EFFECT OF ORGANICS AND CEMENT DEGRADATION ON ^{63}Ni SOLUBILITY IN CEMENT PORE WATERS

CAMELIA ICHIM, CRINA BUCUR, MIRELA OLTEANU, IONUȚ FLOREA
Institute for Nuclear Research (RATEN ICN) Piteşti, Romania
e-mail: camelia.ichim@nuclear.ro

Abstract

Cementitious materials are widely used in repositories for L/ILW radioactive waste. Radionuclide migration depends, among other, on the interaction of dissolved radionuclides with backfill materials and organic matter. In order to predict the radionuclide release into the far field, their concentrations in cement pore waters are of critical importance. In cement-based repositories for radioactive waste, nickel isotopes are considered to have a safety relevant role in performance assessment. The presence of organic materials in cement pore waters has the potential to influence radionuclide solubility and influence the performance of the disposal system. In this study, the solubility of nickel in cement pore waters has been investigated in experiments performed under conditions corresponding to the initial stage of cement degradation. A more advanced state of cement degradation and the influence of organic molecules has been assessed. The organics considered is the formic acid, potentially released in the disposal environment by spent ion exchange resins degradation.

Keywords: *Radionuclide Migration, Nickel, Solubility, Cement, Organic Molecules*

Introduction

In the design of L/ILW (Low /Intermediate Level Waste) radioactive waste repositories, cementitious materials are widely used as construction materials of the engineering barrier system and also as waste conditioning matrices. The multi-barrier concept for radioactive waste disposal is designed so as to prevent and limit the radionuclide migration. Its safety function relies on mechanical and physical properties of cement-based materials. Cementitious materials present in all disposal concepts may also contribute to the containment of radioactivity and to limit water ingress into the repository after its closure. Due to their favourable chemical properties, these materials have the potential to retain a variety of radionuclides by sorption, incorporation or precipitation.

Cement-based materials will degrade in time in the context of waste disposal, inducing a large range of alkaline pH conditions, according to their degradation stage. Geochemical evolution of the near field is dictated by the infiltrating groundwater and its interaction with cement paste, generating changes in the pore water composition.

Generally speaking, the cement degradation follows a pattern associated with three stages, each degradation stage being characterized by a decrease of pore water pH. In the first stage of cement degradation (State I), the pore water chemistry is dominated by alkali hydroxides which derives a pH of about 13.3. For the second stage of degradation (State II), the pore water composition is controlled by the solubility of portlandite with a pH value of about 12.5 and the total Ca concentration buffered at 2×10^{-2} M. After portlandite complete dissolution, in the third stage of degradation (State III), the pH drops continuously until a value of 10 is reached.

Organic materials are present in some radioactive waste and as admixtures in cement-based materials. They can potentially influence the performance of a geological disposal system, especially in the context of low and intermediate level waste disposal. The hyperalkaline conditions derived by the cementitious environments can determine the polymeric materials degradation and ageing phenomena, causing subsequent production of organic molecules. It is well recognized that potential effect of organic molecules is caused by formation of complexes in solution with radionuclides of interest that can increase the radionuclide solubility and decrease their sorption [1].

Organic substances require increased attention since a significant quantity exists in the waste and in cementitious materials, with a large degree of chemical diversity.

Inside the reaction vessel of a nuclear reactor, depending on the irradiation history, nickel found especially in the stainless-steel components is susceptible to neutron activation, thus becoming a critical activation product. ^{63}Ni is produced by neutron activation of stable isotope ^{62}Ni found in structural materials and irradiated metallic components in a nuclear reactor. In performance assessments, nickel radioisotopes present in the LILW repositories are considered to be safety-relevant.

Hydraulic and chemical properties of fresh hardened cement pastes (HCPs) are to be considered in the case of cement waste matrix or container material, while the properties of aged HCPs are important for the performance evaluation of the engineered barriers system. The presence of organic materials in cement pore waters has the potential to influence the solubility of some radionuclides, including Ni isotopes, and influence the performance of the disposal system [2].

In performance assessment studies it is considered that the source term for radionuclide migration into the host rock is determined by a combination of solubility and sorption constraints in the cementitious near field [3]. Thus, the uptake of radionuclides by hardened cement pastes (HCP) and cement minerals plays a decisive role in limiting and retarding their release from the near field.

The effect of organic molecules and cement degradation on nickel solubility has been evaluated in this work. The main objective of the study was to determine the highest ^{63}Ni concentrations that can be introduced in the batch sorption experiments dedicated to assess the ^{63}Ni sorption properties, in order to avoid precipitation phenomena which can occur in cement suspensions.

The tests conducted in the frame of this study to evaluate the solubility limit of ^{63}Ni in the cementitious pore waters were carried out using ^{63}Ni labelled solutions in artificial cement pore waters (ACW) at pH = 13.3 and in cement pore waters resulted from the HCP (based on CEM I) degradation test (pH = 11.3). For the ACW, the potential effect of organic molecules has been assessed. The organic fraction of ^{14}C source term is mainly found as short chained carboxylic acids. ^{14}C-labelled formic acid has been identified as the main organic compound which can originate from the reactor coolant and/or from the degradation of spent ion exchange resins.

Materials and methods

2.1. Pore water composition

In radionuclide migration studies, radionuclide properties in solution are derived by their speciation and solubility. The solubility of nickel, in alkaline conditions determined by cement-based materials, has been reported in a series of studies in literature. Based on most of these studies, it can be concluded that at pH greater than 12, the concentration of the dissolved nickel is usually less than 10^{-6} M.

Artificial Cement pore Water preparation and composition

The composition of the simulated solution in equilibrium with HCP based on CEM I, corresponding to the first stage of cement degradation, was prepared according to the procedure used by Wieland [3]. Briefly, the composition of a pore water in equilibrium with HCP with respect to the main cement-derived cations at pH = 13.3, ACW (artificial cement pore water), is summarized in Table 1.

The ACW stock solution was obtained by weighting and dissolving adequate amounts of KOH and NaOH in 2 L of ultrapure water, followed by addition of calcite and portlandite. The solution obtained was shaken for 2 weeks in closed glass bottles. At the end of the contacting period, the solution was filtered through 0.22 μm Nylon filters, in nitrogen atmosphere inside a glove box to avoid contact with CO_2(g). 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 being used in wet chemistry experiments.

Table 1. Composition of ACW stock solution in equilibrium with HCP

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

Degradation protocol of HCP based on CEM I and Degraded Cement pore Water (DCW) composition

The Hardened Cement Paste used in this solubility study is based on CEM I 52.5 (OPC, LAFARGE, Val d'Azergues factory), prepared at a water/cement ratio of 0.38 and kept in saturated portlandite water until being used, in order to avoid carbonation. The powdered HCP material involved in the present study was obtained from this bulk samples by crushing and grinding followed by sieving to collect the size fraction ≤ 63 μm and obtain the powdered samples and pore waters for the degraded state of the cement paste. In order to avoid the contact of cement samples with CO_2, in the degradation test double distilled degassed (DDW) water has been used, and all operations were performed in a glove box flushed with nitrogen. Both cement pastes and waters were stored in Duran closed glass bottles.

Data from literature and experiments performed by other teams of experimentalist [4] indicate that a solid to liquid ration (S/L), in the range of 0.03 to 12 g/L, is relevant for obtaining degradation states free of portlandite ($Ca(OH)_2$).

The degradation state has been obtained by mixing HCP powders with degassed deionized water at a S/L of 0.4 g/L, for an equilibration period of 3 months (see Table 2.). At the beginning of the hydrolyse process, the pH of the solution is controlled by Na^+ ($-OH^-$) and K^+($-OH^-$) concentrations, until the pH of the solution saturated in portlandite is achieved. Thus, the contacting time of the suspension has been established by continuously monitoring the pH of the solutions.

At the end of the equilibration step, phase separation has been achieved through filtration, inside a glove box flushed with nitrogen. The resulted waters, having a pH of 11.30 at the end of the equilibration period, were used in the test performed to assess the solubility limit of ^{63}Ni in pore waters corresponding to cement degradation stage.

Table 2. Experimental parameters for HCP degradation protocol

Solid/liquid ratio [g/L]	HCP mass [g]	DDW Volume [mL]	Contacting time [days]
0.4	0.8	2000	90

2.2. ^{63}Ni solubility study in cement pore waters with and without organic molecules addition

One of the main processes controlling radionuclide migration and organic molecules interactions in cementitious environments is represented by their solubility in cementitious pore water. According to International Union of Pure and Applied Chemistry conventions, the analytical composition of a saturated solution, expressed in terms of the proportion of a designated solute in a designated solvent, is the solubility of that solute. The solubility may be expressed in a number of ways: concentration, molality, mole fraction, or mole ratio [1].

The chemical composition of the pore water has the potential to influence the type of the chemical species radionuclides will form. Chemical species formed by radionuclides under alkaline conditions can also have a different chemical behaviour. Regarding the speciation/ solubility of radionuclides in the presence of organic molecules, the impact is determined by radionuclides complexation reactions and it depends on the organic type and concentration, on the composition of the aqueous phase providing the pH, types of ions in solutions, etc.

In order to evaluate the operational solubility limit of ^{63}Ni in cement pore waters with and without formic acid addition, three types of laboratory experiments have been performed:

- ^{63}Ni solubility evaluation limit in artificial cement pore water corresponding to Stage I (ACW), at pH = 13.3, without organic molecules addition in the system;
- ^{63}Ni solubility evaluation limit in artificial cement pore water corresponding to Stage I (ACW), at pH = 13.3, with organic molecules (formic acid -HCOOH) addition in the system;
- ^{63}Ni solubility evaluation limit in cement pore water resulted from de degradation test of the HCP based on CEM I (DCW), at pH = 11.3.

Table 3 presents the general experimental conditions applied in the tests performed to evaluate the solubility of ^{63}Ni in cement pore waters, for the binary system (radionuclide-cement) and for the ternary system (radionuclide-cement-organics). All solubility tests have been conducted in duplicate, in centrifuge tubes previously pre-washed, inside of a glove box with nitrogen atmosphere (O_2< 0.1%), at room temperature (22 ± 3^0 C).

Taking into account the findings presented in [3], upon contacting the HCP with ACW, the nickel bound to cement based material could be released into solution. These solubility tests were conducted using ^{63}Ni labelled solutions.

The total nickel concentration in the experiment ranged between 10^{-8} M – 10^{-5} M. For this domain range, four nickel concentrations have been selected and obtained by preparing stock solution of 10^{-4} M $NiCl_2$ and a stock of ^{63}Ni tracer solution. Appropriate volumes from the stock solutions have been added in ACW and DCW (the total volume in a centrifuge tube was 40 mL).

The total concentration of formic acid used in the tests designated to evaluate the influence of short carboxylic acids (HCOOH) on ^{63}Ni solubility limit, was kept constant in all experiments (10^{-3} M). The centrifuge tubes have been intermittently shaken for 30 days. At the end of the testing period, the solutions were sampled and after centrifugation step of the solutions, aliquots were withdrawn from each solution, acidified and analysed for total nickel concentration in the system, by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES iCAP 6000 series)/ Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Table 3. Experimental conditions for the solubility study

Experimental conditions	
Atmosphere	N_2
[Ni] initial	$6 \cdot 10^{-8}$ M – 10^{-6} M
[ORG]	10^{-3} M
ACW	pH = 13.3
DCW	pH = 11.3
Equilibration time	30 days
Phase separation	Filtration
Total Ni concentration measurement	ICP-OES/ICP-MS

3. Results and discussions

In the frame of this study, nickel operational solubility limit in cement pore waters evaluation was not intended to be a rigorous solubility study because no attempt was undertaken to identify the solid phase(s) limiting the solubility of nickel in cement waters.

The main objective of this study was to determine the highest amount of ^{63}Ni which can be introduced in the batch sorption experiments without leading to a precipitation in the ^{63}Ni-cement suspensions.

The results of ^{63}Ni solubility test in ACW and DCW, with and without formic acid addition in the system, are presented in Table 4.

Table 4. Nickel total and in solution concentrations in solubility type test

Ni initial concentration [M]	Ni concentration in ACW [M]	Ni concentration in ACW with HCOOH addition [M]	Ni concentration in DCW [M]
6.826E-08	5.119E-08	5.119E-08	8.532E-08
3.328E-07	1.959E-07	2.218E-07	1.536E-07
2.876E-06	8.533E-07	7.850E-07	3.959E-06
4.300E-06	1.570E-06	9.727E-07	5.188E-06

From the results obtained in this experimental solubility study the following observations can be derived:

- In the cement pore water, ACW (pH = 13.3), nickel total and in solution concentrations agree well up to a total nickel concentration of 2 x 10^{-7} M. Above this value, the formation of a precipitate or a fraction of colloidal nickel could have been occurred, determining lower nickel concentrations in ACW, after the centrifugation and filtration steps. Inside the testing tubes, no macroscopically nickel precipitate was visually observed.
- In the cement pore water, ACW (pH = 13.3), when formic acid is added in the system, as the main spent ion exchange resin degradation compound, nickel total and in solution concentrations are not significantly influenced comparing with those obtained in the solubility test conducted without HCOOH addition (see Fig. 1).
- Nickel concentration mean value in solution was calculated as $[Ni]_{aq}$ = (1.2 ± 0.3) x 10^{-7} M. From this operational nickel solubility limit in ACW, the concentrations for batch sorption test have been selected, in order to avoid precipitation phenomena that could occur in these complicated cement systems.
- In cement pore waters resulted from HCP degradation tests (pH = 11.3), nickel total and in solution concentrations are in good agreement up to a total nickel concentration of 5 x 10^{-6} M. Thus, the pore water composition and the pH, respectively, have a significant influence on nickel solubility limit (see Fig. 2).
- The mean value for nickel concentration in DCW has been calculated as $[Ni]_{aq}$ = (2.3 ± 0.46) x 10^{-6} M.

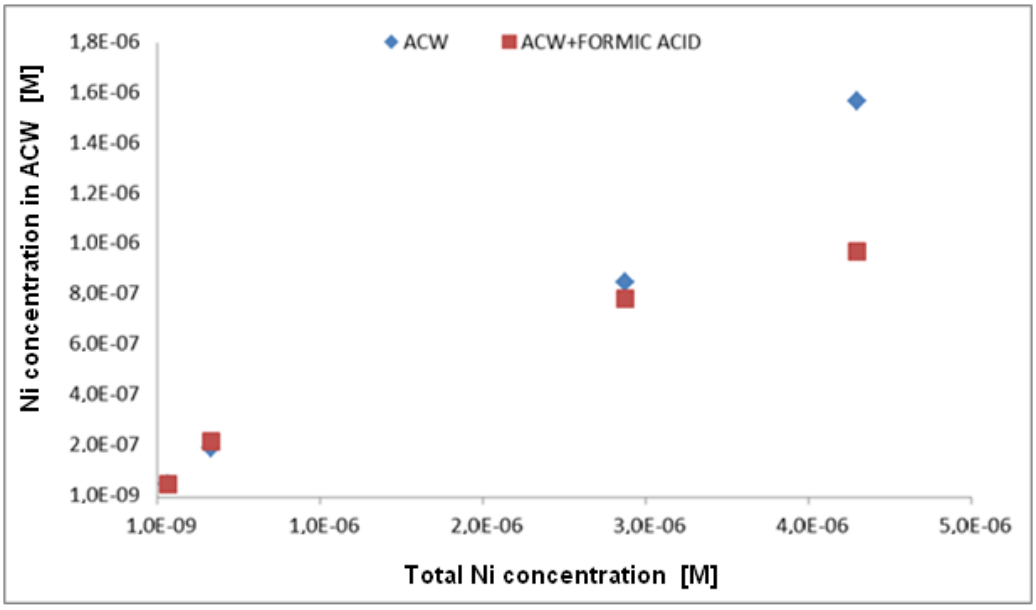


Fig. 1. Effect of organic molecules addition on nickel solubility limit in cement pore water at pH = 13.3

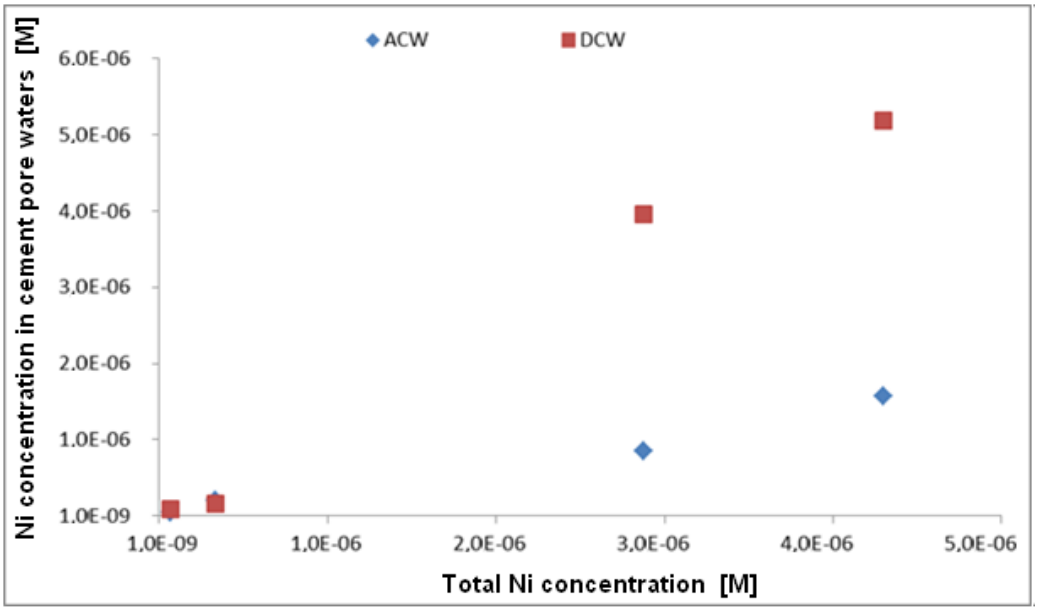


Fig. 2. Nickel concentrations in cement pore waters at pH = 13.3 (ACW) and pH = 11.3 (DCW)

Comparing this study results with other published results, it has to be noted that the mean calculated value of nickel concentration in solution, at pH = 13.3, is consistent with the findings of Wieland & Tits, $[Ni]_{aq}$ = 7 x 10^{-7} M, [3]. Pilkington & Stone are reporting an experimental nickel solubility limit of 5 x 10^{-8} mol/L, for a pH = 13.2, [5]. Other experimental solubility study carried out by Mattigod et al. [6] reports a nickel solubility limit between 6.5 x 10^{-6} mol/L and 8.5 x 10^{-8} mol/L, in cement pore waters with a pH = 12.94. Obviously, experimental conditions are different from one study to another, and the mean values calculated from the results have been considered reasonable indications on nickel operational solubility limit in ACW and DCW, contributing to the selection of nickel concentrations for the batch sorption experiments.

Conclusions

This paper summarizes the experimental studies performed to assess solubility limit of nickel in cement pore waters, under the relevant conditions anticipated in the near field of a cementitious repository.

The solubility of nickel in cement pore waters has been investigated under experimental conditions corresponding to the initial stage of cement degradation, and to a more advanced stage of cement degradation. The influence of organic molecules addition in the system has been also assessed.

At high nickel concentrations, a Ni-containing precipitate could form and limits the concentration of dissolved Ni in ACW to (1.2 ± 0.3) x 10^{-7} M, at a pH = 13.3. Organic molecules addition in the studied system seems to have a minor influence on nickel solubility limit in cement pore water at pH = 13.3. By contrary, degradation of cement and by consequence pore waters composition have effect on Ni solubility at pH = 11.3, giving higher Ni aq. concentrations, and a higher aqueous concentration mean value - one order of magnitude higher.

The mean solubility values calculated in this study will be used to select the range of ^{63}Ni concentrations in kinetic and sorption/desorption tests that will be further performed. The mean values obtained for the operational nickel solubility limit in the cement pore waters are significantly different at various pH values corresponding to cement pore water composition characteristic for the two cement degradation stages considered in this work.

No macroscopic solid phase could be observed in the testing tubes, but it is possible that nickel concentrations in solutions to be governed by meta-stable solids. The phase transformations of these solids have the potential to form new complexes, possibly having different solubility.

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