U.P.B. Sci. Bull., Series B, Vol. 87, Iss. 4, 2025 ISSN 1454-2331

SORPTION ISOTHERMS OF ^{63}Ni ON CEMENTITIOUS ENGINEERED BARRIERS OF A RADIOACTIVE WASTE DISPOSAL FACILITY

Camelia ICHIM[1,2], Crina BUCUR[2], Ionut FLOREA[2], Simona LALIU[2], Daniel DUPLEAC[3]

This paper focuses on the effect of iron and organic molecules on ^{63}Ni uptake by CEM I Hardened Cement Paste investigated through batch type experiments performed in chemical conditions characteristic to the initial stage of cement degradation. The experimental results indicated that by adding iron and formic acid in the system, under the experimental condition considered, nickel uptake on cement paste is slightly enhanced. This improvement could be due to either a nickel precipitation process, or the formation of secondary phases and highly stable complexes. ^{63}Ni sorption isotherms were also fitted with different models and compared to experiment.

Keywords: CEM I HCP, nickel, sorption isotherms.

1. Introduction

Any disposal concept for radioactive waste, either geological or near-surface must ensure the retaining of radionuclides and prevent their release into the biosphere. In many cases, a disposal facility relies on an engineered barrier system and a natural barrier system (geosphere) to achieve the fundamental objective of waste confining for a period of time long enough to allow the decay of the radionuclides contained in the waste disposed. Each component of the in-depth defense strategy for the safe disposal of radioactive waste fulfils certain safety functions, either alone or in synergy [1,2].

As the radionuclides sorption in cement-based materials system is an important uptake mechanism for many radionuclides, in the design of most disposal concepts, especially in the context of low and intermediate level waste (L/ILW), the engineered barrier system comprises cementitious materials which are used as

---

[1] PhD Student, National University of Science and Technology POLITEHNICA Bucharest, Faculty of Energy Engineering, Doctoral School of Energy Engineering, Bucharest, Romania, e-mail: camelia.ichim@nuclear.ro

[2] Eng., Technologies for Nuclear Energy State –Owned Company, Institute for Nuclear Research Pitesti, corresponding author, e-mail: crina.bucur@nuclear.ro, ionut.florea@nuclear.ro, simona.laliu@nuclear.ro

[3] PhD Eng., National University of Science and Technology POLITEHNICA Bucharest, Faculty of Energy Engineering, Doctoral School of Energy Engineering, Bucharest, Romania, e-mail: daniel.dupleac@upb.ro

conditioning matrix, as well as long term confinement and consolidation barrier. For construction purposes, high amounts of iron materials will be involved in the near field of a repository, either as waste or materials for drums and reinforcement in concrete walls [3].

Based on their origins, radioactive waste can incorporate different types of contaminants and organic components. Under hyperalkaline conditions ($10 \leq pH \leq 13$) imposed and developed by the cementitious material it is expected that small organic compounds will play an important role in radionuclide migration through the near and far field of a radioactive waste repository. Based on the outputs of European CAST (CArbon-14 Source Term) Project for Spent Ion Exchange Resins, the organic fraction of the ^{14}C source term is mainly found as short chained carboxylic acids. Formic acid ($H^{14}COOH$) was identified as one of the main organic low molecular weight compounds. Its origin can arise from reactor coolant and/or from the degradation of spent ionic exchange resins.

Nickel is an important contaminant present in the repositories for radioactive waste with barriers based on cement materials. Nickel radioisotopes present in irradiated metallic components from nuclear power plants are considered to be safety relevant and in performance assessment calculations, the mobility of these radionuclides on cementitious materials must be properly addressed. In literature, distribution ratio reported for ^{63}Ni (half-life=101 years) in cementitious systems ranges over a large domain, i.e., 0.01 to 10 000 Lkg^{-1}, for different experimental conditions [4]. Nevertheless, information regarding ^{63}Ni uptake in cement-based materials in the presence of formic acid and influence of this organic molecule on its retention are not available. In general, under the hyperalkaline conditions of the cement environment, low molecular weight organic molecules have a high solubility and a high negative charge. In addition to the formation of complexes, sorption of organic substances to the sorption sites of cement materials and therefore competition with radionuclides can occur [5].

The study of radionuclide mobility in cementitious environment is a key issue for safety assessment of disposal facilities. The proper parametrization of the radionuclide mobility in cementitious environments may become challenging taking into account the complexity and diversity of interactions that occur in these systems as well as the dynamic of the cementitious materials themselves [5,6].

This paper presents the results of sorption experiments carried out by batch method with the aim of investigating and quantifying ^{63}Ni sorption parameters in a cementitious environment, as well as the effect of iron and organic molecules to elucidate their role on ^{63}Ni uptake in the experimental system investigated. Iron is regarded as having a potentially large impact on cement barrier [7].

2. Materials and methods

The Hardened Cement Paste (HCP) samples used in ^{63}Ni uptake experiments are of CEM I type (CEMEX Prachovice, Czech Republic) prepared with a cement/water ratio of 0.45. The powdered HCP samples for sorption experiments were obtained from this bulk samples received from UJV Rez in the frame of CORI (Cement-Organics-Radionuclide-Interactions) project by crushing and grinding followed by sieving to collect fraction with particle size less than 63 μm. The procedure of obtaining powdered HCP material has been conducted in controlled conditions inside a glove box, under CO_2 free conditions to avoid the samples carbonation. CO_2 free conditions have been ensured by permanent purge of nitrogen gas and oxygen concentration monitoring.

Cement pore water. The composition of the solution in equilibrium with CEM I HCP was prepared according to the procedure of Wieland et all [8]. The composition of the pore water in equilibrium with non-degraded CEM I HCP with respect to the main cement-derived cations at pH 13.3 is summarized in Table 1. The Artificial Cement Pore Water (ACW) stock solution was obtained by weighting and dissolving adequate amounts of KOH and NaOH in a 2 L volume of ultrapure water, followed by addition of calcite and portlandite. The solution was shaken for 2 weeks in closed glass bottles and at the end of the equilibration period, was filtered through 0.22 μm Nylon filters, in nitrogen atmosphere inside a glove box. Finally, to complete the ACW stock solution adequate amounts of Na_2SO_4 and $Al_2(SO_4)_3$ have been added and the solution was kept until required for use in the uptake experiments.

Table 1

Composition of ACW stock solution in equilibrium with CEM I HCP

[K]t	[Na]t	[Ca]t	[Al]t	[S]t	[Si]t	pH
180 mM	114 M	1.6 M	0.05 mM	2 mM	0.05 mM	13.3

2.1. Description of the work – experimental setup

By the experimental approach adopted, a combination of systems has been selected and studied. The first part of the experimental study is aiming at investigating the binary system interaction of the radionuclide of interest (^{63}Ni) with CEM I hardened cement paste. The second one, focuses on the ternary system interactions of the radionuclide of interest with CEM I HCP and organic molecules (formic acid) addition in the system (CEM I HCP+^{63}Ni+HCOOH) and also on the quaternary system interactions: CEM I HCP-radionuclide (^{63}Ni)-organic molecule (HCOOH)-iron.

Two types of batch sorption experiments have been conducted for the experimental systems mentioned above:

- ✓ Sorption kinetic tests, to evaluate the time needed to achieve equilibrium or a steady state, taking into account that equilibrium is not always achieved in the complicated and complex cementitious systems;
- ✓ Sorption isotherm tests, varying tracer concentration and maintaining constant all other parameters. Sorption isotherms are curves describing sorption at different concentrations, aiming to evaluate distribution coefficient/ratio dependence of radionuclide concentration.

These sorption experiments have been conducted for a solid-to-liquid ratio (S/L) of 5 g/L. All sorption experiments conducted to study ^{63}Ni uptake on CEM I HCP have been carried out at room temperature ($T = 23 \pm 3^0$C), under controlled nitrogen atmosphere ($O_2 < 1\%$), inside a glove box. The experiments were carried out in duplicate, in polypropylene (PP) centrifuge tubes, which were prewashed, left overnight in a solution of 0.1 molar (M) hydrochloric acid (HCl), and thoroughly rinsed with de-ionized water before use.

For batch sorption experiments, a stock solution using carrier-containing ^{63}Ni radiotracer ($NiCl_2$ in 0.1 M HCl) has been prepared from a radioactive source with the total activity of $3.841 \cdot 10^6$ Bq. The total nickel concentration added in the system have been selected and calculated so that ^{63}Ni plus carrier concentrations are well below the solubility limit.

Sorption kinetic experiments were conducted for an initial total nickel concentration (^{63}Ni plus carrier) of 10^{-8} M. The evolution of ^{63}Ni activity concentration was analyzed in the aqueous phase at different equilibration time periods (t_{eq} = 1-17 days). The interpretation of the results has been performed in terms of percentage uptake (A_{ti}) and distribution ratio (Rd) values evolution.

The kinetics of ^{63}Ni sorption on CEM I HCP (State I, pH = 13.3) in the presence of iron and organic molecules has been evaluated for 5mg/L Fe concentration addition in the experimental system respectively formic acid concentration of 10^{-3} M and (all other experimental parameters–held constant). Iron concentration in the experimental system has been selected based of information published in EURAD ACED (Assessment of Chemical Evolution of ILW and HLW Disposal Cells) work package, Deliverable 2.13 – Intermediate level radioactive waste packages - characterization of waste and backfill degradation experiments [9]. Formic acid concentration was selected taking into account the fact that effects on nickel behaviour have been observed due to the presence of organics, especially at high organic concentrations [10].

Since both ^{63}Ni and ^{14}C are beta emitters, to avoid experimental difficulties in Liquid Scintillation Counting (LSC) and a supplementary separation procedure of samples analyzed for ^{63}Ni activity concentration, in all experiments with ^{63}Ni, it was avoided to use ^{14}C labelled formic acid and its stable form was added in the system. Due to its low beta energy (67 keV), the signal from ^{63}Ni can overlap with the one of ^{14}C (low-energy electrons having energy up to 156 keV), leading to potential interferences during measurement. In particular, the separation of the two beta emitters is critical when using LSC.

The sorption isotherm test was performed in similar conditions with the kinetic ones with the only varied parameter being the concentration of nickel: four nickel concentrations have been selected and obtained by preparing from the stock ^{63}Ni tracer solution. Appropriate volumes from the stock solutions have been added in the suspensions test tubes. The range of nickel concentration in the systems studying sorption isotherms was 10^{-9} M ≤ $[RN]_0$ ≤ 10^{-8} M. The suspension in the centrifuge tubes was shaken intermittently for a total equilibration time of 17 days. During the equilibration periods the test tubes have been placed on a shaker at 110 rpm (revolutions per minute).

After equilibration, test tubes have been centrifuged for phase separation, aliquots from duplicate experiments were sampled and the total radionuclide concentration activity in the suspensions has been determined by LSC counting, using Ultima Gold scintillation cocktail and Canberra Packard Tri-Carb 5110 TR liquid scintillation analyzer. Samples counting was performed until the uncertainty of $\%\sigma \leq 0.5$ was achieved.

All operations except sampling for ^{63}Ni measurement and equilibration of the suspensions (centrifuge tubes were closed and parafilm foil sealed inside the glove box) were carried out under nitrogen atmosphere.

2.2. Interpretation of the experimental results

Sorption kinetic has been evaluated through the percentage uptake (A_{ti} [%]), representing the percentage of radionuclide retained on the solid phase related to the initial amount of contaminant initially present in solution.

$$A_{ti} = \frac{C_{aq}(ti) - C_0}{C_0} \times 100 \qquad (1)$$

The uptake of ^{63}Ni by CEM I HCP as well as the effect of formic acid and iron was quantified in terms of the radionuclide distribution between solid and liquid phase in terms of a distribution ratio, R_d (m^3/kg), which is the ratio of the amount of radionuclide sorbed and the radionuclide concentration in solution. R_d values were obtained using the following equation:

$$R_d = \frac{C_0 - C_{eq}}{C_{eq}} \times \frac{V}{m}\ (\mathrm{m^3/kg}) \qquad (2)$$

where C_o and C_{eq} denote radionuclide initial concentration and respectively the equilibrium concentration measured in solution after equilibration and centrifugation steps, at equilibrium. V and m denote the volume of the suspension (m^3) and the mass of solid phase (kg).

If precipitation is not the uptake process involved, and the equilibrium is achieved, the distribution ratio, R_d, corresponds to the distribution coefficient, K_d. The distribution coefficient (K_d) it is an important parameter in safety assessments of radioactive waste disposal. It helps predicting contaminant transport and potential environmental impact.

For the interpretation and modelling of sorption isotherm experimental data, the correlation with three sorption models were analysed, searching for a model that fits the data well and provides accurate predictions: linear, Freundlich and Langmuir models.

First, for the linear description of isotherms, the linear K_d model was assessed:

$$A_{eq} = K_d \cdot C_{eq} \tag{3}$$

where A_{eq} (Bq/kg) is the equilibrium concentration in the solid phase, C_{eq} (Bq/L) is the equilibrium concentration in the liquid phase and K_d (L/kg) is the distribution coefficient derived from isotherm slope. Linear distribution coefficient is constant over the given range of concentrations.

In order to describe non-linear form of ^{63}Ni isotherm, the non-linear expression of Freundlich isotherm model was assessed, as illustrated below:

$$A_{eq} = K_F \cdot C_{eq}^{1/n} \tag{4}$$

where K_F (Freundlich constant) and n are the constants, measuring the adsorption capacity and intensity. By plotting log (A_{eq}) versus log (C_{eq}), a straight line is produced and the constants are derived from the slope and intercept. K_F and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models [12].

The linear forms of Langmuir model, Equation (5) have been tested to fit the experimental data obtained in the investigated systems. By plotting 1/A_{eq} versus 1/C_{eq} it is possible to determine the value of Langmuir constant, K_L and A_{max} - the model maximum attainable concentration of ^{63}Ni in the solid phase under the given conditions.

$$\frac{1}{A_{eq}} = \frac{1}{A_{max}} + \frac{1}{A_{max} K_L} \frac{1}{C_{eq}} \tag{5}$$

For each model, the Mean Total Error (MTE) has been calculated with Equation 6 in order to assess the corelation between the measured parameters and the parameters derived from sorption isotherms modelling. The correlation coefficient (R^2) has been also used to determine the best-fitting isotherm to the experimental data. The highest R-squared values indicate smaller differences between the sample data and the fitted values.

$$\xi\,\% = \frac{\sum_{i=1}^{n}\left|\left(C_i^{exp} - C_i^{estim}\right)\right|}{\sum_{i=1}^{n} C_i^{exp}} \times 100 \tag{6}$$

where: C^{exp} is the experimental concentration of ^{63}Ni calculated at time i (Bq/g), and C^{estim} is ^{63}Ni concentration estimated from the theoretical curve at the same time (Bq/g), (i) the number of experimental data sets.

3. Results and discussions

The results of ^{63}Ni sorption kinetics on CEM I HCP in the presence of iron and formic acid are reported in Fig. 1, as percentage uptake evolution with time.

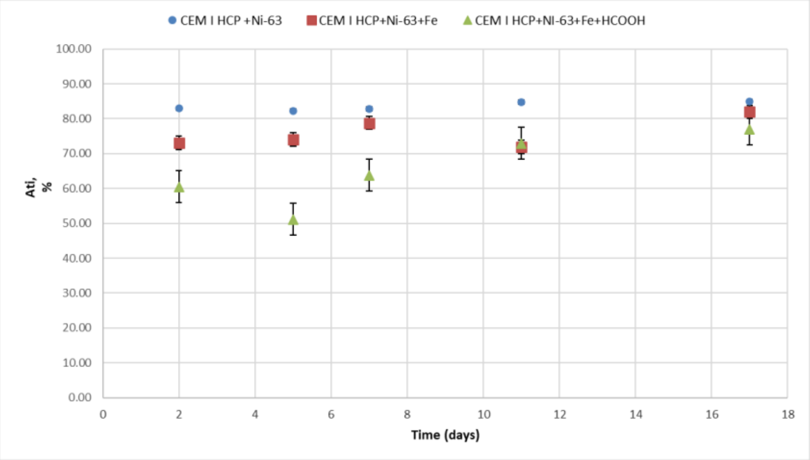

Fig. 1. Kinetics of ^{63}Ni on CEM I HCP (pH=13.3). Experimental conditions: S/L ratio = 5g/L, $[Ni]_{tot} = 1 \cdot 10^{-8}$ M, [Fe]=5 mg/L, [formic acid] $_{tot}= 10^{-3}$M

The results presented in Fig. 1 show fast ^{63}Ni sorption kinetics in all three systems, with percentage uptake values almost identical (in the range of experimental errors) after 17 days of equilibration, meaning that at 5 mg/L and 10^{-3}M of Fe respectively formic acid concentration in the corresponding experimental conditions, does not affect the rate of sorption equilibrium establishment.

Batch isotherm studies performed in order to understand the relationship between the amount of the ^{63}Ni adsorbed per unit mass of CEM I HCP and the ^{63}Ni concentration in the solution at equilibrium investigating also the role and effect of iron and formic acid on the mobility show some very interesting results.

The sorption isotherms of ^{63}Ni obtained by modelling with linear sorption model (A_{eq} vs. C_{eq}) are presented in Fig. 2, and the corresponding distribution coefficients (K_d) for each system are reported in Table 2. Also, in Table 2, experimental data correlation coefficients (R^2) with the linear model are presented, together with the values obtained for MTE as calculated with Equation (6) are reported.

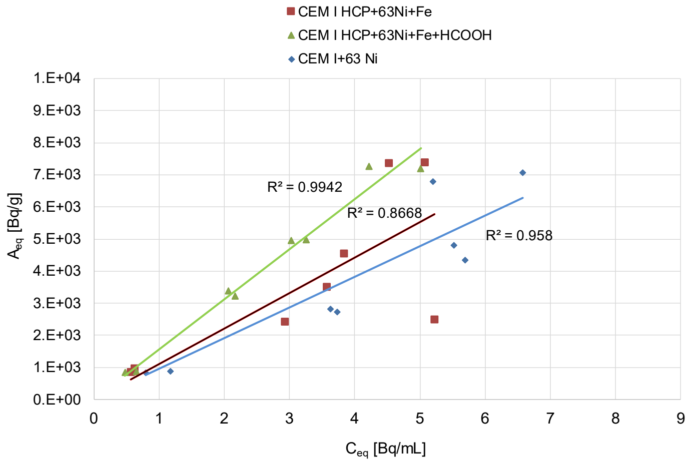

Fig. 2. Fitting of ^{63}Ni sorption experiments on CEM I HCP (pH = 13.3) with linear isotherm model. Experimental conditions: S/L ratio = 5g/L, $1 \cdot 10^{-9}$ M $\leq [Ni]_{tot} \leq 1 \cdot 10^{-8}$ M, [Fe]=5 mg/L, $[\text{formic acid}]_{tot} = 10^{-3}$M, eq. time = 17 days.

Table 2

^{63}Ni sorption parameters in the investigated systems derived from the linear 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

Data presented in Fig. 2 and Table 2 for this model, show good correlation coefficient (R^2) for binary and quaternary system, but with high value for total errors in CEM I HCP-^{63}Ni system (19.62%). The calculated K_d values from the fitting of experimental data with the linear sorption model show a lower sorption of ^{63}Ni on CEM I HCP than in the system with iron and iron and formic acid addition (Kd binary system < K_d ternary system < K_d system with 5 mg/L Fe and 10^{-3} M HCOOH). This may suggest that with addition of iron and formic acid, under these experimental conditions, nickel precipitation may start to play a role in ^{63}Ni removal from liquid phase. Normally, this should not be the case taking into account the fact that the total nickel concentrations in the system were low. Another possible explanation is the appearance of other enhancing sorption processes, like secondary phases and strong stable complexes formation in these already complex systems.

Freundlich isotherm is applicable to processes occurring on heterogenous surfaces, giving an expression which defines also the exponential distribution of active sites and their energies. The Freundlich model describes non-ideal and reversible adsorption [11,12]. The results of modelling the experimental data obtained in this study is presented in Fig. 3 and the sorption data characterizing this sorption model are presented in Table 3.

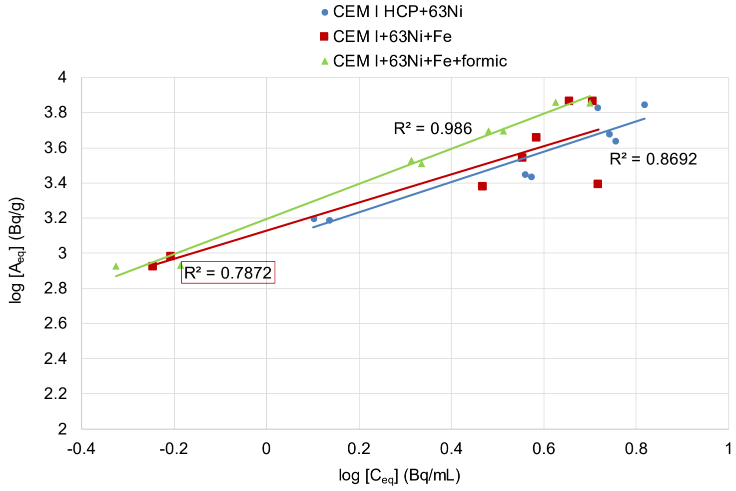

Fig. 3. Sorption isotherms of ^{63}Ni on CEM I HCP (pH=13.3) fitted with non-linear Freundlich model. Experimental conditions: S/L ratio = 5g/L, $1\cdot10^{-9}$ M $\leq[\mathrm{Ni}]_{tot}\leq 1\cdot10^{-8}$ M, [Fe]=5 mg/L, $[\text{formic acid}]_{tot}= 10^{-3}$M, eq. time = 17 days.

Table 3

^{63}Ni sorption parameters in the investigated systems derived from non-linear Freundlich model

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 analyzed fitted data using Freundlich model for ^{63}Ni uptake on CEM I HCP shows good experimental data correlation coefficients (R^2) of 0.986 only for the system with formic acid addition. In all three systems investigated values of 1/n are below one, indicating a normal adsorption process. Specifically, the linear least-squares method and the linearly transformed equations are widely applied to correlate sorption data where 1/n is a heterogeneity parameter. The smaller 1/n, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/n = 1. This is the case for ^{63}Ni uptake on CEM I HCP in the system with iron and also formic acid addition. In the other two systems, n is slightly higher than 1, this indicating a favorable sorption process. From the data in Table 3, the values of 1/n are 0.869; 0.787; 0.999 from the simplest to the more complex system while n=1.15; 1.27; 1.001 with R^2 values of 0.869; 0.787 and 0.986, indicating that sorption of ^{63}Ni on CEM I HCP is not best estimated by Freundlich model for all three investigated system.

The experimental data for ^{63}Ni uptake on CEM I HCP with/without iron and iron and formic acid addition analyzed using Langmuir model gives the best correlation. In Fig. 4 and Table 4, the highest R^2 values for all three system were obtained by fitting experimental data into the Langmuir isotherm model, suggesting that this model is the best-fitting isotherm to the experimental data. Table 4 presents the corresponding isotherm parameters, their correlation coefficients (R^2) and the related mean total errors.

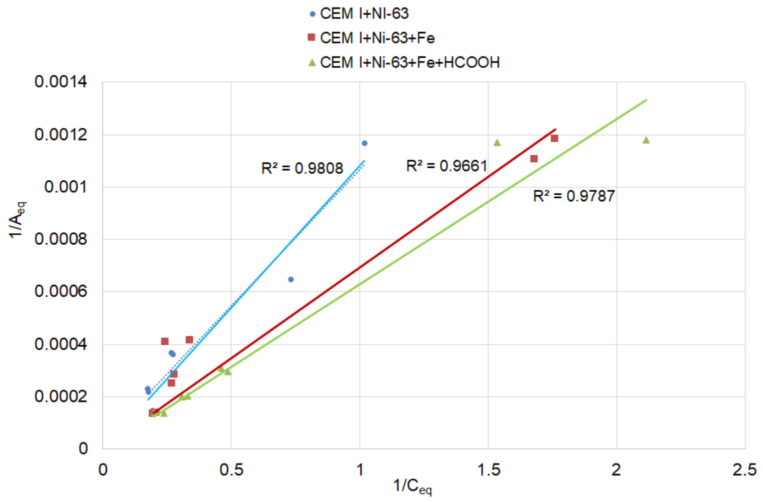

Fig. 4. Sorption isotherms of ^{63}Ni on CEM I HCP (pH=13.3) fitted with Langmuir model (Lineweaver–Burk). Experimental conditions: S/L ratio = 5g/L, $1\cdot10^{-9}$ M $\leq[\mathrm{Ni}]_{tot}\leq 1\cdot10^{-8}$ M, [Fe]=5 mg/L, [formic acid]$_{tot}$= 10^{-3}M, eq. time = 17 days.

Table 4

^{63}Ni sorption parameters in the investigated systems derived from 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	0.979	11.27

Experimental data obtained for the ternary system (CEM I HCP-^{63}Ni-Fe) could be fitted with a good R^2 value of 0.966 only with this model (compared to R^2 values of 0.867 and 0.787 in linear respectively Freundlich models).

Meanwhile, the values of MTE for parameters obtained in Freundlich and Langmuir isotherm models suggest that both Langmuir isotherm model and the Freundlich isotherm model can generate a satisfactory fit to the experimental data, for two of the investigated system (CEM I HCP+^{63}Ni and CEM I HCP+^{63}Ni+Fe+HCOOH), while for the ternary system (CEM I HCP+^{63}Ni+Fe) only Langmuir model gives accurate correlation with the experimental data set. As shown in Table 4, the values of maximum adsorption capacity determined using Langmuir model was $3.33\cdot10^4$, $1\cdot10^4$ and $1\cdot10^5$ for the binary, ternary and quaternary system respectively. These values are near the experimental retained on solid calculated concentrations which indicates that the modelling the sorption with Langmuir model for the systems is acceptable. Therefore, by comparison, the order of isotherm that best fits all sets of experimental data in this study is Langmuir >Freundlich > linear model.

The Langmuir model assumes uniform energies of adsorption onto the surface and describes quantitatively the formation of a monolayer adsorbate on the outer surface of the cement particles, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of nickel ions between the solid and liquid phases and the sorption isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites [13,14].

Studies suggest that a mixed Ni-Al LDH (nickel-aluminum layered double hydroxides) phases may form in cement systems. Therefore, Ni-Al LDHs are regarded as solid phases, being potentially present in the waste matrix and governing nickel uptake. The chemical nature of the Ni-Al LDH phase formed in cement paste, which controls nickel solubility and the retention of radionickel in cementitious systems, is still poorly known, but most probably, cementitious near field of a cement-based repository is determined by solubility-limiting rather than adsorption-type processes [8, 15, 16].

4. Conclusions

This paper dealt with the investigation and quantification of ^{63}Ni sorption parameters in a cementitious environment and the effect of iron and organic molecules, with the aim to elucidate their role on nickel uptake in the experimental system investigated.

In this regard, two types of batch sorption experiments were performed for solid to liquid ratio of 5 g/L, constant concentrations for iron (5 mg/L) and formic acid (10^{-3} M) in the system.

The experimental data for ^{63}Ni uptake on CEM I HCP corresponding to State I of degradation, at pH 13.3, for a S/L ratio of 5g/L^{-1} with and without Fe, and Fe and HCOOH, are best estimated by Freundlich and Langmuir models. The sorption experimental data indicated that both iron and formic acid seem to have a minor but not negligible effect on nickel uptake under alkaline near-field conditions. But this effect is opposite to the expected impact of increasing solubility and decreasing sorption. This effect may be due to the formation of strong complexes, especially determined by iron addition in the ternary and quaternary systems.

Iron can influence nickel uptake in CEM I hardened cement paste (HCP) through several mechanisms. Iron has the potential to alter the oxidation state of nickel, affecting its solubility and sorption behavior, by promoting in cementitious hyper alkaline environments the formation of double layered hydroxides, which in turn seems to enhance nickel retention. Moreover, iron oxides or hydroxides present in cement can provide additional binding sites for Ni (II), increasing its sorption capacity – surface complexation. The presence of iron may lead to the precipitation of Ni-Fe hydroxides, reducing nickel mobility in cement pore water by controlling the solubility of the secondary phase.

Formation of Fe-HCOOH complexes is also a possibility, since formic acid can act as a ligand, forming complexes. These compounds may have an impact on iron solubility in cement pore waters. Also, nickel can form secondary phases (nickel-formate complexes), affecting ^{63}Ni mobility in cementitious environments. As shown, the presence of iron may further modify these interactions.

Although the available data are limited to only a few radionuclides relevant to near field conditions, these suggest that corrosion products on the canister surface will promote reduction and immobilization [17].

In order to improve the overall understanding of sorption mechanism and effective design of the systems studied, interpretation and understanding the sorption isotherms remains an important issue. The overall sorption process of contaminants on solid phases can be hardly defined by one single clearly defined mechanism. Thus, it is very difficult to strictly differentiate between various mechanisms and this is especially true in the complicated and complex system represented by the interactions in cementitious environment [11,12].

REFERENCES

[1]. *W. Falck and K.-F. Nilsson,* Geological Disposal of Radioactive Waste: Moving towards Implementation*,* 2009.

[2]. *N. OECD,* Safety Cases for Deep Geological Disposal: Where do we stand? Paris, France, 2007.

[3]. *A. Mancini,* Thermodynamic and spectroscopic investigations of ferric and ferrous iron in cementitious systems, Zurich: Research Collection ETHZ, 2020.

[4]. *M. Ochs, D. Mallants and L. Wang,* Radionuclide and Metal Sorption on Cement and Concrete, **vol. 29**, Springer International Publishing Switzerland, 2016, 2015.

[5]. *R. E. Guidone*, "Impact of formate, citrate and gluconate on the retention behavior of Pu (III/IV) and Eu (III) by cement phases," Karlsruher, 2023.

[6]. *B. Drtinová, J. Kittnerová, K. Bergelová, M. Burešová and L. Baborová*, Sorption of lead on cementitious materials in presence of organics, Frontiers in Nuclear Engineering 1:1095233, 2023.

[7]. *E. Wieland*, Sorption Data Base for the Cementitious Near Field of L/ILW and ILW Repositories for Provisional Safety Analyses for SGT-E2, 2014.

[8]. *E. Wieland and J. Tits*, Experimental evidence for solubility limitation of the aqueous Ni (II) concentration and isotopic exchange of ^{63}Ni in cementitious systems, Radiochim. Acta, pp. 2-36, 2006.

[9]. *Mladenovic, A., E. Neeft, R. Dähn, Y. Gu, and L. Markku*, Intermediate level radioactive waste packages – Characterization of waste and backfill degradation experiments. Final version as of 18 March 2024 of deliverable D2.13 of the HORIZON 2020 project EURAD. EC Grant agreement No.: 847593, 2022.

[10] *Hummel W, Andereeg G, Rao L et al*, Chemical thermo dynamics of compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands. Elsevier Science, Amsterdam, 2005.

[11] *A. O. Dada and A. P. Olaleken*, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk, IOSR Journal of Applied Chemistry, **vol. 3**, no. 1, pp. 38-45, 2012.

[12]. *N. Ayawei, A. Newton Ebelegi and D. Wankasi*, Modelling and Interpretation of Adsorption Isotherms, Hindawi Journal of Chemistry, 2017.

[13]. *C. Xunjun*, Modelling of Experimental Adsorption Isotherm Data, Information, **vol. 6**, pp. 14-22, 2015.

[14]. *B. Allard, K. Andersson and B. Torstenfelt*, The Distribution Coefficient Concept and Aspects on Experimental Distribution Studies, SKB, 1983.

[15] *Wieland, E., Tits, J., Spieler, P., Dobler, J.P. & Scheidegger, A.M.*, Uptake of nickel and strontium by a sulphate-resisting Portland cement. In: D. Rammelmair, J. Mederer, Th. Oberthür, R.B. Heimann, H. Pentinghaus (eds.): Applied Mineralogy. 2, 705-708, 2000.

[16] *Wieland, E. & Van Loon, L.R.,* Cementitious near-field sorption data base for performance assessment of an ILW repository in Opalinus clay, PSI Bericht 03-06, Paul Scherrer Institut, Villigen PSI, Switzerland.

[17] *P. Wersin, L.H. Johnson, B. Schwyn, U. Berner, E. Curti*, Redox Conditions in the Near Field of a Repository for SF/HLW and ILW in Opalinus Clay, NAGRA, Technical Report 02-13, 2003.