Experimental evidence for solubility limitation of the aqueous Ni(II) concentration and isotopic exchange of ^{63}Ni in cementitious systems

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Summary. Ni radioisotopes are present in cementitious repositories for radioactive waste and considered to be safety relevant in performance assessment. The behaviour of non-radioactive nickel and ^{63}Ni in cement systems has been investigated in batch-type experiments under conditions corresponding to the initial stage of cement degradation. Solubility tests using ^{63}Ni labelled solutions mixed with an artificial cement pore water (ACW) at pH 13.3 revealed that a Ni-containing precipitate was formed at high Ni concentrations, which limits the concentration of dissolved Ni to $(2.9 \pm 0.5) \times 10^{-7} \text{ M}$. The concentration of dissolved Ni in cement suspensions, however, was controlled by the partitioning of non-radioactive Ni between the hardened cement paste (HCP) and ACW. The concentration of dissolved Ni was found to be independent of the solid-to-liquid (S/L) ratio in the range between $10^{-6} \text{ kg L}^{-1}$ and 0.13 kg L^{-1} ($(7.3 \pm 3.9) \times 10^{-8} \text{ M}$). The concentration of dissolved Ni could not be modelled on the assumption that Ni partitioning is a reversible linear sorption process. The experimental data and the modelling indicate that a solubility-limiting process controls the concentration of dissolved Ni in the cement systems. Measurements of the sorption isotherm showed only a small increase in the concentration of dissolved Ni from about $5 \times 10^{-8} \text{ M}$ to about $8 \times 10^{-7} \text{ M}$ while the concentration of added Ni varied over several orders of magnitudes (10^{-6} M – $5 \times 10^{-2} \text{ M}$). This finding supports the idea that a solid-solution aqueous-solution system involving Ni may account for the behaviour of Ni in cement systems.

The distribution ratio for the partitioning of ^{63}Ni between HCP and ACW was found to be consistent with literature data obtained under similar experimental conditions ($R_d = 0.15 \pm 0.02 \text{ m}^3 \text{ kg}^{-1}$). The R_d value determined on Ni loaded HCP samples ($3.9 \times 10^{-4} \text{ mol kg}^{-1}$ and $4.3 \times 10^{-3} \text{ mol kg}^{-1}$) increased with increasing Ni concentration in HCP. It is shown that the uptake of ^{63}Ni can be interpreted in terms of an isotopic exchange process with the non-radioactive Ni of the cement matrix. The distribution coefficient, α , of the exchange process ranges in value between about 0.02 and about 0.06, indicating that only a small portion of the Ni inventory is accessible to isotopic exchange.

1. Introduction

Cementitious materials are foreseen to be used in the planned deep underground repositories for long-lived intermediate-level (ILW) and low- and intermediate-level (L/ILW) radioactive waste in Switzerland. Similar to the concepts developed worldwide, cement will be employed to condition the waste and to construct the engineered barrier system (components of lining, backfill material). Thus, the near field will consist of about 90 weight percent (wt. %) cementitious materials, of which hardened cement paste (HCP) will be about 20 wt. %. 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 [1]. The uptake of radionuclides by HCP and cement minerals, thus, plays a decisive role in limiting and retarding their release from the near field.

Ni radioisotopes associated with irradiated metallic components from nuclear power plants are present in cementitious repositories for radioactive waste and considered to be safety relevant in performance assessment. Furthermore, non-radioactive Ni, which is present in noticeable quantities in cementitious materials, is an important chemotoxic element. Several studies have reported solubility measurements for Ni under the conditions prevailing in cementitious systems [2–9]. The results from the majority of the studies show that the concentration of dissolved Ni is typically below 10^{-6} M at pH > 12. However, the solubility data could not be interpreted in terms of a consistent thermodynamic model because the uncertainties in the Ni hydrolysis constants are large and the solubility-limiting solid phase is not known [e.g. 6, 10]. Until now only few attempts have been undertaken to identify the solid phase limiting the Ni concentration in cementitious systems [5, 7, 11]. The studies of Glasser and co-workers [5, 7] indicated the formation of a Ni-containing solid phase when a NiCl_2 solution was added to a saturated $\text{Ca}(\text{OH})_2$ solution and aged over a time period of 4 weeks. The Ca : Ni ratio of the new phase was determined to be 4 : 1 using analytical electron microscopy. The morphology and bulk composition of the phase, however, is still unknown. Scheidegger *et al.* [11] used X-ray absorption spectroscopy (XAS) and diffusive reflectance spectroscopy (DRS) to investigate the nature of

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nickel precipitates formed in HCP suspensions. The study indicated that a Ni- and Al-containing hydrotalcite-like solid phase (Ni-Al layered double hydroxide (LDH)) forms in cement suspensions at pH 13.3.

^{63}Ni was employed as a tracer in the relatively few batch-type investigations on Ni uptake by cement [2, 12–15]. This allowed added Ni concentrations to be kept at levels well below solubility limits. In these studies distribution ratios (R_d values) of the partitioning of ^{63}Ni between crushed HCP and cement pore waters were found to range in value between about $0.01 \text{ m}^3 \text{ kg}^{-1}$ and $0.2 \text{ m}^3 \text{ kg}^{-1}$. The differences in the R_d values were attributed to differences in the pH values of the porewaters (pH ~ 12 to 13.3) used in the experiments and the different water-to-cement ratios used for the preparation of HCP. Sorption measurements carried out in suspensions with varying cement concentrations showed that the uptake of ^{63}Ni decreased with increasing solid-to-liquid (S/L) ratio [2, 15]. Consistent with this finding, the distribution ratios determined from diffusion studies on compact cement samples were found to be low ($R_d \sim 0.02\text{--}0.04 \text{ m}^3 \text{ kg}^{-1}$ in [16] and $R_d > 0.002 \text{ m}^3 \text{ kg}^{-1}$ in [13]). At the present time, however, the reason for this apparent dependence of the ^{63}Ni uptake on the cement concentration is unclear.

This paper reports results from wet chemistry experiments carried out to investigate the behaviour of non-radioactive Ni and ^{63}Ni in cementitious systems. We will show that knowledge of the behaviour of Ni associated with the cement matrix as an impurity element is essential for the mechanistic interpretation of the ^{63}Ni immobilization. The findings from these investigations, together with sorption experiments with ^{63}Ni on HCP and isotopic exchange experiments, allow an uptake mechanism for ^{63}Ni by the cement matrix to be proposed.

2. Materials and methods

2.1 Hardened cement paste and porewater composition

Commercial sulphate-resisting Portland cement CEM I 52.2 N HTS, denoted as HTS cement (HTS = Haute Teneur en Silice, Lafarge, France), was used for the preparation of the HCP according to a procedure described earlier [17]. The powdered HCP material used in the experiments was prepared from bulk samples by grinding in a mortar under CO_2 -free conditions and sieving the crushed material to collect the size fractions $\leq 63 \mu\text{m}$. The effective size fraction was determined to be $\leq 70 \mu\text{m}$ from particle size analysis using a Mastersizer X (Malvern, UK). The average surface area was determined to be $57 \pm 4 \text{ m}^2 \text{ g}^{-1}$ based on N_2 sorption BET measurements on four replicates using a Micrometrics Gemini 2360 analyzer.

Throughout this study the solutions were prepared using Fluka or Merck “pro analysis” chemicals. Milli-Q water, generated by a Millipore water purification system, was used for the preparation of the solutions and standards, and for sample dilution. The centrifuge tubes used for the wet chemistry experiments were pre-washed, left overnight in a solution of 0.1 M HCl, and thoroughly rinsed with de-ionised water before use.

The concentration of Ni in HCP was determined from a single sample solution, which was prepared from acid dissolution of HCP using HF, HNO_3 and H_3BO_4 . Acid digestion was carried out as follows: 0.5 g of HCP (size fraction $\leq 70 \mu\text{m}$) was added to a 40 mL FEP Oak-ridge type centrifuge tube (FEP = Perfluorethylen-propylenpolymers, Nalgene Int., USA). 5 mL Milli-Q water and 5 mL HNO_3 (65%), and thereafter, 10 mL Milli-Q water and 2.5 mL HF (40%) were added to the solid. Stepwise addition was required due to CO_2 generation during the dissolution of HCP in acidic solution. The tube was tightly closed and heated in a muffle furnace at 95°C . Occasionally the tube was removed from the furnace and carefully shaken for about one minute. The dissolution of the cement was completed within 4 hours. After cooling the sample to room temperature, the solution was quantitatively transferred into a 250 mL FEP flask containing 100 mL H_3BO_4 (1.25%). A 5 mL aliquot of HNO_3 was then added. The flask was heated in a water bath until the sample solution was completely clear, and then made up to 250 mL with Milli-Q water. The Ni concentration was determined using plasma spectrometric methods. Prior to the Ni analysis the concentration of the main matrix elements (Na, K, Ca) were determined using a radial inductively coupled plasma optical emission spectrometer (ICP-OES), type VistaPro (Varian). The spectrometers used in trace and ultra-trace determinations were a quadrupole-ICP-MS ELAN 6000 (Perkin Elmer/Sciex) and a high-resolution magnetic sector field ICP-MS ELEMENT II (ThermoFinnigan), both operated under standard hot plasma conditions. High-purity acids (suprapure, Merck) and high-purity water ($18.2 \text{ M}\Omega \text{ cm}$) generated by a Milli-Q Gradient A10 System (Millipore) were used for sample and standard preparation. Standards were prepared from single and multi-element standards in ICP-quality (Merck and Alfa Aesar). Rhodium was used for internal standardisation.

Prior to the uptake studies, the composition of the solution in equilibrium with HCP was determined. For this, powdered HCP material was mixed with artificial cement pore water (ACW), which had the composition of a porewater in equilibrium with HCP with respect to the main cement-derived cations at pH 13.3, *i.e.*, Na, K, Ca (see below). The suspensions were equilibrated for a period of 30 days under CO_2 -free conditions. The S/L ratio ranged between $10^{-5} \text{ kg L}^{-1}$ and 0.13 kg L^{-1} . Preliminary kinetic tests showed that equilibrium was attained within a time period of 7 days. After equilibration, solid and liquid phase were separated by centrifugation (60 min at 95 000 g), and the total concentrations of the main cement-derived elements in the supernatant were determined by plasma-emission spectroscopy using an Applied Research Laboratory ARL 3410D inductively coupled plasma optical emission spectrometer (ICP-OES). From these tests the following composition of ACW in equilibrium with HCP was determined: $[\text{K}]_t = 0.18 \text{ M}$, $[\text{Na}]_t = 0.114 \text{ M}$, $[\text{Ca}]_t = 1.6 \times 10^{-3} \text{ M}$, $[\text{Al}]_t = 5 \times 10^{-5} \text{ M}$, $[\text{S}]_t = 2 \times 10^{-3} \text{ M}$, $[\text{Si}]_t = 5 \times 10^{-5} \text{ M}$. The basic preparation of ACW is described elsewhere [18]. The main aspects are briefly as follows: 23.8 g KOH (Merck AG, 87%) and 9.2 g NaOH were dissolved in 2 L Milli-Q water, and an excess of CaCO_3 and $\text{Ca}(\text{OH})_2$ (4 g of each solid) added. The solution was pre-equilibrated with CaCO_3 to fix the CO_3^{2-} concentration in solution at

a level corresponding to saturation with respect to CaCO_3 ($[\text{CO}_3^{2-}]_t = 1.2 \times 10^{-4} \text{ M}$ at pH 13.3). For this, the solutions were shaken for at least one week in closed containers in air. After filtration under N_2 atmosphere through 100 nm polyethersulfone membrane filters (Criticap-MTM, Gelman Sciences, USA), Na_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$ were added to obtain the final composition of ACW. The ACW was stored under N_2 atmosphere until required for use.

2.2 Batch-type solubility and sorption experiments

All experiments were carried out in duplicate in 40 mL polyallomere centrifuge tubes in a glovebox under a controlled N_2 atmosphere (O_2 and $\text{CO}_2 \leq 2 \text{ ppm}$) at room temperature ($T = 23 \pm 3^\circ \text{C}$). For the uptake experiments labelled solutions were prepared using carrier-containing ^{63}Ni radiotracer ($t_{1/2} = 100 \text{ y}$) purchased from Amersham International Plc. (UK) or Isotope Products Europe Blaseg GmbH (Germany). Radio assays to a counting uncertainty of $\% \sigma \leq 0.5$ were performed using a Canberra Packard Tri-carb 2250 CA liquid scintillation analyzer (β counter). The ^{63}Ni samples for radio assay were prepared by mixing 5 mL aliquots with 15 mL scintillator (Ultima Gold XR, Packard Bioscience S.A.).

2.2.1 Solubility tests

Solubility tests using Ni solutions labelled with ^{63}Ni were carried out to determine the solubility limit of Ni in ACW. For this, appropriate quantities of 10^{-3} M and 10^{-4} M NiCl_2 stock solutions were added to 20 mL ACW and labelled with $100 \mu\text{L}$ ^{63}Ni tracer solution. The centrifuge tubes were then made up to 40 mL by adding ACW. The total Ni concentration in the experiment ranged from 10^{-8} M to 10^{-5} M . The tubes were tightly closed and shaken end-over-end for 7 and 28 days. Three aliquots were withdrawn from each solution before and after centrifugation (60 min at 95 000 g) and, together with standards, counted.

2.2.2 Ni background concentration

Non-radioactive Ni, associated with the cement matrix, may be released from HCP after contacting with ACW and, thus, determine the concentration of dissolved Ni. To assess the influence of this process on the Ni concentration in ACW, HCP suspensions with S/L ratios ranging between $10^{-6} \text{ kg L}^{-1}$ and 0.13 kg L^{-1} were prepared and equilibrated. For the sample preparation powdered HCP was weighted into centrifuge tubes, or appropriate aliquots were withdrawn from a vigorously stirred stock suspension (0.05 kg L^{-1} crushed HCP in ACW) and pipetted into the tubes. The tubes were then made up to 40 mL by adding ACW and shaken end-over-end for 30 days. After centrifugation (60 min at 95 000 g) aliquots were sampled from the supernatant and analysed for Ni using ICP-MS.

2.2.3 Determination of the sorption isotherm

These experiments were conducted to determine the uptake of Ni by HCP at increasing Ni concentrations (sorption isotherm). The Ni concentration added to the HCP suspensions ranged between 10^{-6} M and $5 \times 10^{-2} \text{ M}$. For the

sample preparation appropriate aliquots of a NiCl_2 stock solution were added to the suspensions (S/L ratio = $2.5 \times 10^{-2} \text{ kg L}^{-1}$) and shaken end-over-end for 7 and 30 days. After centrifugation (60 min at 95 000 g) aliquots were withdrawn from the supernatant solutions and analysed for Ni using ICP-MS or ICP-OES.

2.2.4 ^{63}Ni uptake by Ni loaded HCP

The uptake of ^{63}Ni by Ni loaded HCP were performed to quantify isotopic exchange of ^{63}Ni with the non-radioactive Ni of the cement matrix. A series of sorption isotherm samples were prepared as described in the above section. The samples had a S/L ratio of $2.5 \times 10^{-2} \text{ kg L}^{-1}$ (1 g crushed HCP in 40 mL ACW). The Ni concentrations added to the suspensions were 10^{-6} M or 10^{-4} M . After equilibration for 7 and 30 days on an end-over-end shaker the suspensions were labelled with ^{63}Ni (^{63}Ni plus carrier concentration = $5 \times 10^{-9} \text{ M}$). The ^{63}Ni labelled samples were then shaken end-over-end and sampled at regular time intervals over a period of 60 days. Three aliquots were withdrawn from the supernatant solutions after centrifugation (60 min at 95 000 g) and, together with standards, radio assayed.

3. Results

Fig. 1 shows the results from the solubility tests using ^{63}Ni labelled solutions. The tests were carried out to determine the solubility limit of Ni in ACW. In Fig. 1 the concentration of dissolved Ni in ACW is shown as a function of the total Ni in the system for two different equilibration periods. The Ni concentrations in ACW before and after centrifugation, *i.e.*, total and aqueous Ni concentrations, respectively, agree well up to a total Ni concentration of about $3 \times 10^{-7} \text{ M}$. Above this limit, however, the formation of a Ni precipitate or a colloidal Ni fraction occurred, thus giving rise to lower Ni concentrations in ACW after centrifugation. The aqueous Ni concentration ranges in value between about $1.5 \times 10^{-7} \text{ M}$ and $4.5 \times 10^{-7} \text{ M}$. Although the concentrations tend to be lower after 28 days equilibration, the

Fig. 1. Ni concentration in solution after centrifugation as a function of the total Ni(II) inventory after 7 and 28 days equilibration. The shaded area indicates the Ni background in ACW.

observed difference is considered not to be significant within the uncertainties in the data. Therefore, the mean value was calculated using all of the data in the concentration range $> 7 \times 10^{-7} \text{ M}$ ($[\text{Ni}]_{\text{aq}} = (2.9 \pm 0.5) \times 10^{-7} \text{ M}$).

For the present study it was considered that, upon contacting HCP with ACW, Ni inherently associated with the cement matrix is released into the pore water. Thus, the partitioning of Ni between HCP and ACW controls the Ni concentration in solution. This speculation was supported from in-house studies on Sr partitioning between HCP and ACW [19]. It was observed that the Sr concentration in ACW, which was controlled by the release of Sr from HCP, depended on the S/L ratio of the cement suspension. This finding prompted the following investigations of the partitioning of Ni between HCP and ACW at increasing S/L ratios. Fig. 2 shows that the concentration of dissolved Ni is close to the background concentration in ACW ($\sim 2 \times 10^{-8} \text{ M}$ – $\sim 4 \times 10^{-8} \text{ M}$). The concentration increases to about $2 \times 10^{-7} \text{ M}$ at S/L ratio = 0.13 kg L^{-1} . It should be noted that, except for the samples with the highest S/L ratio ($= 0.13 \text{ kg L}^{-1}$), the Ni concentrations in solution are significantly lower than the concentration limit determined in the solubility tests.

Investigations of the partitioning of Sr between HCP and ACW showed that the Sr concentration in ACW can be predicted based on mass balance considerations and by assuming linear reversible Sr sorption onto HCP [19]. The approach proposed in [19] is also applied to predict the partitioning of Ni between HCP and ACW. The mass balance in the HCP systems can be written as:

$$n_t = n_s^0 + n_l^0 = n_{s,\text{eq}} + n_{l,\text{eq}} = m_c c_s^0 + V c_l^0 = m_c c_{s,\text{eq}} + V c_{l,\text{eq}} \quad [\text{mol}] \quad (1)$$

- n_t : total mole numbers in the HCP suspension [mol]
- n_s^0 : initial mole number associated with the HCP matrix [mol]
- n_l^0 : initial mole number in ACW [mol]
- $n_{s,\text{eq}}$: mole number in the HCP matrix at equilibrium [mol]
- $n_{l,\text{eq}}$: mole number in ACW at equilibrium [mol]
- m_c, V : mass of HCP [kg] and volume of ACW [m^3]
- c_s^0, c_l^0 : initial concentrations in HCP [mol kg^{-1}] and ACW [mol m^{-3}]
- $c_{s,\text{eq}}, c_{l,\text{eq}}$: equilibrium concentrations in HCP [mol kg^{-1}] and ACW [mol m^{-3}].

The initial Ni concentration (c_s^0) in HCP was determined to be $19.9 \pm 1.3 \text{ ppm}$ ($= (3.39 \pm 0.22) \times 10^{-4} \text{ mol kg}^{-1}$) following the procedure described in the experimental section for the acid digestion of the cement material. The initial concentration in ACW (c_l^0) prior to equilibration with HCP was determined to be $1.8 \pm 0.6 \text{ ppm}$ ($= (3.1 \pm 1.0) \times 10^{-8} \text{ mol L}^{-1}$) using ICP-MS.

The partitioning of Ni between solid and liquid phase is described in terms of a distribution ratio (R_d), which is defined as follows:

$$R_d = \frac{c_{s,\text{eq}}}{c_{l,\text{eq}}} = \left(\frac{c_s^0 - c_{l,\text{eq}}}{c_{l,\text{eq}}} \right) \left(\frac{V}{m_c} \right) \quad [\text{m}^3 \text{ kg}^{-1}] \quad (2)$$

The symbols correspond to those given in Eq. (1). It should be noted that the definition of the distribution ratio as given

Fig. 2. Ni concentration measured in solution shown as a function of the S/L ratio of the HCP suspensions (pH = 13.3) after 30 days equilibration. The dashed line indicates the increasing inventory of Ni in the HCP suspensions, which is associated with HCP. The solid and broken lines represent predictions made for the concentration of dissolved Ni based on mass balance and using R_d values of 150 L kg^{-1} and 1600 L kg^{-1} , respectively. The shaded area indicates the Ni background in ACW.

by Eq. (2) and used in the present study does not imply a specific sorption process. In general terms, Eq. (2) accounts for the relationship between the Ni taken up by the solid and the concentration of dissolved Ni at equilibrium. Thereby, the difference between the Ni concentration added to the suspension (c_s^0) and the concentration determined in the supernatant ($c_{l,\text{eq}}$) corresponds to the amount of Ni taken up by the solid.

Re-arranging Eq. (1) and replacing $c_{s,\text{eq}}$ by $R_d \times c_{l,\text{eq}}$ (R_d in L kg^{-1}) according to Eq. (2) yields the following expression for the Ni concentration at equilibrium, $c_{l,\text{eq}}$:

$$c_{l,\text{eq}} = \frac{m_c c_s^0 + V c_l^0}{m_c R_d + V} \quad [\text{mol L}^{-1}] \quad (3)$$

The following parameters were used for the predictive modelling of the partitioning of Ni between HCP and ACW: $V = 0.04 \text{ L}$, $c_s^0 = 19.9 \text{ ppm}$ ($= 3.39 \times 10^{-4} \text{ mol kg}^{-1}$), $c_l^0 = 3 \times 10^{-8} \text{ mol L}^{-1}$, $R_d = 150 \text{ L kg}^{-1}$ and 1600 L kg^{-1} . Upper and lower bound R_d values are considered in these calculations to account for uncertainties in the modelling. The lower bound value was obtained from tracer studies of ^{63}Ni on pristine HCP (Fig. 4), whereas the upper limit corresponds to the maximum value reported in [2]. Fig. 2 shows that, independent of the R_d value used, the experimental data at S/L ratios $> 10^{-4} \text{ kg L}^{-1}$ are significantly below the expected Ni concentrations (solid and broken lines), indicating that the partitioning of Ni between HCP and ACW cannot be interpreted in terms of a linear reversible sorption process.

Sorption isotherms show the relationship between the bulk activity (concentration) of adsorbate and the amount adsorbed at constant temperature. In the Langmuir adsorption model the initial slope of the isotherm is unity (double logarithmic plot), implying a proportional increase in the concentration of sorbed species with increasing bulk activity of the adsorbate. The slope is less than unity in

Fig. 3. Ni sorption isotherm on HCP in ACW (pH = 13.3). (a) The concentration of dissolved Ni is plotted as a function of the concentration of Ni added, (b) Ni taken up by HCP is shown as a function of the concentration of dissolved Ni. Experimental conditions: S/L ratio = $2.5 \times 10^{-2} \text{ kg L}^{-1}$; equilibration time = 7 and 30 days. The shaded area indicates the Ni background in ACW.

Fig. 4. Time-dependent uptake of ⁶³Ni by pristine HCP (data taken from [14]) and HCP loaded with non-radioactive Ni in ACW. The Ni concentrations added to the HCP suspensions (S/L ratio = $2.5 \times 10^{-2} \text{ kg L}^{-1}$) were 10^{-6} M and 10^{-4} M. The Ni containing HCP suspensions had been pre-equilibrated for 7 and 30 days before ⁶³Ni was added.

the Freundlich-type sorption model. In this study sorption isotherm measurements were conducted to determine the Ni uptake by HCP at increasing Ni concentrations in ACW. The Fig. 3a and b show experimental results from sorption isotherm measurements on HCP ($S/L = 2.5 \times 10^{-2} \text{ kg L}^{-1}$). The data correspond to duplicate measurement of the sorption of non-radioactive Ni at the given concentrations. The Ni concentration in solution was found to increase by about one order of a magnitude from $\sim 5 \times 10^{-8}$ M to $\sim 8 \times 10^{-7}$ M while the concentration of added Ni varied over several orders of magnitudes (10^{-6} M– 5×10^{-2} M) (Fig. 3a). The results presented in Fig. 3b show that Ni uptake by HCP cannot be interpreted in terms of a linear sorption isotherm as the slope is > 1 . The results, however, suggests that solubility limitation rather than an adsorption-type process could account for the observed behaviour of Ni in the cementitious system. Furthermore, the experimentally determined solution concentrations of $\sim 5 \times 10^{-8}$ M to $\sim 8 \times 10^{-7}$ M at added Ni concentrations $> 10^{-4}$ M exceed the Ni concentrations in the solubility tests ($(2.9 \pm 0.5) \times 10^{-7}$ M, Fig. 1) or from solubility measurements with Ni(OH)₂(cr) as reported in an earlier study (3.1×10^{-7} M, [6]). Note further that a dependence of the Ni concentration in cement pore water on the added Ni concentration was already observed by Carlsson and co-workers [9].

Uptake studies of ⁶³Ni on Ni loaded HCP were carried out to investigate the influence of the Ni inventory of the cement matrix on ⁶³Ni binding. In Fig. 4 the results are compared with earlier measurements on HCP as reported in Wieland *et al.* [14]. Fig. 4 shows the distribution ratios of ⁶³Ni, R_{d,M^*} , determined on pristine HCP and the Ni loaded cement samples at a S/L ratio = $2.5 \times 10^{-2} \text{ kg L}^{-1}$. The partitioning of ⁶³Ni was quantified according to Eq. (2). The difference between the ⁶³Ni activity added to the suspension (A_i) and the activity of the supernatant solution after centrifugation ($A_{i,eq}$) was taken as measure of the tracer activity on the solid. Note that in all these tracer experiments, wall sorption of ⁶³Ni was found to be negligible, and the added ⁶³Ni concentration (5×10^{-9} M) was significantly lower than the concentration of non-radioactive Ni in equilibrium with HCP ($\geq (7.3 \pm 3.9) \times 10^{-8}$ M).

In all uptake studies equilibrium was attained within less than 7 days after ⁶³Ni addition, indicating fast kinetics of the ⁶³Ni uptake. Wieland *et al.* [14] determined an R_d value of $0.15 \pm 0.02 \text{ m}^3 \text{ kg}^{-1}$ on pristine HCP, which is consistent with values previously determined on cements at similar S/L ratios [2, 13]. In the case of the Ni loaded samples the R_d value of ⁶³Ni showed no dependence on the equilibration time (7 and 30 days) used for the preceding sorption step with Ni. Nevertheless, the distribution ratio of ⁶³Ni was found to increase with increasing concentration of sorbed Ni added, *i.e.*, from about $0.20 \pm 0.02 \text{ m}^3 \text{ kg}^{-1}$ to about $1.2 \pm 0.1 \text{ m}^3 \text{ kg}^{-1}$ (Table 1). Note that the concentrations of sorbed Ni in these samples were 22.1 ppm and 255.3 ppm at added Ni concentrations of 10^{-6} M and 10^{-4} M, respectively.

Isotopic exchange of ⁶³Ni with a small fraction of non-radioactive Ni in the cement matrix was considered to be responsible for the uptake of ⁶³Ni by HCP in the above experiments. In the case of isotopic exchange the partitioning of ⁶³Ni between HCP and ACW is described in terms of

Table 1. Isotopic exchange of ^{63}Ni in HCP suspensions.

Conditions	R_{d,M^*} [$\text{m}^3 \text{kg}^{-1}$]	$R_{d,M}$ [$\text{m}^3 \text{kg}^{-1}$]	α
No Ni addition	0.15 ± 0.02	4.6 ± 2.3	$(3.3 \pm 1.7) \times 10^{-2}$
$[\text{Ni}]_{\text{add}} = 10^{-6} \text{ M}$			
7 days equilibration	0.22 ± 0.02	4.9 ± 1.0	$(4.5 \pm 1.0) \times 10^{-2}$
30 days equilibration	0.20 ± 0.02	6.9 ± 1.4	$(2.9 \pm 0.6) \times 10^{-2}$
$[\text{Ni}]_{\text{add}} = 10^{-4} \text{ M}$			
7 days equilibration	1.1 ± 0.1	38.6 ± 7.5	$(2.8 \pm 0.6) \times 10^{-2}$
30 days equilibration	1.2 ± 0.1	26.8 ± 5.4	$(4.5 \pm 1.0) \times 10^{-2}$

a partition coefficient, α [20]:

$$\alpha = \frac{(n_{s,M^*}/n_{s,M})}{(n_{l,M^*}/n_{l,M})} = \frac{R_{d,M^*}}{R_{d,M}} \quad [-] \quad (4)$$

n_{s,M^*} and $n_{s,M}$ denote the mole number of ^{63}Ni or non-radioactive Ni, respectively, in HCP, whereas n_{l,M^*} and $n_{l,M}$ denote the respective mole numbers in ACW. Note that the distribution coefficient, α , equals 1 if the total inventory of Ni in HCP is accessible to isotopic exchange. As mentioned above, the distribution ratio of ^{63}Ni , R_{d,M^*} , is given by Eq. (2). Rearranging Eq. (3) leads to the following expression for the distribution ratio of non-radioactive Ni, $R_{d,M}$:

$$R_{d,M} = \frac{m_c c_s^0 + V (c_1^0 - c_{1,\text{eq}})}{m_c c_{1,\text{eq}}} \quad [\text{m}^3 \text{kg}^{-1}] \quad (5)$$

The symbols correspond to those given in Eq. (1). It should be noted that the initial concentration in solution, c_1^0 , corresponds to the total concentration of the background concentration of Ni in ACW and the concentration of added Ni. In Table 1 the distribution ratios, R_{d,M^*} , are listed together with the corresponding $R_{d,M}$ values for Ni. The R_{d,M^*} values correspond to the mean values deduced from the kinetic tests shown in Fig. 4 using the experimental data after 14 days equilibration. The $R_{d,M}$ values were calculated from the sorption isotherm data shown in Fig. 3 and by using Eq. (5). The partition coefficients, α , determined for the different experimental conditions and quantified according to Eq. (4), are listed in Table 1. The table shows that the distribution coefficient, α , ranges in value between $(2.8 \pm 0.6) \times 10^{-2}$ and $(4.5 \pm 1.0) \times 10^{-2}$.

4. Discussion

Knowledge of the retention mechanism of ^{63}Ni in HCP systems is essential for predicting the long-term behaviour of nickel radioisotopes in cementitious repositories for radioactive waste. In earlier studies it was proposed that the uptake of ^{63}Ni can be quantified in terms of a distribution coefficient (K_d value), which implies that an adsorption-type process accounts for the interaction of ^{63}Ni with HCP [2, 12, 13]. The experimental evidence provided from the sorption isotherm measurements performed in this study (Fig. 3a), however, contradict the idea that the uptake of ^{63}Ni by HCP is controlled by linear sorption. The results from the ^{63}Ni uptake measurements at different Ni inventories (Fig. 4) rather suggest that isotopic exchange of ^{63}Ni with the non-radioactive Ni in HCP takes place and determines the interaction of the radiotracer with the cement matrix. Isotopic

exchange of ^{63}Ni with the Ni inventory in HCP can be expressed in terms of a distribution coefficient, α , which ranges in value between $(2.8 \pm 0.6) \times 10^{-2}$ and $(4.5 \pm 1.0) \times 10^{-2}$ as determined in this study. It should be noted that the observed variation is small compared to the large variation in the Ni inventory in these experiments, *i.e.* 19.9 ppm in pristine HCP, and 22.1 ppm and 255.3 ppm, respectively, in the Ni loaded HCP samples. This indicates that the same portion of the Ni inventory is accessible to isotopic exchange at different Ni loadings. Furthermore, α was found to be significantly less than unity, indicating that only a small portion of the Ni inventory in the cement matrix, *i.e.*, between $2.8 \pm 0.6\%$ and $4.5 \pm 1.0\%$, is accessible to isotopic exchange under the given experimental conditions.

The findings from this study indicate that isotopic exchange accounts for the ^{63}Ni uptake by HCP. Isotopic exchange of ^{63}Ni , however, is determined by the total Ni concentration in ACW and the inventory of exchangeable Ni in the HCP. Therefore, Ni, which is present as impurity in the cement matrix, plays an important role in the immobilization of ^{63}Ni in cementitious systems. This implies that, in addition to studies on ^{63}Ni partitioning between HCP and ACW, complementary studies of the behaviour of non-radioactive Ni in cementitious systems are essential for a thorough interpretation of the radiotracer data. In particular, identification of the Ni solid phase that is limiting the Ni concentration in the HCP system and the determination of the thermodynamic data are required.

Previous work indicated that $\beta\text{-Ni}(\text{OH})_2(\text{cr})$ may be the solid phase limiting the Ni concentration [2, 4, 6]. To test this assumption, the solubility of $\beta\text{-Ni}(\text{OH})_2(\text{cr})$ at pH 13.3 was calculated using the set of consistent solubility and hydrolysis constants published earlier by Plyasunova *et al.* [21] and recently used by Hummel and Curti [10] (Table 2) and compared with the experimental data of this study. The solubility constants deduced in [21] were obtained from solubility measurements using thermodynamically stable or “aged” modifications of $\text{Ni}(\text{OH})_2(\text{cr})$, *i.e.*, presumably $\beta\text{-Ni}(\text{OH})_2(\text{cr})$. The speciation calculations revealed that the solubility limit of Ni is about $2 \times 10^{-6} \text{ M}$ at pH 13.3 ($I = 0.3 \text{ M}$). However, by taking into account the uncertainties associated with the nickel hydrolysis constants [10, 21], the range of Ni concentrations consistent with solubility limitation by $\beta\text{-Ni}(\text{OH})_2(\text{cr})$ extends over four orders of magnitude, *i.e.*, from $2 \times 10^{-8} \text{ M}$ to $2 \times 10^{-4} \text{ M}$. This covers the entire range of Ni concentrations determined experimentally in this study, *e.g.*, $[\text{Ni}]_{\text{aq}} = (2.9 \pm 0.5) \times 10^{-7} \text{ M}$ as measured in the solubility tests (Fig. 1), $[\text{Ni}]_{\text{aq}} = (7.3 \pm 3.9) \times 10^{-8} \text{ M}$ as determined from measurements of the Ni background

Table 2. Thermodynamic constants for solubility and speciation calculations ($T = 25\text{ }^{\circ}\text{C}$).

Chemical equilibrium	Plyasunova <i>et al.</i> [21] log K^0
$\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$	-9.5 ± 0.36
$\text{Ni}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-18.0 ± 1.4
$\text{Ni}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{NiOH}_3^- + 3\text{H}^+$	-29.7 ± 2.0
$\text{Ni}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_4^{2-} + 4\text{H}^+$	-44.96 ± 0.88
$\text{Ni}(\text{OH})_2(\text{cr}) + 2\text{H}^+ \rightleftharpoons \text{Ni}^{2+} + 2\text{H}_2\text{O}$	10.52 ± 0.59

a: For the speciation calculations, the thermodynamic complexation constants log K^0 were corrected for ionic strength $I = 0.3\text{ M}$ using the Davies equation with $b = 0.3$ in the correction term.

concentration (Fig. 2), and $[\text{Ni}]_{\text{aq}} \sim 10^{-7}\text{ M} - \sim 10^{-6}\text{ M}$ as obtained from the sorption isotherm data. Thus, due to the large uncertainties associated with the hydrolysis constants, it is believed that the thermodynamic data in Table 2 are of very limited use for developing a mechanistic interpretation of the behaviour of Ni in cementitious systems.

The experimental data reported in this study contradict the idea that a pure phase, such as $\beta\text{-Ni}(\text{OH})_2(\text{cr})$, controls the Ni concentration in cementitious systems. If this were the case then the Ni concentration in solution should have a constant value independent of the Ni inventory. The results from the sorption isotherm measurements, however, show increasing concentrations of dissolved Ni at increasing concentrations of total Ni in the HCP system (Fig. 3b). This indicates that the Ni concentration is limited by a solid phase with variable composition (solid solution) rather than a fixed bulk composition (pure solid phase) [*e.g.*, 22].

According to X-ray absorption spectroscopy (XAS) studies performed on HCP samples, hydrotalcite-like solid phases, such as mixed Ni-Al layered double hydroxides (LDH), form in cementitious systems [11]. The Ni loadings of the samples investigated in the study of Scheidegger *et al.* [11] were estimated to be about 23 000 ppm, which corresponds to a concentration of sorbed Ni of about 0.39 mol kg^{-1} (Fig. 3a). It should be noted that, in the study of Scheidegger *et al.* [11], the concentration of Ni bound to HCP was about three orders of magnitude higher than the concentration of Ni in pristine HCP ($3.4 \times 10^{-4}\text{ mol kg}^{-1}$). High Ni loadings were required due to limitations in the sensitivity of the EXAFS beamline used for the measurements. The spectroscopic data reported in [11] revealed the formation of predominantly Ni-Al LDH (> 91%) with minor impurities of $\beta\text{-Ni}(\text{OH})_2(\text{cr})$ in the Ni-containing HCP suspensions initially oversaturated with respect to $\beta\text{-Ni}(\text{OH})_2(\text{cr})$. Further evidence in support of the formation of Ni-Al LDH was provided by diffuse reflectance spectroscopy [11], and very recently from investigations on the speciation of Ni in compacted HCP using micro XAS [23]. Thus, spectroscopic evidence has been presented in these studies that Ni-Al LDH could play an important role in the immobilization of Ni in HCP. The results from the wet chemistry studies reported here are consistent with the proposal that the concentration of dissolved Ni in the HCP systems is controlled by a solid-solution aqueous-solution equilibrium system, most likely involving a Ni-Al LDH-type solid phase with variable Ni:Al stoichiometry. At the present

time, however, comprehensive sets of thermodynamic data for Ni-containing hydrotalcite-like phases are still lacking. These data will be required in the future with a view to long-term predictions of the immobilization of Ni in a cementitious repository for radioactive waste made on the basis of the thermodynamic modelling of the Ni retention in HCP systems.

5. Conclusions

This study emphasises the need for re-assessing the uptake mechanism of ^{63}Ni by HCP and detailed investigations of the partition of non-radioactive Ni between the cement matrix and the pore water. The results from the wet chemistry experiments presented here indicate that the concentration of dissolved Ni appears to be controlled by a solubility limiting rather than an adsorption-type process as proposed in earlier studies. Experimental evidence has been provided that $\beta\text{-Ni}(\text{OH})_2(\text{cr})$ may not be the solid phase limiting the concentration of dissolved Ni, further supporting the proposal that a Ni-Al LDH-type phase is involved in controlling the concentration of Ni in cementitious systems [11]. The uptake of ^{63}Ni by HCP occurs *via* isotopic exchange with the non-radioactive Ni in the cement matrix. However, it appears that only a small portion of the Ni inventory is accessible to isotopic exchange. The results from this study suggest that the behaviour of non-radioactive Ni has to be taken into account for predictions of the long-term immobilization of nickel radioisotopes in a cementitious repository for radioactive waste. Implications for performance assessments will be discussed in details in a forthcoming publication.

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