

Effect of competition from other metals on nickel complexation by α -isosaccharinic, gluconic and picolinic acids

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ABSTRACT

The effect of competition from other metal ions on the complexation of Ni with isosaccharinic acid, gluconic acid and picolinic acid, at high pH, is described. The competing metal ions used were divalent Co, trivalent Eu and tetravalent Th. In the majority of cases, competition from these metal ions followed the predicted pattern, with most anomalies seeming to be caused by sorption of Ni to the many different solid phases formed in presence of the competing ions. The Ni solid phase was shown to change with time during the course of the study. No major unexplained competition effects were found.

KEYWORDS: modelling, engineered barrier, europium, isosaccharinic acid, gluconic acid, picolinic acid, nickel, radionuclide transport, thorium.

Introduction

AN objective of the Nuclear Decommissioning Authority (NDA) in the UK is to provide safe, environmentally sound and publicly acceptable options for the long-term management of radioactive waste. The NDA has developed a deep underground geological disposal facility (GDF) concept that makes use of a combination of engineered and natural barriers (Tweed, 2012). Physical containment of radionuclides will be achieved by immobilization and packaging of the wastes, mostly in stainless steel containers. Geological isolation will be achieved by emplacement of the waste packages in vaults excavated deep underground within a suitable geological environment, before a decision is made either to retrieve the waste, or to seal it by backfilling the GDF with Nirex reference vault backfill (NRVB) (Nirex, 2003). The cementitious backfill will

provide a high pH environment for at least one million years and abundant surfaces for sorption (Nirex, 2003). This alkalinity greatly reduces the solubility of many inorganic toxic or hazardous species, and inhibits most microbiological processes (Bath *et al.*, 2010).

After closure, the GDF will become saturated with groundwater and a highly alkaline pore water will develop, with an initial pH of ~13.4. The pH will decrease to 12.5 (Arcos *et al.*, 2003) as sodium and potassium hydroxides are removed. Eventually, calcium hydroxide and calcium silicate hydrate gels will dominate the aqueous geochemistry. The release of many radionuclides from the GDF vaults will be reduced by their limited solubility in the highly alkaline cement pore water (from which they will precipitate as oxides and hydroxides), and their sorption onto cementitious surfaces.

Organic ligands are likely to be present in the pore fluids that develop in the GDF, some of these are inherent components of the wastes (e.g. those arising from decontamination operations), but the

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majority will form as a result of degradation of solid organic materials, particularly cellulose. Among the anthropogenic ligands, picolates are likely to be present in certain waste streams due to the use of picolinic acid (PA) as a decontamination agent (Dey *et al.*, 1992). It has been shown that the presence of cellulose degradation products, particularly α -isosccharinic acid (ISA), which is the main degradation product under alkaline conditions, can substantially increase the solubility of radionuclides (Warwick *et al.*, 2003). Gluconic acid (GA) is included in this study as: (1) it is structurally similar to ISA (i.e. polyhydroxylated); (2) a strong ligand which is useful for comparison purposes; (3) readily obtained at high purity; and (4) may occur in the GDF if it is used as a cement additive, as has been proposed for a Swiss GDF.

Many studies have investigated systems containing a single radionuclide and a single organic ligand. These studies are crucial for understanding the thermodynamics and kinetics of such systems. However, in a GDF many radionuclides and ligands will be present. The interaction of nickel with the three chosen ligands, isosccharinic, gluconic and picolinic acid, is relatively well understood, our objective is to determine whether this understanding can be expanded to predict its behaviour in systems in which nickel is in competition with other radionuclides. From the performance assessment point of view, it is necessary to know whether the processes occurring in these systems are predictable and capable of interpretation.

At the pH values investigated in this study (11.5 to 13.5), which are representative of the near field of an intermediate-level waste (ILW) GDF, Ni has a low solubility (Evans *et al.*, 2004). Previous studies have shown that the three ligands increase its solubility by forming aqueous complexes. However, complexation of organics with competing inactive metal ions could also reduce their impact on near-field performance. The metals chosen as competitors were tetravalent thorium, trivalent europium and divalent cobalt. Predictions of Ni solubility were made for each system, as an aid to understanding the results, and the interpretation of competitive effects.

Experimental

Deionized water produced by a Barnstead NANOpure purification system was used throughout. The sodium salt of isosccharinic acid (NaISA) was prepared using the procedure

described by Whistler and BeMiller (1958). Analytical reagent grade $\text{Th}(\text{NO}_3)_4$, CoCl_2 , EuCl_3 , NiCl_2 , sodium gluconate and picolinic acid were purchased from Fisher Scientific (Loughborough, UK). The experiments were conducted in 15 cm³ polycarbonate centrifuge vials. Three sets of NiCl_2 solutions spiked with ⁶³Ni were prepared at concentrations of 10⁻², 10⁻³ and 10⁻⁴ mol dm⁻³. The ligands, ISA, PA and GA, were added to produce equimolar concentrations with the Ni. Competing metal ions were added to produce a concentration of 10⁻³ mol dm⁻³ in all of the vials, resulting in one set of solutions with Ni at a tenfold excess over the competing metal ion; one set with an equal concentration of Ni and the competing metal ion; and one set with the competing metal ion at a tenfold excess over Ni.

Sodium hydroxide (NaOH) was added to produce four different pH values in the range 11.5 to 13.5 for each permutation of metal ions and concentrations. For example, the Ni–GA system was studied at 10⁻², 10⁻³ and 10⁻⁴ mol dm⁻³ with all three concentrations run at four different pHs between 11.5 and 13.5. For each concentration/pH combination three replicates were performed. Control samples without ligands were also studied. The vials were equilibrated for two weeks before sampling. Carbonate was not specifically excluded from these experiments, although the vials were kept sealed during equilibration.

For each system of Ni–ligand concentration and competing metal ion, three vials were set up. Each of the three vials for each system was sampled in triplicate after equilibration. Before sampling, the pH of the solution was measured, the vials were then centrifuged for five minutes. An 8 cm³ sample was withdrawn with a syringe and filtered through a Millex 0.02 μm syringe filter, with the first 3 cm³ being discarded to waste to allow for sorption onto the filter. Three 1 cm³ aliquots from the filtered solution were then added to 10 cm³ of Ecoscint, neutralized with HCl to reduce chemiluminescence, shaken on a Fisons Whirlimixer for 1 minute and allowed to light-adjust for 1 hour. The ⁶³Ni activity was measured by liquid scintillation counting on a Canberra Packard TRI-Carb 2750TR/LL.

Calculated Ni Solubility

Speciation calculations were performed using the *JCHESS* (Van der Lee, 2003) programme for each system. Stability constants values used were from

the *HATCHES* database (version NEA16) (Bond *et al.*, 1997).

Nickel speciation

In order to interpret the experimental results, it is necessary to have an understanding of the expected behaviour of each metal ion in the absence of other cations across the pH range studied. Figure 1 shows that Ni solubility increases at high pH due to the formation of $\text{Ni}(\text{OH})_3^-$ (aq). Picolinic acid complexes strongly with Ni, but it has a declining effect as pH rises (Evans *et al.*, 2004). Above pH 13.5, the most significant Ni species is $\text{Ni}(\text{OH})_3^-$. Gluconic acid is a very strongly complexing ligand, which dominates the speciation of Ni and causes its solubility to be at inventory level across the pH range studied. Isosaccharinic acid has a significant effect on the solubility of Ni only above pH 13. Although PA is strongly complexing with divalent ions such as Co^{2+} , its effect rapidly diminishes above pH 12. As a result, the increase in Co solubility above pH 13 is due to the hydrolysis products $\text{Co}(\text{OH})_3^-$ and $\text{Co}(\text{OH})_4^{2-}$. Gluconic acid complexes very strongly with Co and this leads to the prediction that all the Co should be in solution as a Co–GA complex. Isosaccharinic acid also complexes very strongly with Co. This implies that all the Co should be in solution as a Co–ISA complex. Gluconic acid complexes strongly with Eu above pH 13, but ISA only weakly. The hydrolysis products $\text{Eu}(\text{OH})_4^-$ and $\text{Eu}(\text{OH})_3(\text{aq})$ dominate the speciation. Picolinic

acid complexes very weakly with Th; from pH 11.5 to 14 Th speciation is dominated by the hydrolysis product $\text{Th}(\text{OH})_4(\text{aq})$. This calculation was performed assuming thorianite to be the solid phase formed. Thorium complexes strongly with ISA in the pH range studied, forming the Th–ISA[−] complex, although its effects diminish above pH 13 as hydrolysis products become more significant (Evans *et al.*, 2004).

Results

In many of the systems it was apparent that more than one metal ion was forming a solid phase. This may have been a mixed hydroxide, and so the Ni solubility was not necessarily being determined above a pure Ni phase. This may have influenced the solubility values obtained. The calculated values for the mixed metal systems represent the concentrations above Ni (hydr)oxide phases, so this could introduce an additional uncertainty when comparison is made between the calculated values and the measured concentrations. The measured solubilities are given as the mean ± 1 standard deviation from 3 results for each experiment, except where noted. The predicted Ni solubility in the absence of competing metal ions is shown in each figure. Although the speciation, performed using *JCHESS*, began with a Ni^{2+} concentration of $10^{-2} \text{ mol dm}^{-3}$, the calculated concentration of Ni in solution is around $6 \times 10^{-7} \text{ mol dm}^{-3}$ at pH 12, due to the precipitation of $\text{Ni}(\text{OH})_2(\text{am})$.

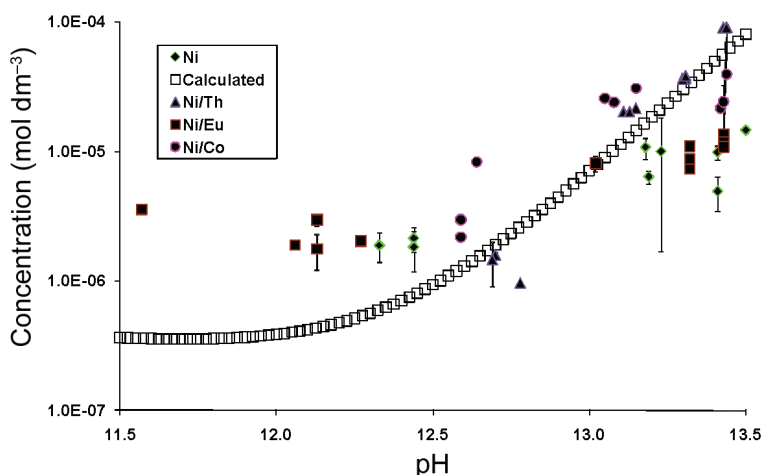


FIG. 1. System with total $[\text{Ni}] = 10^{-3} \text{ mol dm}^{-3}$ in absence of ligands, showing effect of competing metal ions. Calculated values from *JChess*.

In the absence of organic ligands, the measured Ni solubilities in the systems with total Ni equal to 10^{-2} , 10^{-3} and 10^{-4} mol dm⁻³ showed the predicted increase at high pH, due to the formation of hydrolysis products, an example is shown in Fig. 1. There appeared to be no significant effect due to other metal ions and/or solid phases being present. All values were within one order of magnitude of the 'calculated value'. Variations may have been caused by differences in the Ni(OH)_{2(am)} solid phase.

Picolinic acid systems

The competing metal ions used in the Ni-PA systems were Th and Co; Eu was not used as trivalent cations have very little affinity for PA at high pH.

Total [Ni] = 10^{-2} mol dm⁻³

For this system, the effect of Co and Th on Ni solubility was calculated to be virtually zero, hence all three 'calculated' plots lie over each other. When comparing these with the experimental values, the calculated Ni solubility trend was followed as shown in Fig. 2, with variations from the calculated values being much less than an order of magnitude.

Calculations predicted no effect of Co on Ni solubility, as Ni is predicted to be complexed more strongly. However, the experimental results indicate that Co slightly reduced the Ni solubility across the pH range studied, below both the experimental and calculated values. It should be

noted that very slight changes in the picolinate, or hydrolysis, or solubility product constants could account for this small discrepancy. This may also be due to stronger than predicted Co complexation with picolinate. Thorium was predicted to have no effect on Ni solubility. When compared to the measured values, this appeared to be the case, although the solubility with and without Th was less than predicted by about 50%.

Total [Ni] = 10^{-3} mol dm⁻³

When the total concentration of Ni was reduced to 10^{-3} mol dm⁻³, changes were observed in both the calculated and the experimental solubility values, and, in general, the calculated trend in Ni solubility was followed (Fig. 3). The solubility was slightly less than predicted, most markedly at the lower end of the pH range. The experiment results are consistent with the absence of the competitive effects predicted by the models; although the overall Ni solubility was slightly less than predicted, it is within the same order of magnitude in all cases.

Total [Ni] = 10^{-4} mol dm⁻³

In these experiments the competing metal ion is in tenfold excess over the initial [Ni]. In the absence of competing metal ions the [Ni]_(aq) remains at $\sim 10^{-5}$ mol dm⁻³ across the pH range (Fig. 4). Above pH 13 all the metal ions caused a significant reduction in Ni solubility, of about one order of magnitude. This may be due to sorption to the solid phases, or co-precipitation with the Ni being scavenged out as the lowest inventory

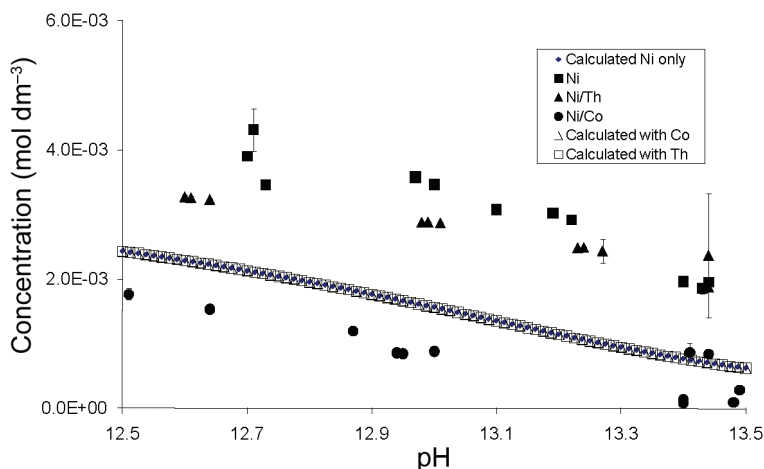


FIG. 2. System with total [Ni] = 10^{-2} mol dm⁻³ with PA and competing metal ions.

NICKEL COMPLEXATION

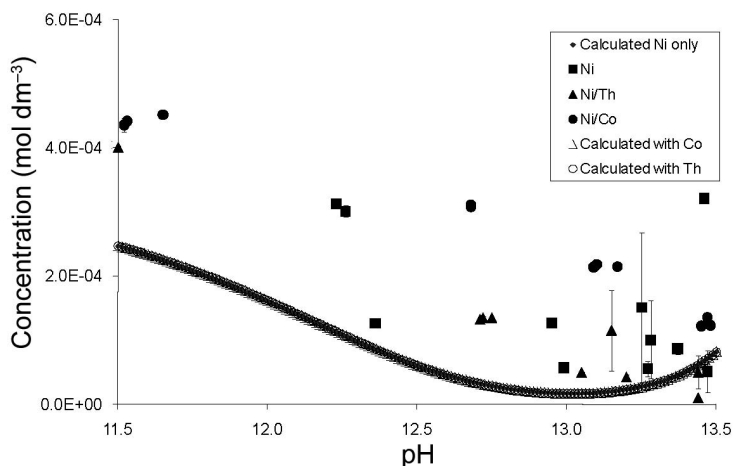


FIG. 3. System with total $[Ni] = 10^{-3} \text{ mol dm}^{-3}$ with PA and competing metal ions.

metal. The Ni solubility is suppressed at high pH, probably by sorption or co-precipitation. Cobalt was predicted to have no effect on Ni solubility, which was the case up to pH 13.1, when sorption begins to occur. This effect increased with pH. It may be that the speciation (hydrolysis) of these metal ions is not fully understood at high pH. Thorium was predicted to have no effect on Ni solubility, which was the case up to pH 13.1, when sorption began to occur (Fig. 4). This effect increased with pH, as for Co.

Gluconic acid systems

No stability constants were available for Th–GA complexes, so no predictions could be made on

their effects on Ni solubility. Gluconic acid complexes very strongly with Ni, so it would be expected that the $[Ni]$ in solution would be approximately the same as its inventory in each system (Figs 5–7).

$$\text{Total } [Ni] \text{ in system} = 10^{-2} \text{ mol dm}^{-3}$$

The measured $[Ni]_{(aq)}$, in the absence of competing metal ions, indicated that all the Ni was complexed with GA in solution (Fig. 5). Cobalt and thorium, consistently reduced $[Ni]_{(aq)}$ by around 10 and 20%, respectively, across the pH range. This latter figure could be explained by the formation of a Th–GA₂ species. Although, Co was predicted to have no effect on $[Ni]_{(aq)}$, the measured values show some reduction in Ni in

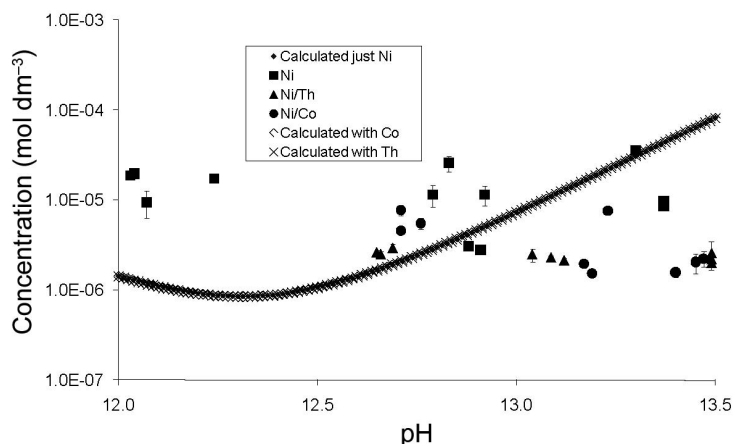


FIG. 4. System with total $[Ni] = 10^{-4} \text{ mol dm}^{-3}$ with PA and competing metal ions.

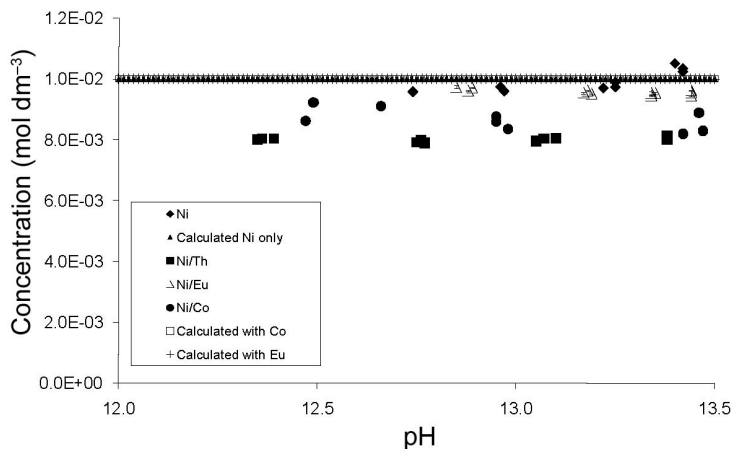


FIG. 5. System with total $[\text{Ni}] = 10^{-2} \text{ mol dm}^{-3}$ with GA and competing metal ions.

solution. Although it is possible that this is due to sorption onto a Co solid phase, it seems more likely that the Co is complexing with gluconate, reducing the amount available for Ni complexation. Given that $[\text{Co}]$ is 10% of the $[\text{Ni}]_{(\text{aq})}$ in these systems, this seems the more probable explanation. Europium was predicted to have no effect on $[\text{Ni}]_{(\text{aq})}$, as observed (Fig. 5). The measured values showed a very slight reduction in Ni in solution, but this does not appear to be significant, and may have been caused by sorption, rather than complexation reactions.

Total [Ni] in system = $10^{-3} \text{ mol dm}^{-3}$

When the Ni inventory in the system was $10^{-3} \text{ mol dm}^{-3}$, and in the absence of competing metal

ions, the $[\text{Ni}]$ in solution was roughly as predicted (Fig. 6). In these systems, the Ni and competing metal ions were in equimolar quantities. However, in general, $[\text{Ni}]$ in solution was not affected any more than in the previous system by the presence of other cations (e.g. the results in the presence of Co are virtually identical). The Th results are the most difficult to explain. At $[\text{Ni}] = 10^{-2}$ and $10^{-4} \text{ mol dm}^{-3}$, Th affected $[\text{Ni}]_{(\text{aq})}$ as though it was forming strong complexes with GA. However, this did not seem to happen in this system. Europium reduced the $[\text{Ni}]$ in solution by ~20% across the pH range, in comparison with both the measured and calculated values. This suggests that either there was sorption of Ni species to the Eu solid phase, or that a degree of

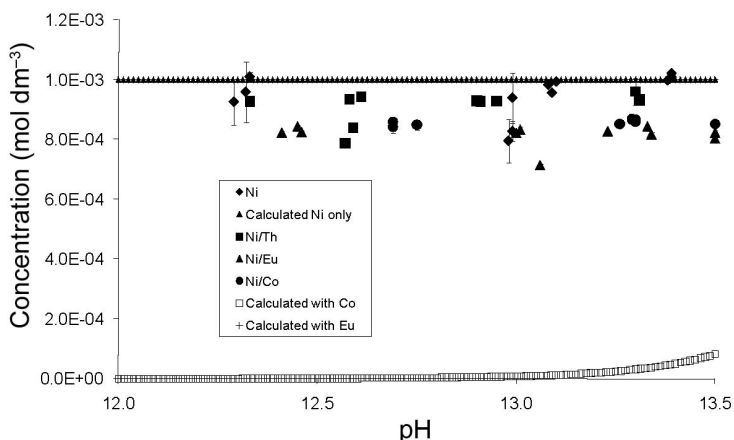


FIG. 6. System with total $[\text{Ni}] = 10^{-3} \text{ mol dm}^{-3}$ with GA and competing metal ions.

Eu–GA complexation occurred, above that which was predicted.

Total [Ni] in system = 10^{-4} mol dm $^{-3}$

In the experiments where the competing metal ions are in tenfold excess over the starting [Ni], and the absence of competing metal ions, the $[\text{Ni}]_{(\text{aq})}$ was roughly as predicted at 10^{-4} mol dm $^{-3}$ (Fig. 7). All the competing metal ions significantly reduced the [Ni] in solution. As was the case in the 10^{-2} mol dm $^{-3}$ Ni system, Th appeared to have complexed strongly with GA, causing the Ni to precipitate, presumably as an (oxy)hydroxy species. Cobalt significantly reduced the $[\text{Ni}]_{(\text{aq})}$ in line with its predicted effect. Europium had a significant effect on $[\text{Ni}]_{(\text{aq})}$ reducing it from the predicted 1×10^{-4} to approximately 1.5×10^{-6} mol dm $^{-3}$. This would indicate that significant Eu–GA complexation occurred, despite the speciation suggesting that Ni forms stronger complexes than Eu. An alternative explanation would be the formation of stable Eu–GA octanuclear clusters, which have not been accounted for in the speciation calculations (Permin and Ibers, 1997).

Isosaccharinic acid systems

Total [Ni] in system = 10^{-2} mol dm $^{-3}$

In general the Ni solubility followed the calculated trend, both with and without the presence of competing metal ions when the total concentration of Ni was 10^{-2} mol dm $^{-3}$ (Fig. 8).

The only exception was that Co and Eu reduced the $[\text{Ni}]_{(\text{aq})}$ in solution more than predicted above pH 13.2. This may again be explained by an insufficient understanding of hydrolysis speciation at high pH, or the production of a different solid phase. Another possibility is that Th is forming mixed complexes with Ni and ISA at high pH. However, this seems unlikely as the Ni is in tenfold excess over the other cations. Speciation predictions suggested that Co should have little effect on Ni solubility. Thorium was predicted to have no effect on the Ni solubility, as can be seen in Fig. 8, the two predicted concentration lines lying on top of one another. This was borne out by the experimental results.

Total [Ni] in system = 10^{-3} mol dm $^{-3}$

When the total inventory of Ni was 10^{-3} mol dm $^{-3}$, the competing metal ions have little or no effect on Ni solubility from pH 11.5 to 13.2. Above 13.2, Co seemed to reduce the solubility of Ni below the predicted level (Fig. 9), but it should be noted that the control samples with no competing metal ion present gave the same results. Cobalt was predicted to reduce the $[\text{Ni}]_{(\text{aq})}$ by preferentially complexing with ISA. This appears to have been the case, although the effect was more marked than was calculated. The experimental data for Eu competition were more scattered, but basically followed the calculated pattern of having no effect on Ni solubility. Thorium had no impact on Ni solubility as predicted.

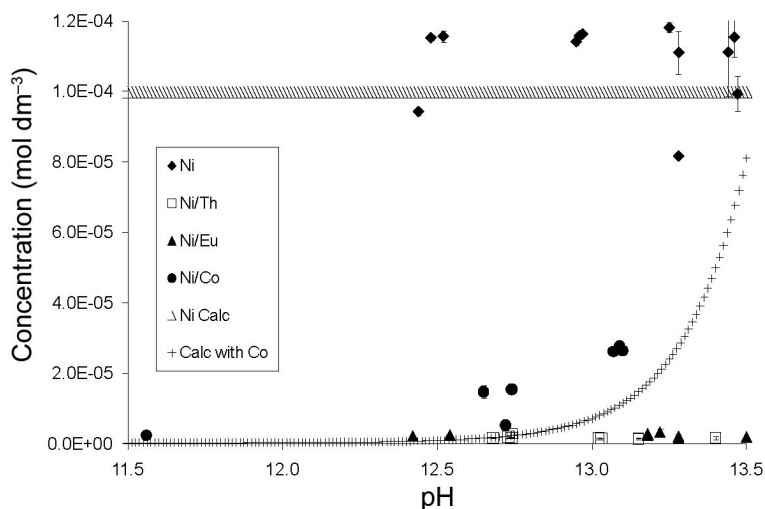


FIG. 7. System with total $[\text{Ni}] = 10^{-4}$ mol dm $^{-3}$ with GA and competing metal ions.

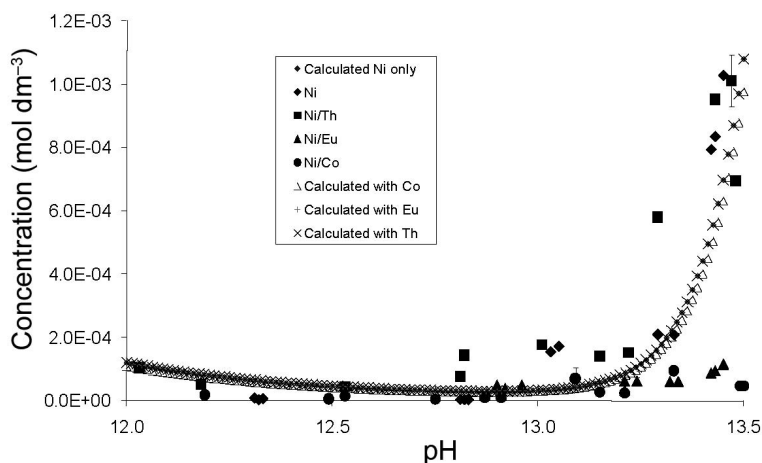


FIG. 8. System with total $[\text{Ni}] = 10^{-2} \text{ mol dm}^{-3}$ with ISA and competing metal ions.

Total [Ni] in system = $10^{-4} \text{ mol dm}^{-3}$

Even when the competing metals were in tenfold excess compared with the total Ni inventory, the data for all metal ions broadly followed the calculated pattern, of having little or no impact on Ni solubility (Fig. 10).

Conclusions

The measured Ni concentrations in the absence of competing metal ions showed good correlation with the calculated values. In the absence of organic ligands, there was evidence for slight sorption of Ni to Th- and Eu-bearing phases

above pH 13 in some systems. There appeared to be no significant effect due to other metal ions and/or solid phases being present.

The calculated Ni solubility trend was generally followed with PA. Except for Co, the measured solubilities were slightly higher than calculated. As would be expected from its low affinity for PA, Th had little effect. However, when the competing ions were in tenfold excess in comparison to the Ni inventory ($10^{-4} \text{ mol dm}^{-3}$) all metal ions caused a significant reduction in $[\text{Ni}]_{(\text{aq})}$ above pH 13, which may be due to sorption to solid phases, or co-precipitation, with Ni being scavenged as the lowest inventory metal.

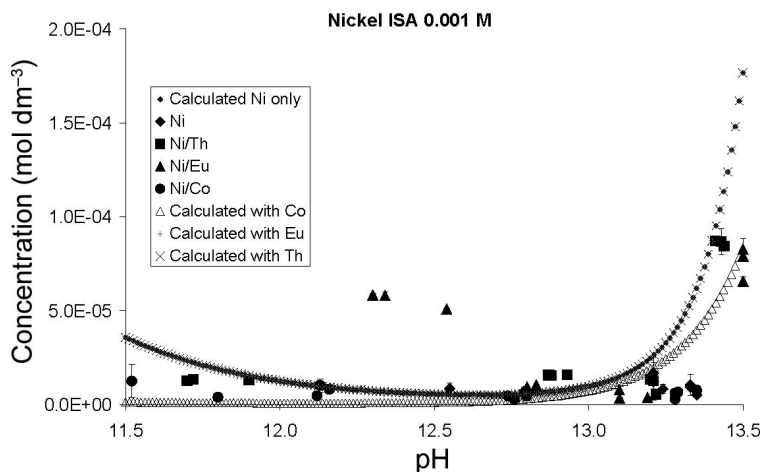


FIG. 9. System with total $[\text{Ni}] = 10^{-3} \text{ mol dm}^{-3}$ with ISA and competing metal ions.

NICKEL COMPLEXATION

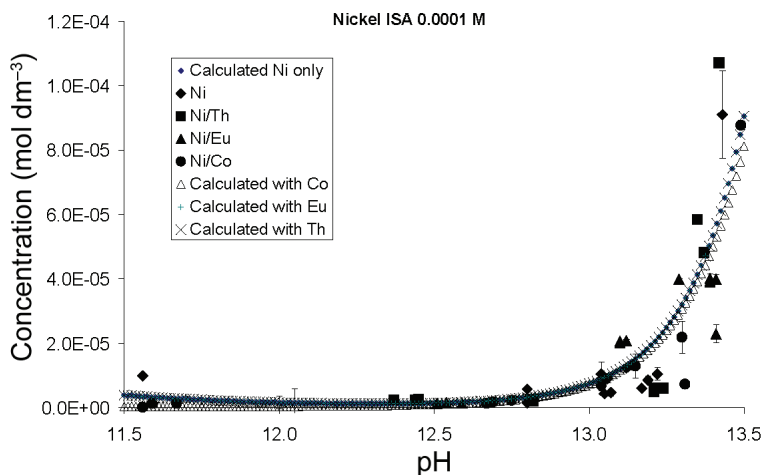


FIG. 10. System with total $[\text{Ni}] = 10^{-4} \text{ mol dm}^{-3}$ with ISA and competing metal ions.

All Ni was complexed with GA in solution, and in the absence of competing ions the concentration of Ni in solution equalled the total inventory. Europium had no significant effect at $[\text{Ni}] = 10^{-2} \text{ mol dm}^{-3}$. Cobalt and thorium reduced $[\text{Ni}]_{(\text{aq})}$ across the pH range, probably due to complexation with GA. Europium had a marginally greater effect at $[\text{Ni}] = 10^{-3} \text{ mol dm}^{-3}$, suggesting a very slight amount of complexation. The Th results are the most difficult to explain. At $[\text{Ni}] = 10^{-2}$ and $10^{-4} \text{ mol dm}^{-3}$, Th affected $[\text{Ni}]_{(\text{aq})}$ as though forming strong GA complexes, but this was not the case at $[\text{Ni}] = 10^{-3} \text{ mol dm}^{-3}$. At $[\text{Ni}] = 10^{-4} \text{ mol dm}^{-3}$, all competing metal ions significantly reduced $[\text{Ni}]_{(\text{aq})}$. Thorium complexed strongly with GA, causing Ni to precipitate. The presence of Co significantly reduced $[\text{Ni}]_{(\text{aq})}$ in line with predictions. Europium had a significant effect on $[\text{Ni}]_{(\text{aq})}$ reducing it from the predicted 1×10^{-4} to approximately 1.5 to $2.5 \times 10^{-6} \text{ mol dm}^{-3}$. This suggests significant Eu–GA complexation occurred.

In general, the Ni solubility with ISA followed the calculated trend, with and without competing metal ions, except where Co and Eu reduced $[\text{Ni}]_{(\text{aq})}$ more than predicted above pH 13.2. This may be due to an insufficient understanding of hydrolysis speciation, or production of a different solid phase. From pH 11.5 to 13.2, the competing metal ions had little or no effect at an equimolar concentration of Ni and the competing ions. Above pH 13.2, Co seemed to reduce the Ni solubility below the predicted level, but the control samples gave the same results. As

predicted, Eu and Th had no effect. At the lowest Ni concentration, all metal ions broadly followed the calculated pattern, of having little or no impact on Ni solubility. It is intended to extend this study to the effect of iron and calcium in the future to mimic more accurately the real aqueous chemistry in a cementitious GDF. The differences observed between predicted and experiments values indicated that there is a need to improve the knowledge and understanding of the stability constants for complexes formed in these high pH systems and the formation of mixed species.

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