of calcium facilitates uranium sorption in the cement-based material system, with the distribution coefficient (Kd) values, determined from the slope of the isotherms, shown in Table 3-1. The obtained values were found to decrease with the decreasing of the C/S ratio.

Table 0-1 Distribution coefficients of uranium on C-S-H phases

Raport C/S	Kd (L/kg)
1	**$1{,}06 \cdot 10^{2}$**
1,6	**$1{,}66 \cdot 10^{2}$**
1,8	**$2{,}66 \cdot 10^{2}$**

Uranium is well retained on all the C-S-H phases investigated in the laboratory experiments (C/S = 1.8; 1.6; 1.0), with distribution coefficient (Kd) values ranging from 266 L/kg to 106 L/kg under the conditions present in the cement-based materials system.

The results of the batch experiments conducted in this study suggest a surface-controlled sorption behavior: rapid reaction kinetics and sorption approximated by the linear model. However, uncertainties arising from the batch sorption experiments, particularly in the cement-based materials system, may obscure the identification of other structural incorporation processes. The aqueous speciation of hexavalent actinides under alkaline conditions, in the presence of calcium, it is not sufficiently explored, but it is assumed that ternary complexes are formed, with calcium uranate being the most likely solubility-limiting solid phase.

Sorption of ^{14}C-Labeled Formic Acid on Cement Pastes

In order to optimize the experimental parameters, preliminary tests proposed solid-to-liquid (S/L) ratios in the range of 1–10 g/L for conducting laboratory sorption experiments using the batch method. The sorption tests were performed in duplicate, using a solid-to-liquid ratio (S/L) of 4 g/L, established as a constant experimental parameter throughout the suspension contact stage.

To investigate the sorption process, three initial concentrations of ^{14}C-labeled formic acid ($H^{14}COOH$) were selected, ranging from 6.7×10^{-7} to 1.3×10^{-6} mol/L. In this experimental set, after equilibration periods of 3 and 9 months, no detectable uptake of $H^{14}COOH$ was observed on CEM I hardened cement pastes. Considering the uncertainties associated with the measurements, the ^{14}C activity determined in the analyzed solutions was practically identical to the initially added activity, indicating the absence of a sorption process.

Subsequently, the solid-to-liquid ratio in the experimental system was increased to ~100 g/L by suspending 1 g of cement with particle size ≤ 63 µm in 10 mL of solution. The powdered HCP samples were suspended and pre-equilibrated with 9 mL of simulated cement pore water (ACW) or with the corresponding solutions obtained from the degradation of the cement pastes. Afterwards, 1 mL volumes of ^{14}C-labeled formic acid solution were added to each test tube.

Additionally, in the laboratory experiments, tests were conducted to evaluate the influence of iron ions addition on the ^{14}C-labeled formic acid (H^{14}COOH) uptake on CEM I cement pastes, using the CEM I HCP Cemex Prachovice sample. The experimental protocol adopted was the same as described previously: solid-to-liquid ratio (S/L) – 100 g/L, added Fe concentration – 5 mg/L, and ^{14}C-labeled formic acid concentration – 3.96×10^{-7} mol/L.

The results obtained from the ^{14}C-labeled formic acid sorption experiments on CEM I 52.5 cement pastes corresponding to Degradation Stage II, as well as on carbonated cement pastes (Figure 3-5), demonstrated good reproducibility of the experimental data. This consistency was observed for the parallel samples, across different sampling periods, and during the monitoring of ^{14}C activity concentrations.

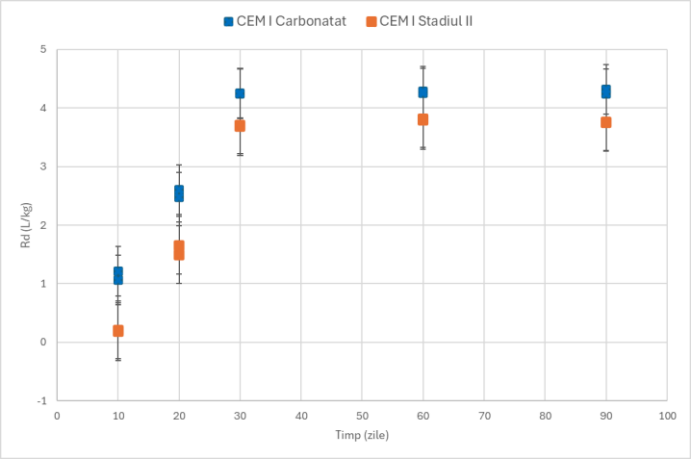


Figure 0-5 H ^{14}COOH uptake on CEM I 52,5 hardened cement paste, as a function of time and cement degradation state

The distribution ratio values did not change significantly after 30 days of equilibration and monitoring of H^{14}COOH concentrations in the suspensions within the test tubes. The results obtained for the carbonated CEM I 52.5 samples show slightly higher Rd values (2,4÷4,2 L/kg) under the same experimental conditions. These results indicate that the degradation state of the cement may have an impact on the adsorption of H^{14}COOH on CEM I 52.5 hardened cement pastes.

In the experiments investigating the influence of added iron ions on the retention of ^{14}C-labeled formic acid on CEM I cement pastes (CEM I UJV) from a different source (Cemex Prachovice) with a w/c ratio of 0.45 and the same solid-to-liquid ratio of 100 g/L, it was observed that the obtained distribution ratio values correlate very well with those obtained for non-degraded CEM I 52.5 cement paste (LAFARGE) (Rd = 1.03÷3.7 L/kg). Furthermore, in this system, the influence of iron on the sorption values was evaluated, showing a decrease in sorption (Rd,max = 1.88 L/kg) (Figure 3-6).

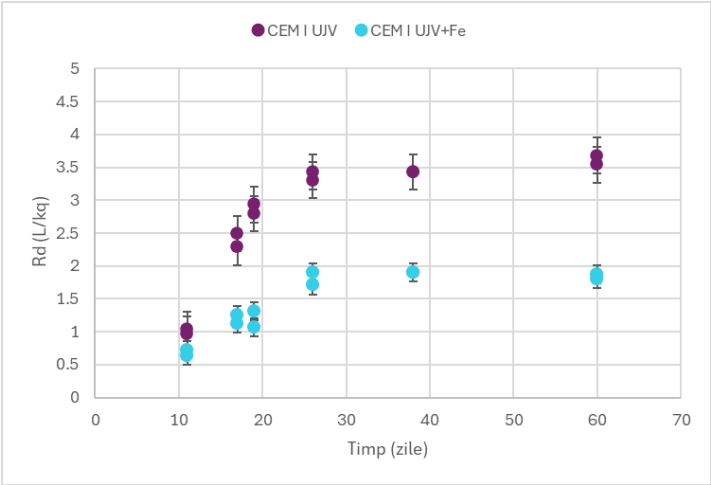


Figure 0-6 Sorption of H^{14}COOH on CEM I Cement Pastes in the Ternary Cement–Organic–Fe System as a Function of Contact Time

The reduction effect on sorption is quantified by the sorption reduction factor (SRF), calculated as the ratio between the Rd values obtained in the presence and in the absence of iron ions in the system (Equation 3-1).

$$\boldsymbol{FRS} = \frac{R_d(RN)}{R_d(RN+Fe)} \qquad (3\text{-}1)$$

The sorption reduction factor values calculated for this system are very close to 2. In general, for SRF values < 2, the sorption decrease effect is considered negligible, SRF = 1 indicates no effect, SRF = 2 is considered a moderate effect, and values greater than 2 indicate a significant sorption reduction effect.

The sorption reduction factor is specific to a given set of experimental conditions. For this dataset, the reduction effect on H^{14}COOH sorption on CEM I cement pastes is weak to moderate.

The results of the sorption experiments conducted to investigate the uptake of ^{14}C-labelled formic acid on CEM V/A 32.5 cement pastes are shown in Figure 0-7 both for samples subjected to the degradation protocol and for non-degraded samples (Rd = 0.9–3.09 L/kg). The results also show a slightly higher retention tendency of H^{14}COOH on cement paste samples subjected to the degradation protocol (Rd = 1.63–4.66 L/kg).

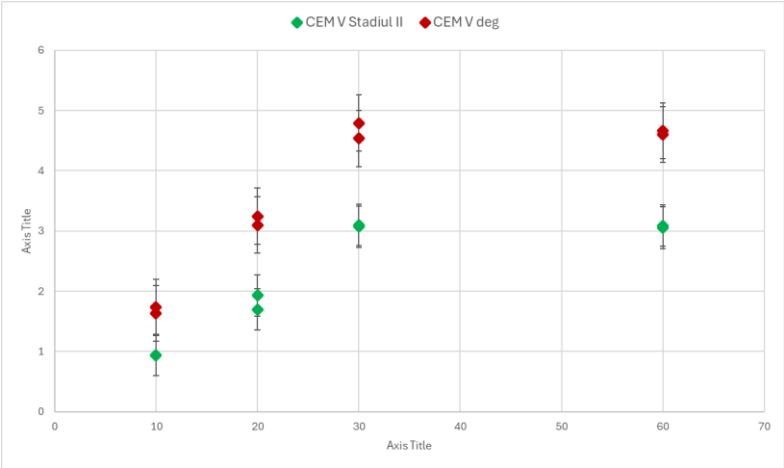


Figure 0-7 Distribution ratio (Rd) values obtained for the sorption of H^{14}COOH on CEM V HCP

In Table 3-2 evolution as a function of time of all distribution ratio values obtained in the different experimental systems studied for H^{14}COOH retention is illustrated.

Table 0-2 Distribution ratio values obtained for the sorption of H^{14}COOH in the studied experimental systems

HCP	Rd L/kg
CEM I Cemex Prachovice, ratio w/c = 0,45 - Stage I	3.61
CEM I Cemex Prachovice, ratio w/c = 0,45 - Stage I + Fe	1.84
CEM I 52,5 Lafarge, ratio w/c = 0,38 - Stage II	3.76
CEM I 52,5 Lafarge, ratio w/c = 0,38 - carbonated	4.28
CEM V/A, Holcim, ratio w/c = 0,38 - Stage II	3.09
CEM V/A, Holcim, ratio w/c = 0,38 - Stage III	4.63

The Rd values for each individual system, estimated as the average of the values obtained for the parallel samples, were calculated to derive the order of distribution ratio values characteristic for formic acid uptake on the investigated cement pastes, as follows: $Rd_{CEM\ I}$ = 3.76 L/kg; $Rd_{carbonated\ CEM\ I}$ = 4.28 L/kg; $Rd_{CEM\ I\ UJV}$ = 3.61 L/kg; $Rd_{CEM\ I\ UJV+Fe}$ = 1.84 L/kg; $Rd_{CEM\ V}$ = 3.09 L/kg; $Rd_{degraded\ CEM\ V}$ = 4.63 L/kg. This results in the following retention order of H^{14}COOH in the studied systems: degraded CEM V > carbonated CEM I > CEM I UJV > CEM V > CEM I UJV+Fe.

4. Investigation of Nickel Sorption in the Cement–Radionuclide–Organic System

Sorption of ^{63}Ni on CEM I Cemex Prachovice Cement Pastes

The laboratory experiments conducted to study ^{63}Ni uptake on CEM I hardened cement paste prepared at a w/c ratio of 0.45 were performed in duplicate, in 50 mL centrifuge tubes at room temperature. The total Ni concentrations added to the system were selected and calculated to remain below the solubility limit determined in the laboratory experiments.

The nickel concentrations added to the system ranged between 10^{-9} M and 10^{-8} M, and four test concentrations within this range were selected for kinetic and sorption experiments.

The generic and systematic approach of the experimental design led to the identification of the following systems that were studied:

- ✓ Interaction of the radionuclide of interest with the cement paste;
- ✓ Interaction of the radionuclide of interest with HCP and the addition of organic molecules to the system;
- ✓ Interaction of the radionuclide of interest with the previous systems, including the addition of iron to the studied system.

Considering that both ^{63}Ni and ^{14}C are β-emitters, in all experiments investigating the influence of organic compounds, stable formic acid was used to avoid potential experimental difficulties, as well as the need for additional separation steps for the two radionuclides.

The nickel concentration range in the systems for which the characteristic sorption isotherms were studied and modeled is 10^{-9} M ≤ $[RN]_0$ ≤ 10^{-8} M. The results show rapid ^{63}Ni sorption kinetics in all three studied systems, indicating that under these experimental conditions, the addition of 5 mg/L Fe and 10^{-3} M formic acid does not affect the rate at which sorption equilibrium is reached.

^{63}Ni sorption isotherms obtained by modeling the experimental data using the linear sorption model (Aeq vs. Ceq) are shown in Figure 4-1, and the corresponding distribution coefficients, Kd, are presented in Table 4-1, together with the correlation coefficients of the experimental data with the linear sorption model (R^2) and the calculated mean total error values.

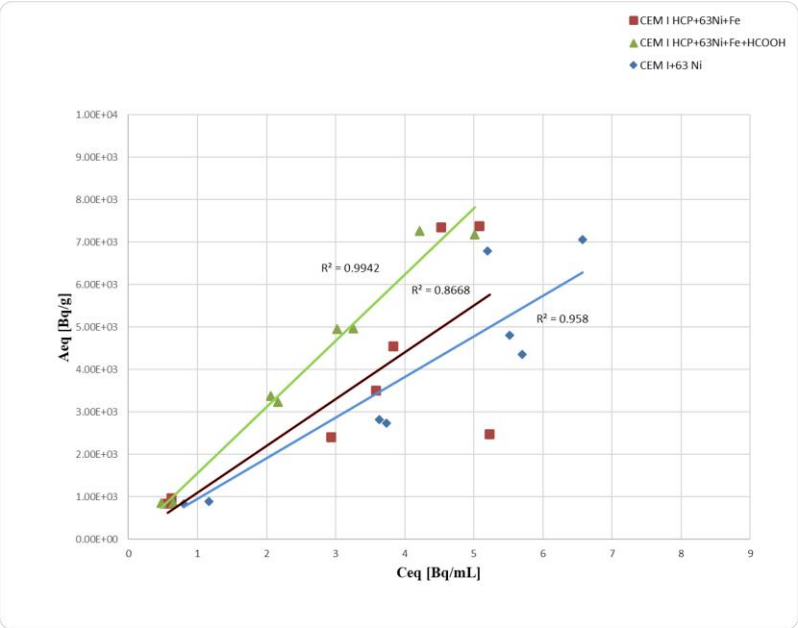


Figure 4-1 ^{63}Ni linear sorption isotherm experimental data on CEM I HCP (Stage I)

Table 4-1 ^{63}Ni sorption parameters in the investigated systems, derived from the linear sorption model

Investigated system	**Linear sorption model $A_{eq} = K_d \cdot C_{eq}$**		
	K_d [L/Kg]	R^2	ζ (%)
CEM I HCP +^{63}Ni	956,4	0,958	19,62
CEM I HCP +^{63}Ni+Fe	1102,6	0,867	32,25
CEM I HCP +^{63}Ni+Fe+HCOOH	1560,3	0,994	6,84

The data reported in Figure 4-1 și Table 4-1 show a good correlation of the experimental data with this sorption model for the binary and quaternary systems (R^2 = 0.985 and 0.994, respectively), although with a mean total error of 19.62% for the ^{63}Ni–CEM I HCP system. The Kd values calculated by fitting the experimental data with the linear sorption model indicate lower ^{63}Ni sorption on CEM I HCP compared to the systems with added Fe and with both Fe and HCOOH, under the adopted experimental conditions (Kd binary system < Kd ternary system < Kd system with 5 mg/L Fe and 10^{-3} M HCOOH).

Freundlich sorption isotherms are applicable to sorption processes occurring on heterogeneous surfaces, resulting in an expression that also defines the exponential distribution of sorption active sites. The Freundlich model describes a reversible, non-ideal adsorption process [8] [9]. The results of experimental data modeling obtained in this study using the Freundlich model are illustrated in Figure 4-2, and the sorption data characterizing this model are presented in Table 4-2.

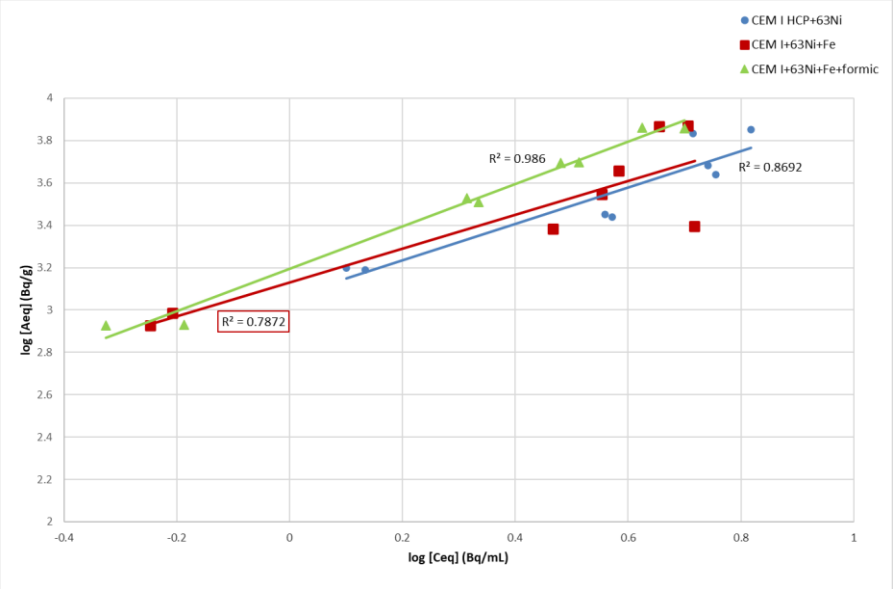


Figure 4-2 ^{63}Ni sorption isotherms on CEM I HCP fitted with the Freundlich model

Table 4-2 ^{63}Ni sorption parameters derived from the Freundlich model for the investigated systems

Investigated system	**Freundlich sorption model** $A_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}}$				
	K_F [L/Kg]	$\frac{1}{n}$	n	R^2	ζ (%)
CEM I HCP +^{63}Ni	1153,72	0,869	1,15	0,869	3,12
CEM I HCP +^{63}Ni+Fe	1348,34	0,787	1,27	0,787	32,30
CEM I HCP +^{63}Ni+Fe+HCOOH	1563,15	0,999	1,001	0,986	9,53

The analysis of the data fitted with the Freundlich model shows a good correlation of the experimental data only for the system with formic acid addition ($R^2 = 0.986$).

The experimental data obtained were analyzed using a third sorption model, the Langmuir model, which provides the best fit to the experimental data. In Table 4-3 and Figure 4-3, the highest R^2 values for all three systems are observed when the experimental data are fitted using this sorption model. In Table 4-3, the sorption parameters corresponding to this model, the correlation coefficients (R^2), and the mean total errors are presented.

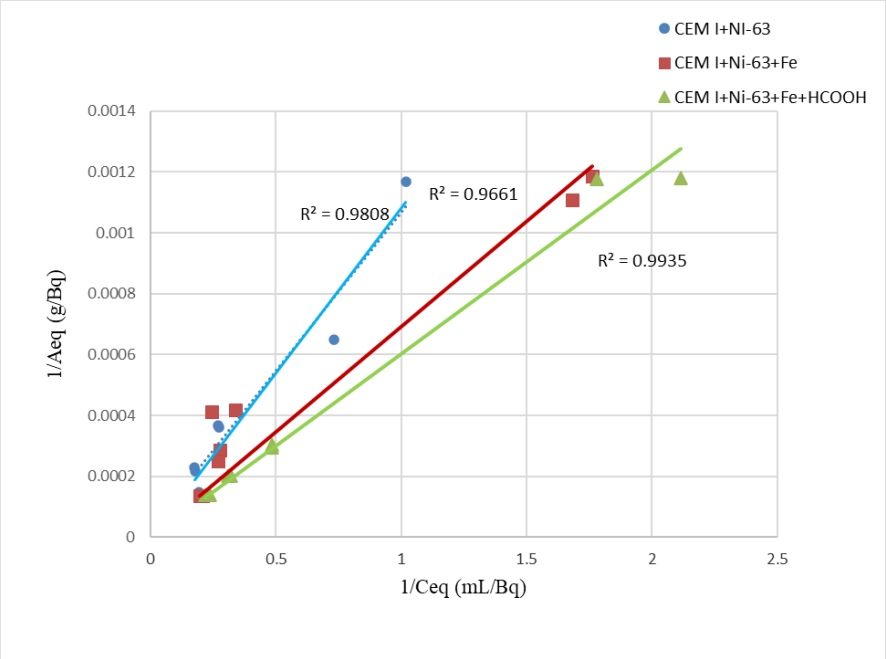


Figure 4-3 ^{63}Ni sorption isotherms on CEM I HCP fitted with the Langmuir model (Lineweaver–Burk)

Table 4-3 ^{63}Ni sorption parameters derived from the Langmuir model

Investigated system	**Langmuir sorption model** $\frac{1}{A_{eq}} = \frac{1}{A_{max}} + \frac{1}{A_{max}K_L}\frac{1}{C_{eq}}$			
	K_L [L/Kg]	A_{max} [Bq/Kg]	R^2	ζ (%)
CEM I HCP +^{63}Ni	0,027	3,33E+04	0,980	12,34
CEM I HCP +^{63}Ni+Fe	1,667	1,00E+04	0,966	12,90

CEM I HCP +^{63}Ni+Fe+HCOOH	0,017	1,00E+05	0,994	11,27

The experimental data obtained in the ternary system (CEM I HCP – ^{63}Ni – Fe) were well fitted only with this sorption model, showing good R^2 values (0.966), compared to the other models (R^2 = 0.867 and 0.787 for the linear and Freundlich models, respectively).

The mean total error values of the characteristic parameters obtained from the Langmuir and Freundlich sorption models suggest that both models satisfactorily fit the experimental data, but only for two of the three investigated systems: CEM I HCP + ^{63}Ni and CEM I HCP + ^{63}Ni + Fe + HCOOH, whereas for the ternary system CEM I HCP + ^{63}Ni + Fe, only the Langmuir model provides a good fit to the experimental dataset.

The experimental data obtained for ^{63}Ni sorption on CEM I HCP (w/c = 0.45) corresponding to the first stage of cement degradation, at pH 13.3 and a solid-to-liquid ratio (S/L) of 5 g/L, with and without the addition of Fe and Fe + HCOOH, are best fitted by the Freundlich and Langmuir sorption models.

Sorption of ^{63}Ni on CEM I 52.5 Cement Pastes – Lafarge

In order to study the sorption of ^{63}Ni on CEM I 52.5 Lafarge cement pastes, sorption kinetics tests were conducted to evaluate the time required to reach equilibrium in solution. The kinetics test was performed at a total nickel concentration of 1×10^{-7} M, and the time evolution of the radionickel activity concentration in the liquid phase was measured at different time intervals: 5, 12, 21, and 30 days after the initial contact of the suspensions in the test tubes. The results were processed, the distribution ratio (Rd) values were calculated, and their evolution over time is depicted in Figure 4-4.

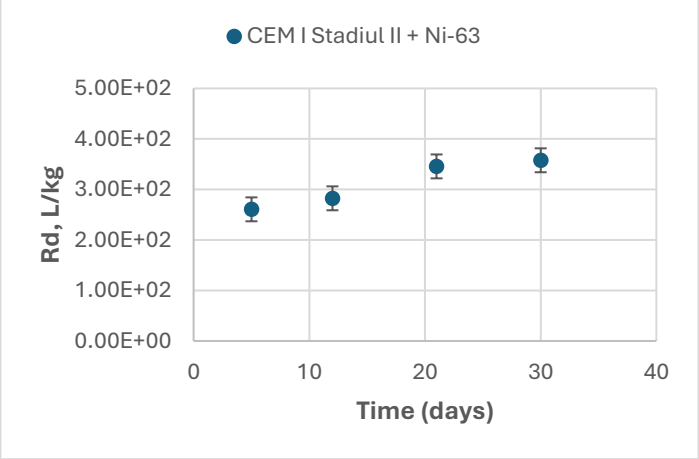


Figure 4-4 Time evolution of the distribution ratio (Rd) values for nickel on non-degraded CEM I cement pastes; S/L = 3 × 10⁻² kg/L

The results of the experimental tests conducted in the ternary system (cement–^{63}Ni–HCOOH), aimed at evaluating the effect of organic molecules on radionickel mobility, were processed, graphically represented, and are shown in Figure 4-5. The results obtained from the sorption kinetics experiments, in the presence and absence of organic molecules, show relatively rapid sorption and confirm the initial hypothesis that sorption is reduced in their presence. A Sorption Reduction Factor (SRF) was calculated as the ratio between the Rd values in the binary system (cement + ^{63}Ni) and those in the ternary system (cement + ^{63}Ni + HCOOH).

The obtained SRF value of 1.94 indicates a negligible but quantifiable sorption reduction effect, with lower distribution ratio (Rd) values observed in the ternary system.

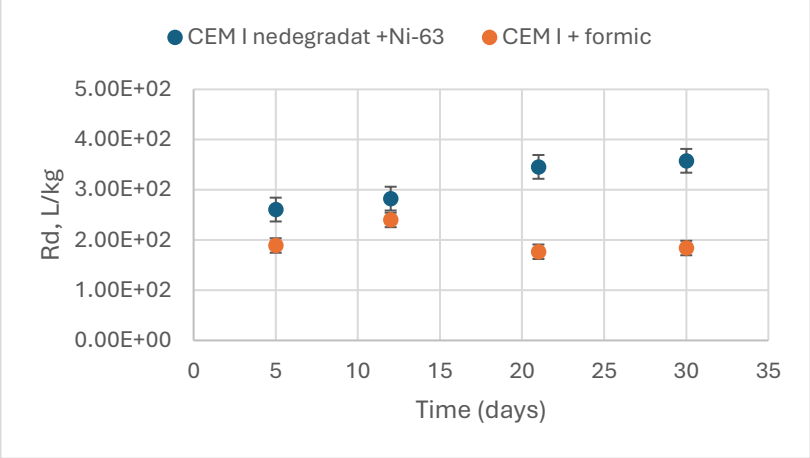


Figure 4-5 Distribution ratio (Rd) values characteristic of ^{63}Ni sorption on CEM I 52.5 cement pastes, Stage II, in the presence of formic acid (10^{-3} M); comparison with the results obtained in the binary system

Sorption of Nickel on Carbonated CEM I 52.5 – Lafarge Cement Pastes

Similar experimental conditions were adopted in the ^{63}Ni sorption kinetics test on carbonated cement pastes, with the evolution of ^{63}Ni concentration in the liquid phase analyzed in both the binary and ternary systems to evaluate the influence of organic molecules on sorption.

The time evolution of the distribution ratio (Rd) values for the two systems is presented in Figure 4-6.

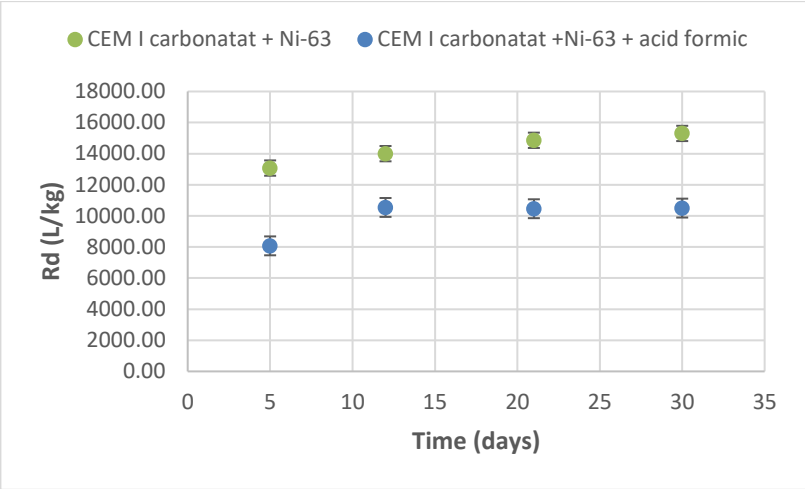


Figure 4-6 Distribution ratio (Rd) values characteristic for ^{63}Ni sorption on carbonated CEM I 52.5 cement pastes in the absence and presence of formic acid (10^{-3} M)

Based on the results presented in Figure 4-6, it can be observed that ^{63}Ni is strongly retained on carbonated CEM I cement pastes, and the degradation state and composition of the cement significantly, and positively, influence radionickel sorption. Although the occurrence of a precipitation process might be initially assumed, it should be noted that the concentration range adopted in these experiments is well below the operational solubility limit determined in the laboratory tests.

The influence of adding organic molecules to the studied system is also quantifiable in this set of laboratory experiments. In the ternary system of carbonated cement–^{63}Ni–HCOOH, the calculated Rd values indicate a higher mobility of the investigated radionuclide, with a Sorption Reduction Factor (SFR) of approximately 1.46. The SRF value indicates a negligible effect of formic acid on radionickel mobility under these experimental conditions.

Sorption of ^{63}Ni on CEM V/A Cement Pastes

The sorption tests aimed at evaluating nickel mobility on non-degraded and degraded CEM V/A cement pastes were also conducted in a controlled atmosphere by purging a small, constant flow of nitrogen inside the glove box.

The sorption kinetics experiments and those aimed at obtaining the characteristic ^{63}Ni sorption isotherms on hydrated CEM V cement pastes were performed at a solid-to-liquid ratio (S/L) of 5 g/L^{-1}.

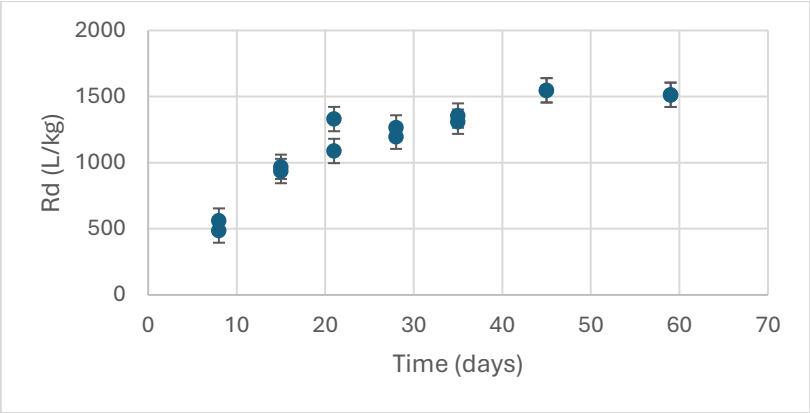


Figure 4-7 ^{63}Ni sorption kinetics on CEM V/A cement pastes

The results of the sorption kinetics test shown in Figure 4-7 illustrate that in this system, the reaction kinetics are slower than in the other studied systems, with equilibrium being reached after 45 days. Therefore, the experiments to obtain the sorption isotherms were conducted with a suspension equilibration time of 50 days. Sorption isotherm experiments to evaluate the distribution coefficient were carried out for five initial nickel concentrations: 5×10^{-9} M, 1×10^{-8} M, 5×10^{-8} M, 1×10^{-7} M, and 5×10^{-7} M.

The obtained results were processed in terms of the concentration in the aqueous phase and the amount sorbed on the cement paste at equilibrium. The experimental data were fitted using known sorption models: the linear model (Figure 4-8) and Freundlich model (Figure 4-9), the only theoretical sorption models that fit the experimental data obtained for evaluating ^{63}Ni mobility on CEM V cement pastes at Degradation Stage II, with good correlation coefficients of 0.97 and 0.984, respectively.

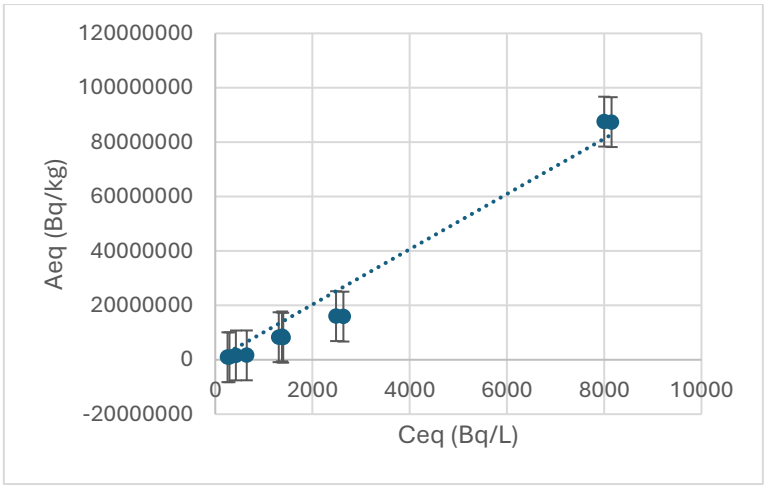


Figure 4-8 Linear sorption isotherm of ^{63}Ni on CEM V/A cement pastes at Degradation Stage II

The sorption parameters derived from fitting this experimental dataset with theoretical sorption models are presented in Table 4-4.

The results of the sorption tests on CEM V cement pastes at Degradation Stage II indicate that ^{63}Ni is much more strongly retained on these pastes compared to CEM I cement paste samples at the same degradation stage.

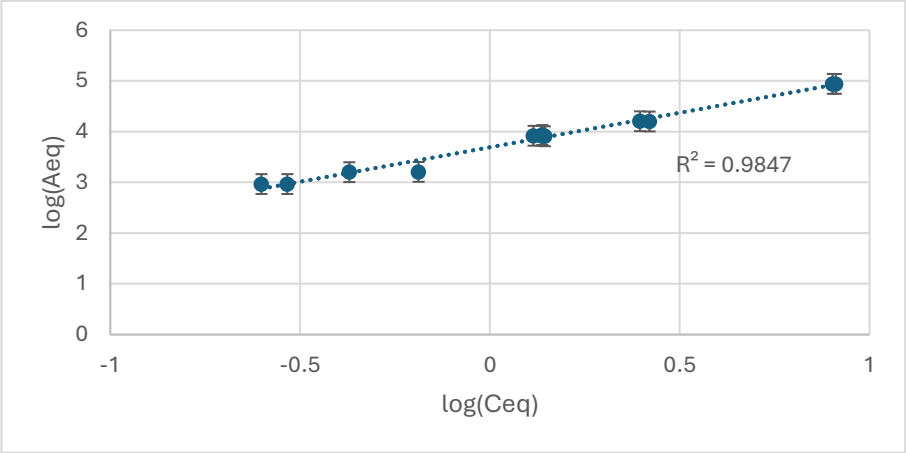


Figure 4-9 Correlation of ^{63}Ni sorption data on CEM V/A cement pastes with the Freundlich sorption model

Table 4-4 Summary of the characteristic sorption parameters of ^{63}Ni on CEM V cement pastes (Degradation Stage II), derived from fitting the experimental data with the linear sorption model and the Freundlich model

Sorption model	**Sorption parameters and associated statistical parameters**	
Modelul liniar: $A_{eq} = K_d \cdot C_{eq}$	K_d [L/kg]	10,16E+03
	R^2	0,9736
	ξ [%]	26,262
Modelul Freundlich: $A_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}}$	K_F [L/kg]	4,925E+03
	1/n	0,74
	R^2	0,9847
	ξ [%]	5,93

Although both models accurately fit the experimental data, the mean total errors obtained from fitting the experimental data with the Freundlich model are lower compared to the mean total error calculated for the linear model.

In the ternary systems (CEM V cement paste–^{63}Ni–formic acid), the influence of organic molecules on the mobility of the radionuclide of interest was evaluated under the same experimental conditions, keeping the formic acid concentration constant.

This experimental dataset was the most challenging to represent and interpret, as the sorption kinetics did not exhibit any clear trend. The results of the ^{63}Ni sorption kinetics experiments on CEM V cement pastes in the ternary system, in which the influence of formic acid was evaluated, were graphically represented and are presented in Figure 4-10, together with the results obtained in the binary system (CEM V HCP–^{63}Ni), to aid in visually assessing the influence of organic molecules on the mobility of the radionuclide under study. In the ternary system, the calculated distribution ratio values are higher than those in the system without added formic acid at certain equilibration times, while toward the end of the equilibration period, the values tend to decrease, confirming the initial hypothesis of reduced sorption and increased mobility of nickel on CEM V cement pastes in the presence of organic molecules.

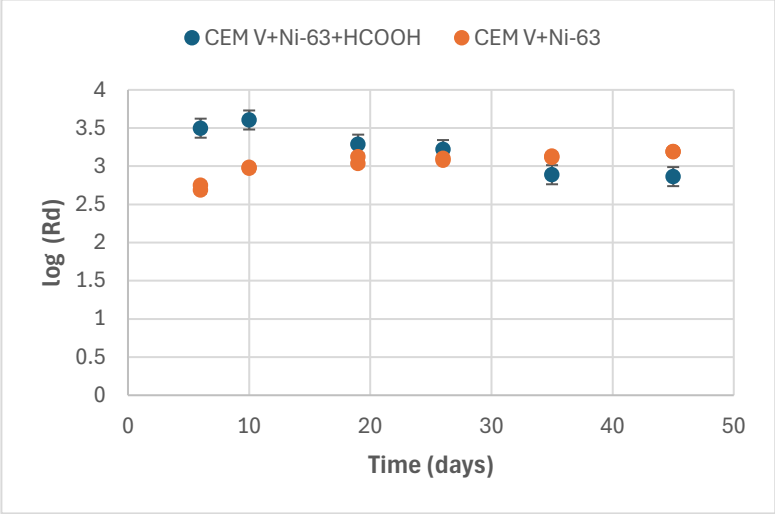


Figure 4-10 Sorption kinetics of ^{63}Ni on CEM V/A cement pastes in the binary and ternary systems (with 10^{-3} M formic acid added to the system)

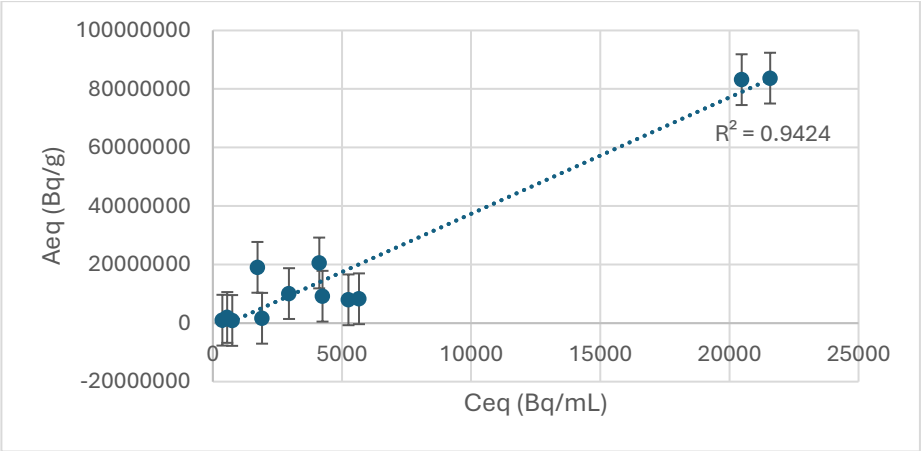


Figure 4-11 Linear sorption isotherm of ^{63}Ni on CEM V cement pastes (Degradation Stage II) in the presence of 10^{-3} M formic acid

The only model that fits the experimental data with a good correlation coefficient (R^2 = 0.9424) is the linear model (Figure 4-11). The distribution coefficient, Kd, characterizing the ^{63}Ni sorption on CEM V cement pastes at Degradation Stage II in the presence of organic molecules, was derived from the slope of the linear isotherm. Its value is 3.976 × 10^3 L/kg, which is lower than the distribution coefficient obtained in the binary system. The mean total error calculated for this dataset is 26.42%.

The laboratory experiments also investigated the influence of the degradation state of CEM V cement paste on the mobility of the radionickel, using the same conditions and keeping the experimental parameters constant. In Figure 4-12 the sorption isotherm of ^{63}Ni on CEM V cement pastes subjected to the degradation protocol is presented, obtained from the processing of an experimental dataset that was difficult to interpret. The correlation coefficient is 0.94, and the distribution coefficient derived from the slope of the isotherm is 1.44 × 10^3 L/kg.

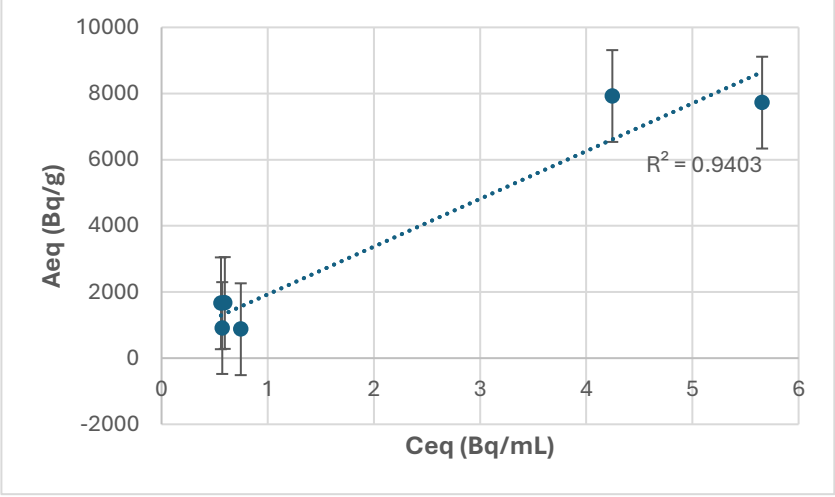


Figure 4-12 ^{63}Ni linear sorption isotherm on CEM V/A cement pastes (Deg. St. III)

Interpreting and drawing conclusions from the experimental results, particularly from the sorption experiments on CEM V/A cement pastes, is very challenging, mainly due to discrepancies observed in the results obtained for parallel samples with the same equilibration period of the suspensions. The distribution ratio values are higher than those in the system without added formic acid at certain equilibration times, while toward the end of the equilibration period, the values tend to decrease.

The linear model is the only model that fits the experimental data with a good correlation coefficient ($R^2 = 0.9424$)—yields a distribution coefficient, Kd, characteristic of ^{63}Ni sorption on CEM V/A cement pastes at Degradation Stage II in the presence of organic molecules, of 3.976×10^3 L/kg. This distribution coefficient is lower than that obtained in the binary system (1.016×10^4 L/kg).

CEM V/A cement pastes exhibit a higher affinity for ^{63}Ni than CEM I cement pastes, a behavior attributed to the fact that hydrated composite cement pastes contain higher percentages of C–S–H phases and lower percentages of portlandite.

5. Conclusions

The results obtained in this work fall within the scope of current research topics both at the national and international level and highlight important aspects, presented below.

The high sorption capacity of hydrated cement-based materials is mainly determined by the significant presence of calcium silicate hydrate (C-S-H) phases. These phases have very large reactive surfaces, which provide a high number of sorption sites accessible to the metallic cations present in radioactive waste for surface complexation.

Uranium is well retained on C-S-H phases with different C/S ratios, corresponding to various stages of cement degradation, the values of the distribution coefficients obtained from the slope of the isotherms being closely related to the calcium/silicon ratios.

The sorption of ^{14}C-labelled formic acid is very low, but not zero, on CEM I cement pastes in degradation stages I and II, with distribution ratio values ranging between 1.6–3.7 L/kg, depending on the testing period. This indicates the presence of sorption sites capable of incorporating, probably within the ettringite structure, a small fraction of the formic acid. The results obtained for carbonated CEM I cement paste samples show slightly higher Rd values (2.4–4.2 L/kg), obtained under the same experimental conditions. The reduction effect of $H^{14}COOH$ sorption in the presence of iron ions was quantified by the sorption reduction factor (SRF), yielding values characteristic of a negligible effect. For CEM V cement pastes, the results also illustrate a slightly higher tendency for $H^{14}COOH$ retention in samples subjected to the degradation protocol (Rd = 1.63–4.66 L/kg).

The experimental data obtained for ^{63}Ni sorption on CEM I HCP corresponding to the first degradation stage of cement, at pH 13.3 for a solid/liquid ratio (S/L) of 5 gL^{-1}, with and without the addition of Fe and Fe plus HCOOH, demonstrate that under the adopted experimental

conditions, iron and formic acid have the potential to influence nickel mobility under the hyper-alkaline conditions existing in the near field of a radioactive waste disposal facility.

The results of the experimental tests obtained in the ternary system (CEM I 52.5 cement – ^{63}Ni – HCOOH), aimed at evaluating the effect of organic molecules on the mobility of radionickel, confirm the initial hypothesis that sorption is reduced in their presence. A Sorption Reduction Factor (SRF) was calculated as the ratio between the Rd values in the binary system (cement + ^{63}Ni) and those obtained in the ternary system (cement + ^{63}Ni + HCOOH).

From the sorption tests of ^{63}Ni on carbonated CEM I 52.5 cement pastes, it is observed that nickel is strongly retained in these systems, with the degradation state and the composition of the cement positively influencing radionickel sorption. In the ternary system (carbonated CEM I cement – ^{63}Ni – HCOOH), the calculated Rd values indicate enhanced sorption of the investigated radionuclide.

The sorption test results on CEM V/A cement pastes in degradation Stage II indicate that ^{63}Ni is retained much more effectively on these materials compared to CEM I cement paste samples corresponding to the same degradation stage.

Original Contributions

In order to perform a safety assessment and evaluate the long-term evolution of a disposal facility, it is necessary to establish a scientific database through which the contaminant migration delay functions can be quantified. Thus, through my own experimental research, I synthesized in the laboratory the main phases present in hydrated cement and evaluated the sorption of uranium onto these phases, obtaining results that could be validated against data published in the scientific literature.

In laboratory solubility experiments, I evaluated the operational solubility limit of nickel in cement pore water under the experimental conditions adopted in the studied systems and tests. The calculated values subsequently served as reference points for selecting concentrations in the sorption kinetics experiments and in those aimed at obtaining sorption isotherms.

I also evaluated the variation of distribution ratios/coefficient values characteristic of radionuclides considered safety relevant for low- and intermediate-level radioactive waste disposal facilities, as a function of the cement hydration phases evolution and the composition of hydrated cement pastes, covering the full range of degradation states.

I correlated the experimental data obtained in sorption experiments with a variety of theoretical models, thus evaluating the best approximation of these data.

By adopting a solid/liquid ratio considered “atypical” at the laboratory sorption experiment scale (100 g/L), but representative of real conditions existing in the near field of a disposal facility with cement-based engineered barriers, I have quantified the interaction of ^{14}C-labelled formic acid with hardened cement pastes and their components, and evaluated the effect of its interaction with iron from the disposal environment. Such data are scarcely available in the scientific literature, or even absent for the specific systems investigated in this work..

I evaluated the impact of organic compounds on radionuclide mobility in cement-based material systems, as well as the impact of other components with potential perturbing or synergistic effects, under experimental conditions that closely simulate those existing in the near field of disposal facilities with engineered barriers made of cement-based materials.

Scientific impact of the thesis

For Romanian near surface and geological disposal facilities, the main category of organic waste to be disposed of consists in spent ion exchange resins (SIERs). ^{14}C-labelled organic molecules are generated by SIERs degradation. ^{63}Ni is one of the safety relevant radionuclides for Romanian near surface disposal facility and the effect of organics on its mobility in the disposal zone (cementitious environment) was not considered in the preliminary performance assessment for the near surface disposal facility (DFDSMA). Through the experimental research and the results obtained, the National Agency for Radioactive Waste can benefit from an improved sorption database, containing distribution coefficient values determined under experimental conditions representative to the disposal environment.

Moreover, the research conducted within this study may contribute to the optimization of cement formulations used in the construction of DFDSMA Saligny disposal modules and cells .

Future perspectives

An important direction for continuing experimental activities aimed at evaluating uranium mobility in cement-based materials involves the laboratory synthesis of additional families of hydration phases present in hardened cement pastes, such as monosulfate (AFm) and ettringite (AFt) phases, and the quantification of uranium sorption onto these phases. Furthermore, experimental research will proceed with studies and tests assessing uranium sorption onto hydration phases in the presence of a diverse range of organic molecules, as well as the impact of these molecules on the structural integrity of the respective phases.

The perspectives of further research on ^{14}C-labelled formic acid the uptake will focus on conducting sorption experiments on individual hydration phases of cement pastes, with the aim of elucidating the mechanisms by which organic molecules are incorporated into their structure.

To evaluate the interactions occurring within ternary systems cement-organic compounds-radionuclides future research activities will concentrate on investigating the order of addition in sorption experiments: (cement + organic molecules) + radionuclide; (organic molecules + radionuclide) + cement, as well as examining the effect on radionuclide sorption of the solid-to-liquid ratio. Another prospective research direction involves assessing the influence of organic molecule concentration on radionuclide mobility, considering that the experiments conducted within this doctoral thesis investigated the impact of a single concentration point of formic acid.

Looking ahead, the continuation perspectives derived from the thematic framework of this thesis also extends toward more complex and broader topics, including the evaluation of radionuclide mobility in mortars and concrete, and the expansion of experimental methodologies

to include diffusion and column transport experiments conducted under realistic conditions characteristic to the cementitious disposal environment.

List of Publications Resulting from the Scientific Research

Articles Published in Web of Science-Indexed Journals

I. C. Florea, C. M. Bucur, C. E. Diaconescu, E. A. Florea, **C. E. Ichim**, „*Analysis of the hydration process of CEM II/B-M composite cement*", Journal of Science and Arts, Vol. 24, Issue 3, ISSN 1844-9581, pp. 735-746, 2024.

II. **C. Ichim** , C. Bucur , I. Florea, S. Laliu, D. Dupleac, „ *Sorption isotherms of ^{63}Ni on cementitious engineered barriers of a radioactive waste disposal facility*" (trimis spre publicare și aflat în proces de revizuire, Scientific Bulletin Series B: Chemistry and Materials Science, articol nr. 16489).

Scientific Articles in Journals Indexed in BDI

I. **C. Ichim**, C. Bucur, M. Olteanu, I. Florea, „*Effect of organics and cement degradation on ^{63}Ni solubility in cement pore waters*", Journal of Nuclear Research and Development (JNRD), mai 2023.

II. **C. Ichim**, C. Bucur, M. Olteanu, „ *Ni-63 uptake on CEM I hardened cement paste – preliminary experimental results*", INE SCIENTIFIC WORKING DOCUMENTS 07, ISSN: 2701-262X, DOI: 10.5445/IR/1000173343.

III. C. Bucur, **C. Ichim**, I. Florea, C. Diaconescu, „*Cementitious materials characterisation by inductively coupled plasma emission spectroscopy*", Journal of Nuclear Research and Development (JNRD), decembrie 2023.

Papers Presented at International Conferences

I. **C. Ichim**, C. Bucur, S. Laliu, C. Manolescu, *„Uptake of ^{63}Ni onto hardened cement paste: effect of iron and organic molecules"*, The 15th Biennial International Conference on Sustainable Development through Nuclear Research and Education 29-31 May 2024 .

II. S. Laliu, C. Bucur, **C. Ichim**, C. Manolescu, *„Current Status of Geological Disposal Programme and a Review of the Potential Candidate Sites in Romania",* The 15th Biennial International Conference on Sustainable Development through Nuclear Research and Education, 29-31 May 2024.

III. **C. Ichim**, C. Bucur, I. Florea, D. Dupleac, „*Formate uptake in cementitious systems*", 6th International Workshop on Mechanisms and Modelling of Waste/ Cement Interactions, Prague, 2023.

IV. I. Florea, C. Diaconescu, **C. Ichim**, I. Prisecaru „*Modelling of Cement Hydration using PHREEQC Code*", The 14th Annual International Conference on Sustainable Development through Nuclear Research and Education, 2022.

V. S. Laliu, C. Bucur, **C. Ichim**, Daniela Rotaru, „*Site selection criteria for the deep geological repository in Romania*", The 14th Annual International Conference on Sustainable Development through Nuclear Research and Education, May 2022, (sesiune poster)

VI. C. Diaconescu, M. Mihalache, I. Florea, **C. Ichim**, „*Efficiency Calibration Methods of GeHP Detector for Gamma Ray Measurements from Solid Radioactive Waste,,*, The 13th Annual International Conference on Sustainable Development through Nuclear Research and Education, Nuclear 2021.

VII. M. Olteanu, C. Bucur, **C. Ichim**, „*Study of technetium sorption on pure clay mineral*, The 13th Annual International Conference on Sustainable Development through Nuclear Research and Education, Nuclear 2021

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