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Invited Review

Nickel Aqueous Speciation and Solubility at Ambient Conditions: A Thermodynamic Elegy

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Summary. This review reveals that, in contrast to the general opinion, the aqueous speciation of nickel is poorly known. Besides the fairly well established first hydrolysis constant, data are scarce and only poor estimates can be derived for higher Ni hydrolysis constants from a few solubility studies. The situation is even worse in the case of aqueous carbonate complexes. No reliable experimental study has been published so far and almost all numbers reported in thermodynamic databases are unacceptable estimates. In this review we scrutinise all these published estimates and propose expectation ranges of nickel carbonate complex stability through correlation with other known thermodynamic constants. Solubility constants for a few simple nickel solids are known or have been estimated from thermochemical data. However, none of these simple solids is of geochemical relevance at ambient conditions. Based on field evidence, classes of solids are identified which potentially govern nickel concentrations in ground and surface waters. Recent spectroscopic data indicate that magnesium clay minerals and layered double hydroxides are the most prominent candidates for nickel-bearing solids at ambient conditions.

Keywords. Thermodynamics; Complexes; Solubility; Transition metals; Carbonate; Alumosilicates.

Introduction

Nickel is an element of environmental concern. It belongs to the suite of toxic heavy metals (Ni, Cu, Zn, Cd, Pb, Hg) which are subject to concentration limits in drinking water [1]. Waste containing these metals has to be treated carefully before disposal, and its long-term behaviour in a surface disposal site or geological repository is of high environmental relevance. Furthermore, large amounts of ^{59}Ni and ^{63}Ni occur as fission products in nuclear waste and thus, the fate of these

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[a] Dedicated to the memory of Prof. *Rolf Grauer*

radionuclides has to be considered in performance assessment studies of planned repositories for nuclear waste [2, 3].

Any geochemical model aiming at a reliable description of the behaviour of nickel in groundwater has to consider, as a minimum, the influence of hydroxide and carbonate on the aqueous speciation of this trace metal. In addition, sound information is required about nickel containing solid phases which potentially govern the concentration of dissolved nickel in groundwater. This minimum set of thermodynamic data [4] is used for estimating solubility limits of toxic and radioactive elements escaping from geological repositories into the geosphere [5, 6]. It also forms a necessary basis for further studies concerning the sorption of nickel on clay minerals [7–11] and the sorption and incorporation of nickel in cement phases [12, 13].

There is a general belief that thermodynamic data for nickel are well established and, therefore, modelling of the geochemical behaviour of nickel in groundwater or in the cementitious environment of a geological repository is considered as a straightforward procedure. However, a close inspection of the published data revealed that this is a myth far from reality. In the following survey we discuss in detail what is really known at present about nickel hydrolysis, carbonate complexation, and nickel-bearing solid phases. Uncertainty ranges of thermodynamic data are estimated and their impact on geochemical models is shown. Finally, the most promising direction of further research in this area is outlined.

The System Ni–H_2O at Ambient Conditions

A First Glance

The influence of hydroxide solubility and aqueous complexation on metal speciation is the subject of the comprehensive monograph "The Hydrolysis of Cations" by *Baes* and *Mesmer* [14], which contains a systematic evaluation of experimental data up to 1973. An entire chapter of this work is devoted to the hydrolysis of nickel. The careful evaluation of *Baes* and *Mesmer* [14] is well documented, and the recommended thermodynamic constants have been adopted in many databases. The nickel stability constants recommended in "Critical Stability Constants" by *Smith* and *Martell* [15, 16] are in close agreement with the *Baes* and *Mesmer* [14] data. More recently, a new set of recommended values on nickel hydrolysis has been published [17], based on the critical evaluation of literature data up to 1993. These authors conclude that their recommended stability constants are, within their estimated uncertainties, in general agreement with the earlier recommendations [14–16] (Table 1). In addition, two careful studies of the solubility of crystalline nickel hydroxide [18, 19] claim to settle the question concerning the large variability in solubility products of $Ni(OH)_2$ published in the older literature (Table 1). Hence, on a first glance the nickel hydrolysis data seem to be well established.

A Detailed Review

However, a closer look at the reported hydrolysis and solubility data quickly darkens this pleasant picture. *Plyasunova et al.* [17] admit in their critical evaluation of

Table 1. Nickel solubility and hydrolysis constants found in literature

Reaction	*Baes* and *Mesmer* [14] $\log K^{\circ a}$	*Smith* and *Martell* [15, 16] $\log K^{\circ a}$	*Plyasunova et al.* [17] $\log K^{\circ a}$	*Mattigod et al.* [18] $\log K^{\circ a}$	*Gamsjäger et al.* [19] $\log K^{\circ a}$
$Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+$	-9.86 ± 0.03	-9.9	-9.50 ± 0.36	-8.35 ± 0.1	–
$Ni^{2+} + 2H_2O \rightleftharpoons Ni(OH)_2(aq) + 2H^+$	-19 ± 1^{b}	-19	$-18.0 \pm 1.4\ (\pm 1.0)^{d}$	–	–
$Ni^{2+} + 3H_2O \rightleftharpoons Ni(OH)_3^- + 3H^+$	-30 ± 0.5	-30	$-29.7 \pm 2.0\ (\pm 1.5)^{d}$	–	–
$Ni^{2+} + 4H_2O \rightleftharpoons Ni(OH)_4^{2-} + 4H^+$	<-44	–	$-44.96 \pm 0.88\ (\pm 0.6)^{d}$	–	–
$2Ni^{2+} + H_2O \rightleftharpoons Ni_2OH^{3+} + H^+$	-10.7 ± 0.5	-9.3 ± 0.2^{c}	-9.8 ± 1.2	–	–
$4Ni^{2+} + 4H_2O \rightleftharpoons Ni_4(OH)_4^{4+} + 4H^+$	-27.74 ± 0.02	-27.7	-27.9 ± 1.0	–	–
$NiO(cr) + 2H^+ \rightleftharpoons Ni^{2+} + H_2O$	12.3	–	10.66 ± 0.65	–	–
$Ni(OH)_2(cr) + 2H^+ \rightleftharpoons Ni^{2+} + 2H_2O$	10.8 ± 0.1	12.8	10.52 ± 0.59	11.9 ± 0.1	11.1 ± 0.2
$NiO(cr) + H_2O \rightleftharpoons Ni^{2+} + 2 \cdot OH^-$	-15.7	–	-17.34 ± 0.70	–	–
$Ni(OH)_2(cr) \rightleftharpoons Ni^{2+} + 2 \cdot OH^-$	-17.2	-15.2	-17.48 ± 0.54	-16.1 ± 0.1	–
$Ni(OH)_2(cr) \rightleftharpoons Ni(OH)_2(aq)$	≈ -7	–	-7.52 ± 0.80	–	–
$Ni(OH)_2(cr) + OH^- \rightleftharpoons Ni(OH)_3^-$	-4.7 ± 0.5	–	-5.2 ± 1.4	–	–
$Ni(OH)_2(cr) + 2 \cdot OH^- \rightleftharpoons Ni(OH)_4^{2-}$	<-5	–	-6.43 ± 0.23	–	–

[a] The uncertainties in Refs. [17–19] refer to the 95% confidence level ($\approx 2\sigma$), whereas in [14–16] 1σ uncertainties are given; [b] This seems to be a computational error. If we combine the $\log K^\circ$ values of $Ni(OH)_2(cr) \rightleftharpoons Ni(OH)_2(aq)$ and $Ni(OH)_2(cr) + 2H^+ \rightleftharpoons Ni^{2+} + 2H_2O$ we get $\log K^\circ \approx -18$; [c] $\log K$ at ionic strength $1\,M$; [d] The uncertainties given in parentheses have been calculated in the present work applying the principle of error propagation; the original uncertainties in [17] had been estimated by simply adding up the individual uncertainties

thermodynamic data that the aqueous chemistry of Ni^{2+} in general, and its hydrolysis in particular, has been poorly investigated as compared to other divalent transition metals like Co. In spite of the general agreement among recommended values, the amount of usable quantitative experimental data to evaluate the thermodynamics of Ni^{2+} hydroxo-complexes is rather limited.

Most experimental studies of hydrolytic equilibria have been made at high total metal concentrations where equilibria are dominated by polynuclear species. In the case of Ni, the existence of the polynuclear species Ni_2OH^{3+} and $Ni_4(OH)_4^{4+}$ is now fairly well established [17]. In contrast, chemical information on mononuclear hydrolysis is scarce. This is unfortunate because the hydrolysis of trace elements is dominated by such species, and polynuclear complexes can safely be ignored in most groundwater modelling studies.

For a long time, $NiOH^+$ was considered to be the only hydrolysis product of Ni (Eq. 1) with a well-known stability constant, due to a fair number of potentiometric studies.

$$Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+ \tag{1}$$

However, most of the experimental determinations of $\log {}^*\beta_1$ according to Eq. (1) were carried out without taking into account the formation of polynuclear species. *Baes* and *Mesmer* [14] solved this problem by relying only upon the work of *Perrin* [20] which "was done in such dilute Ni^{2+} solutions that $Ni_4(OH)_4^{4+}$ could be ignored". They recommend a value of $\log {}^*\beta_1{}^\circ = -9.86 \pm 0.03$ at zero ionic strength. *Plyasunova et al.* [17] reevaluated the available data measured in perchlorate medium by taking into account the effects of polynuclear species and recommend a value of $\log{}^*\beta_1^\circ = -9.50 \pm 0.36$. Despite the increased uncertainty, the first hydrolysis constant of nickel can be considered as the best known equilibrium of the entire series discussed here.

All other mononuclear hydrolysis constants of Ni have been derived from solubility studies of nickel hydroxide in alkaline solutions according to the equilibria shown in Eqs. (2)–(4) with $K_{s,2}$, $K_{s,3}$, and $K_{s,4}$, respectively.

$$\mathrm{Ni(OH)_2(cr)} \rightleftharpoons \mathrm{Ni(OH)_2(aq)} \quad (2)$$

$$\mathrm{Ni(OH)_2(cr)} + \mathrm{OH^-} \rightleftharpoons \mathrm{Ni(OH)_3}^- \quad (3)$$

$$\mathrm{Ni(OH)_2(cr)} + 2\mathrm{OH^-} \rightleftharpoons \mathrm{Ni(OH)_4}^{2-} \quad (4)$$

Baes and *Mesmer* [14] solely relied on the $Ni(OH)_2(cr)$ solubility data of *Gayer* and *Garrett* [21] for their estimates and recommended $\log K_{s,2}^\circ \approx -7$, $\log K_{s,3}^\circ = -4.7 \pm 0.5$, and $\log K_{s,4}^\circ < -5$ (Table 1). *Ziemniak et al.* [22] measured the solubility of NiO(cr) in sodium phosphate solutions. At 290–410 K, NiO(cr) was found unstable and eventually covered by a layer of $Ni(OH)_2(cr)$. The results from experiments with ascending and descending temperature cycles were fitted assuming that $Ni(OH)_2(cr)$ was responsible for the solubility at a temperature up to 440 K. The equilibrium constants are $\log K_{s,2}^\circ = -8.04 \pm 0.06$ and $\log K_{s,3}^\circ = -6.16 \pm 0.35$. *Plyasunova et al.* [17] recommend mean values derived from both studies, *i.e.* $\log K_{s,2}^\circ = -7.52 \pm 0.80$ and $\log K_{s,3}^\circ = -5.2 \pm 1.4$ (Table 1). In addition, they use these constants and *Gayer* and *Garrett*'s [21] solubility data for an elaborate fitting exercise in order to determine the fourth hydrolysis constant. A value of $\log K_{s,4}^\circ = -6.43 \pm 0.23$ was determined, which must be considered as a first guess despite the relatively small statistical uncertainty. Indeed, this value is not only directly dependent on the accuracy of the numbers chosen for $\log K_{s,2}^\circ$ and $\log K_{s,3}^\circ$, it also relies on the validity of the ionic strength correction in solutions up to $15\,M$ NaOH! In most cases extrapolations to zero ionic strength using the specific ion interaction (SIT) method are limited to electrolyte concentrations of about $3\,M$ [23]. The minimum uncertainty of this constant cannot be smaller than the uncertainty of $\log K_{s,3}^\circ$, *i.e.* $\log K_{s,4}^\circ = -6.4 \pm 1.4$. Although this discussion is purely academic (as the reaction described by Eq. (4) is of importance only in concentrated NaOH solutions and will never influence any geochemical modelling of environmental systems) it illustrates how poor the quality of such thermodynamic data may be.

As discussed in detail by *Plyasunova et al.* [17], $Ni(OH)_2(cr)$ is thermodynamically more stable than NiO(cr) at ambient conditions. Therefore, the solubility of NiO(cr) cannot be directly measured at ambient conditions but has to be calculated from thermochemical data determined at high temperatures. *Plyasunova et al.* [17] recommend $\log K_{sp}^\circ = -17.34 \pm 0.70$ for the equilibrium given in Eq. (5).

$$\mathrm{NiO(cr)} + \mathrm{H_2O} \rightleftharpoons \mathrm{Ni^{2+}} + 2\mathrm{OH^-} \quad (5)$$

The large variation in published solubility products of $Ni(OH)_2$ probably results from the existence of different phase modifications, ranging from "freshly precipitated" to "aged" nickel hydroxides. Considering the observed decrease in solubility with ageing time and the qualitative observation that $Ni(OH)_2(cr)$ is more stable than the oxide at ambient temperature, *Plyasunova et al.* [17] recommend a mean value of $\log K_{sp}^{\circ} = -17.48 \pm 0.54$ for the equilibrium shown in Eq. (6).

$$\mathrm{Ni(OH)_2(cr)} \rightleftharpoons \mathrm{Ni^{2+}} + 2\mathrm{OH^-} \qquad (6)$$

Improvement by New Measurements?

The large uncertainties in most hydrolysis constants and solubility products reflect the poor consistency of experimental data. This fact had already been documented by *Baes* and *Mesmer* [14]. The new data evaluation of *Plyasunova et al.* [17] does not remedy this unfortunate situation but rather emphasises it by a detailed discussion of all the inconsistencies in experimental data. The need for new careful studies of nickel solubility and hydrolysis is an obvious consequence of this review.

Mattigod et al. [18] measured the solubility of crystalline $\mathrm{Ni(OH)_2}$, precipitated from $\mathrm{NiCl_2}$ solutions by adding NaOH, in solutions of 0.01 M $\mathrm{NaClO_4}$ at *pH* ranging from 7 to near to 14 (Fig. 1). Equilibrium was approached from both over- and undersaturation, and equilibration times extended from 3 to 90 days. The solubility of $\mathrm{Ni(OH)_2(cr)}$ in the *pH* range of approximately 7 to 11.3 was modelled assuming only $\mathrm{Ni^{2+}}$ and $\mathrm{NiOH^+}$ as aqueous species. Values of $\log K_{sp}^{\circ} = -16.1 \pm 0.1$ for Eq. (6) and of $\log {}^{*}\beta_1^{\circ} = -8.35 \pm 0.10$ for Eq. (1) were determined. At *pH* values above 12, the measured concentrations seem to increase with *pH* (Fig. 1). Unfortunately, also the detection limit of the Ni concentration increases above *pH* 12. Since all measurements at $pH > 12$ are very close to the detection limit, these data must be taken with care, and the existence of higher-order hydrolytic species, including $\mathrm{Ni(OH)_2(aq)}$, $\mathrm{Ni(OH)_3^-}$, and $\mathrm{Ni(OH)_4^{2-}}$ could not be established [18].

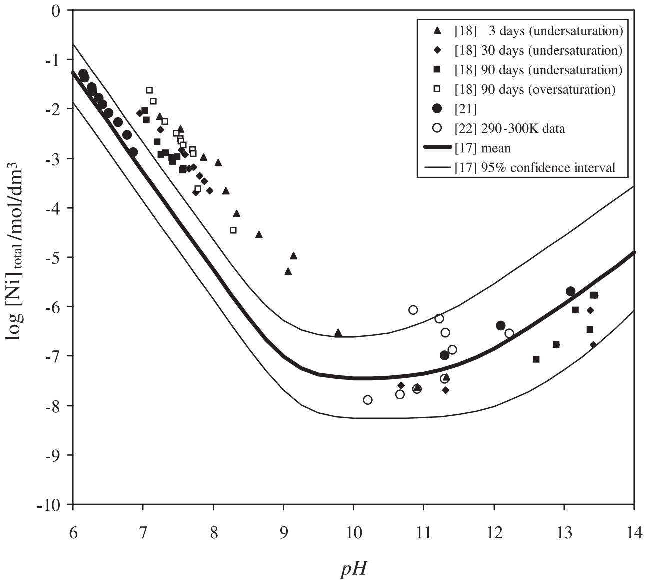

Fig. 1. Solubility of crystalline nickel hydroxide shown as nickel concentration in solution versus *pH*; symbols represent experimental data; the lines have been calculated for ionic strength 0.1 M using constants recommended by *Plyasunova et al.* [17] (Table 1)

As a first consequence, the most uncertain constants, those of the higher-order hydrolytic species, cannot be refined using the data of this new study. To make things worse, both thermodynamic constants derived by *Mattigod et al.* [18] differ by more than one order of magnitude from the values recommended by *Baes* and *Mesmer* [14] and *Plyasunova et al.* [17] (Table 1). According to these new constants, nickel hydrolysis should set on at a much lower *pH* than reported in all previous studies, and the solubility of crystalline nickel hydroxide would be much higher than anticipated by previous reviews.

A close inspection of the solubility data reported by *Mattigod et al.* [18] reveals that the *pH* range where $NiOH^+$ should predominate is rather sparingly covered by experimental data. To be precise, 4 out of 55 experiments (undersaturation experiments with three days equilibrium time) between *pH* 8.5 and 10.5 determine the $NiOH^+$ constant reported by *Mattigod et al.* [18] (Fig. 1). In our opinion, these few solubility data are not sufficient to justify the revision of the first hydrolysis constant, which had been determined fairly well by other investigators through independent potentiometric studies.

However, the discrepancy in the solubility products is much more disturbing since it may point to intrinsic inconsistencies of the whole data set recommended by *Baes* and *Mesmer* [14] and *Plyasunova et al.* [17]. *Mattigod et al.* [18] showed by X-ray powder diffraction data that the equilibrated samples did not differ in phase or crystallinity from the initial solid phase. However, a remarkable detail in the results of *Mattigod et al.* [18] raises the question whether true equilibrium has been reached in their experiments. Their undersaturation experiments reveal systematically decreasing solubilities the longer the experiments lasted (Fig. 1). As pointed out by *Gamsjäger et al.* [19], *Mattigod et al.* [18] worked with a microcrystalline product, and the decreasing solubility in undersaturation experiments may indicate a slow transition towards crystalline products with less active surfaces. The solubility data of *Gayer* and *Garrett* [21], also obtained from under- and oversaturation, are systematically lower by more than one order of magnitude (Fig. 1). Because the solubility data of *Mattigod et al.* [18] refer to a crystalline solid and not to an amorphous substance with higher solubility, the lower solubility reported by *Gayer* and *Garrett* [21] cannot simply be explained by differences in the crystallinity of the solid phases. *Mattigod et al.* [18] tried to solve this enigma by assuming that the *pH* measurements by *Gayer* and *Garrett* [21] were consistently in error by more than one order of magnitude. *Mattigod et al.* [18] "recalculated" these *pH* values by using some analytical data reported by *Gayer* and *Garrett* [21] as input values, letting their equilibrium code dissolve the appropriate amount of $Ni(OH)_2(cr)$ into various species according to their thermodynamic model, and keeping track of the H^+ concentration (*Rai*, personal communication). However, this procedure merely shifts the *Gayer* and *Garrett* [21] data onto their model curve, *i.e.* it simply answers the question "What *pH* values should *Gayer* and *Garrett* [21] have measured in order to produce data entirely consistent with the thermodynamic model of *Mattigod et al.* [18]?". This circular argument does not explain anything.

Recently, *Gamsjäger et al.* [19] reported a new $Ni(OH)_2(cr)$ solubility study. They prepared well crystallized β-$Ni(OH)_2$ (theophrastite), precipitated from $Ni(ClO_4)_2$ solutions in molten NaOH, with crystal sizes of about 0.1 mm. These crystals were used in solubility experiments ranging from *pH* 5 to 7 at ionic strengths varying from 0.5 to 3.0 $\text{mol}\cdot\text{kg}^{-1}$ $NaClO_4$. Due to the notorious inertness of Ni^{2+} at 25°C, the solubility was measured at elevated temperatures (35–80°C) to speed up equilibration. Nickel hydroxo complexes were negligible in the *pH* range considered by *Gamsjäger et al.* [19]. SIT [23] was applied to extrapolate the experimental data to zero ionic strength, and the resulting constants were fitted as a function of temperature.

The solubility product reported by *Gamsjäger et al.* [19] is $\log {}^{*}K_{sp}{}^{\circ} = 11.1 \pm 0.2$ at 25°C, almost one order of magnitude lower than the value reported by *Mattigod et al.* [18] (Table 1). *Gamsjäger et al.* [19] appreciate the careful solubility study of *Mattigod et al.* [18] "but according to their preparative method the respective results refer to a microcrystalline probably chloride containing β-$Ni(OH)_2$". A solid solution $NiCl_x(OH)_{2-x}(s)$ would explain the higher solubility measured by *Mattigod et al.* [18]. Such an increase in solubility has been demonstrated in the case of $PdCl_x(OH)_{2-x}(s)$ [24].

In addition, the old results of *Gayer* and *Garrett* [21], $\log {}^{*}K_{sp}{}^{\circ} = 10.7 \pm 0.2$ according to the reevaluation by *Plyasunova et al.* [17], and the recommended constant $\log {}^{*}K_{sp}{}^{\circ} = 10.5 \pm 0.6$ [17] are compatible with the findings of *Gamsjäger et al.* [19]. However, simply accepting the new solubility value of *Gamsjäger et al.* [19] and retaining all other data recommended by *Plyasunova et al.* [17] leads to a new inconsistency (Table 1): NiO(cr) would now appear in all model calculations as the stable phase, contrary to experimental evidence at temperatures below 200°C [19].

In summary, the new study of *Gamsjäger et al.* [19] has the potential to resolve the enigma of incompatible $Ni(OH)_2(cr)$ solubility data, but a complete reappraisal of all published data is necessary. The goal of such a review would be to supersede the recommendations of *Plyasunova et al.* [17] by new and consistent, but only slightly changed values for $Ni(OH)_2(cr)$ and NiO(cr) solubility. Unfortunately, the solubility studies of *Mattigod et al.* [18] and *Gamsjäger et al.* [19] do not reduce the large uncertainties of the nickel hydrolysis constants, due to nickel concentrations measured at the detection limit at high *pH* in the former study, and the limited *pH* range considered in the latter one.

Consequences for Geochemical Modelling

Nickel concentrations measured in natural waters are generally much lower than predicted by the solubility of $Ni(OH)_2(cr)$. Typical nickel concentrations in natural aqueous solutions range from $\sim 10^{-9}$ to $\sim 10^{-7} M$, with median values close to 10^{-8} (Fig. 2). These concentrations are orders of magnitude below the solubility of nickel hydroxide, indicating that other phases must control the concentration of Ni in natural waters. Nickel concentration profiles in oceanic waters are typical for "nutrient-type" elements [25]. Nickel is depleted through microbiological processes near the surface, but at depths exceeding ∼1000 m the concentration is remarkably constant, *i.e.* ∼6 n*M* in the Atlantic and ∼10 n*M* in the Pacific [25]. Nickel concentrations in continental waters are also close to these values. We can thus safely conclude that the nickel concentration in natural water is not governed by the solubility of $Ni(OH)_2(cr)$.

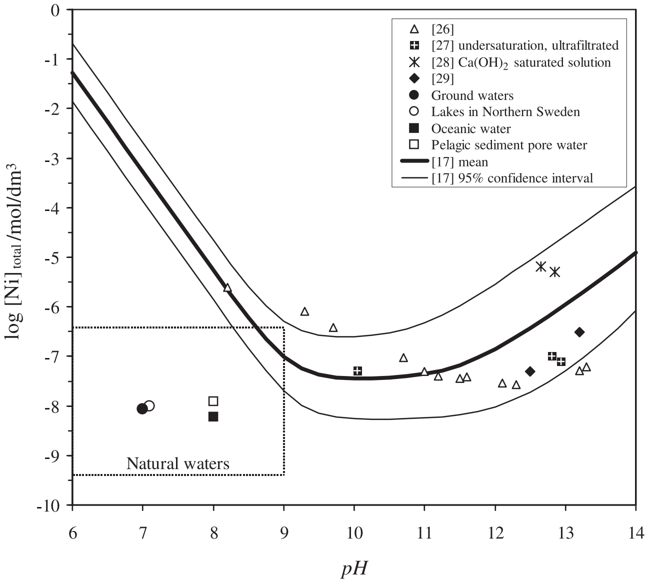

Fig. 2. Nickel concentrations in natural waters and in cementitious systems compared with the solubility of crystalline nickel hydroxide; the lines are taken from Fig. 1; the dotted rectangle represents the maximum variability in natural waters; the symbols in the rectangle denote medians or average values from a large number of concentration data; sources for water concentration data are [25, 103–105]; symbols for [26–29] represent experimental data in cementitious systems

Hence, the above discussion concerning the solubility data of $Ni(OH)_2$(cr) is of no practical consequence for geochemical modelling of natural waters at $pH < 8$. However, at higher *pH* the aqueous speciation of Ni is affected by the large uncertainties of hydrolysis constants derived from solubility experiments, even if the solubility of $Ni(OH)_2$(cr) itself is of no importance in the respective geochemical models.

The solubility of $Ni(OH)_2$(cr) becomes rather low in alkaline waters ($pH > 9$) and the concentration of Ni in this *pH* range may actually be governed by dissolution/precipitation of nickel hydroxide. Unfortunately, the uncertainty range of nickel solubility increases with increasing *pH*. For example, in a cementitious environment at *pH* 12.5 the predicted Ni solubility ranges between $10^{-8} M$ and $10^{-5} M$ (Fig. 2). This uncertainty is too large even for very modest demands on geochemical predictions.

A possible remedy to this unfortunate situation is the direct measurement of nickel concentrations in cementitious systems. At a first glance comparison of our (rather vague) thermodynamic model predictions with direct measurements in cement-equilibrated waters at $pH > 10$ looks rather promising. Measurements [26–29] reveal a fairly consistent pattern of low nickel concentrations close to and slightly below the predicted mean solubility of $Ni(OH)_2$(cr) (Fig. 2).

Pilkinton and *Stone* [26] and *Kulmala* and *Hakanen* [27] report nickel concentrations measured by radiochemical methods using ^{63}Ni tracers. No details about concentration measurements are given by *Glasser et al.* [28]. *Ochs et al.* [29] used ICP-MS analysis to determine dissolved nickel.

We remember that *Mattigod et al.* [18] report a detection limit in ICP-MS analysis of $5 \cdot 10^{-8} M$ Ni, which however increases at $pH > 10$ due to sample dilution. As a consequence, the measured aqueous concentrations in the alkaline region were at or below the instrumental detection limit. *Ochs et al.* [29] used the same analytical methods and thus, their measured aqueous nickel concentrations also were at the instrumental detection limit. Both data sets give hints about upper limits of nickel concentration in high *pH* systems but they cannot be used to refine hydrolysis constants.

Unfortunately, also the data of *Pilkinton* and *Stone* [26] and *Kulmala* and *Hakanen* [27] cannot be used for that purpose. Although the dissolved nickel data (derived by radiometric methods) are probably reliable, in both studies no attempt was made to identify the solid phase in equilibrium with dissolved nickel.

According to investigations of *Glasser et al.* [28], samples aged in $Ca(OH)_2$ containing solutions showed the presence of a new phase. Analysis of this phase by analytical electron microscopy revealed the new phase to have an undefined morphology and a ratio Ca:Ni = 4:1. The particles also contained a small amount of chloride. Of course, no thermodynamic data are known yet concerning this Ca:Ni phase and thus, nickel concentrations measured in cementitious systems cannot be used to refine any hydrolysis constants.

In summary, there is experimental evidence for very low nickel solubility in cementitious systems, but at present these low concentrations cannot be reliably coupled to a thermodynamic model due to large uncertainties in the hydrolysis constants and the lack of thermodynamic data for the Ca:Ni solid which most probably replaces $Ni(OH)_2(cr)$ as the solubility limiting phase in these systems.

The System $Ni–H_2O–CO_2$ at Ambient Conditions

A Pretended Experimental Study

No work comparable to the comprehensive monograph "The Hydrolysis of Cations" by *Baes* and *Mesmer* [14] has been published yet about the influence of carbonate complexation on metal speciation. Considering the ubiquity of carbonate in groundwater systems the lack of a thorough review is somewhat astonishing. However, in "Critical Stability Constants" by *Smith* and *Martell* [16] we find at least stability constants for the complexes $NiCO_3(aq)$ and $NiHCO_3^+$ of $\log K = 3.57$ and 1.59, respectively, apparently measured at 25°C in an ionic medium of $0.7 M$.

A unique reference is given by *Smith* and *Martell* [16] as source of these stability constants, namely *Zhorov et al.* [30]. These authors cryptically state that they determined the mentioned constants by the "*Garrels* method". The reference given for the "*Garrels* method" is a Russian translation of the popular textbook of *Garrels* and *Christ* [31]. A patient search in the 450 pages of the original textbook finally revealed the meaning of the "*Garrels* method". On page 98 in *Garrels* and *Christ* [31] a Fig. 4.3 appears showing a plot of electronegativity versus *pK* of the carbonate complexation constants. A linear correlation is defined there by three (!) points, namely $CuCO_3(aq)$ at the high end and $CaCO_3(aq)$ and $MgCO_3(aq)$ at the low end of the line. In addition, two points for $CaHCO_3^+$ and $MgHCO_3^+$ are plotted in Figure 4.3 but the authors didn't dare to define any straight line using just these two points so close to each other. *Garrels* and *Christ* [31] comment this figure as follows: "Data for the dissociation constants of the divalent metal carbonate ion pairs in solution are sparse, but the line shown is drawn for the three points available. The two points for $CaHCO_3^+$ and $MgHCO_3^+$ are not at the moment susceptible to interpretation, although it should be noted in passing that these two values are open to considerable question, because the probable error in determining these constants is large."

Zhorov et al. [30] provide no further details how they applied the "*Garrels* method". Apparently they used electronegativity numbers of 1.8 for Ni^{2+} and 1.7 for Co^{2+} to read from Fig. 4.3 in *Garrels* and *Christ* [31] values of $\log K^\circ \approx 6.2$ and 5.8 for $NiCO_3(aq)$ and $CoCO_3(aq)$, respectively. In order to derive values for bicarbonate constants it seems that *Zhorov et al.* [30] used the $CaHCO_3^+$ and $MgHCO_3^+$ data in the same Fig. 4.3. Ignoring the warnings of *Garrels* and *Christ* [31] concerning the quality of these bicarbonate data, apparently a value of $pK(MeCO_3(aq))/pK(MeHCO_3^+) \approx 2.2$ was derived which finally gave $\log K^\circ \approx 2.8$ and 2.6 for $NiHCO_3^+$ and $CoHCO_3^+$, respectively.

Zhorov et al. [30] were not primarily interested in determining thermodynamic stability constants but in the computation of predominance diagrams for nickel and cobalt in seawater. Therefore, they extrapolated their estimated values from ionic strength zero to $I = 0.7\,M$ NaCl using "the *Debye-Hückel* formula (*Levchenko* variant)" and finally came up with $\log K = 3.57$ and 1.59 for $NiCO_3(aq)$ and $NiHCO_3^+$, respectively. Note that the "precision" of the estimated numbers has significantly increased during this extrapolation procedure! These estimated numbers were mistaken by *Smith* and *Martell* [16] as experimental data and included in their collection of recommended stability constants.

Ironically, this is not the end of our story. *Foulliac* and *Criaud* [32] were also deceived to take these numbers as experimental data but added a further twist to this already screwy anecdote. They present in their "Critical reevaluation of stability constants" the "selected values" $\log K_1{}^\circ = 4.83$ and 2.22 for $NiCO_3(aq)$ and $NiHCO_3^+$, respectively, which were "corrected to $I = 0$ from *Zhorov et al.* [30]". *Foulliac* and *Criaud* [32] do not state their preferred method of ionic strength correction. After checking various options we think that they most probably used the *Davies* equation with a constant of 0.2. A graphical representation of the entire multi-step estimation process is shown in Fig. 3. Note, that not only the "precision" of the estimated number is increased by extrapolating back and forth in ionic strength using different formulae, but also that the final value dropped by more than one order of magnitude compared to the original number "determined" by the "*Garrels* method".

A Useless Experimental Study

Emara et al. [33] published a spectrophotometric study of nickel and cobalt carbonate systems in mixtures of water and methanol, including pure water. They report to have investigated the equilibrium shown in Eq. (7) and give a final result

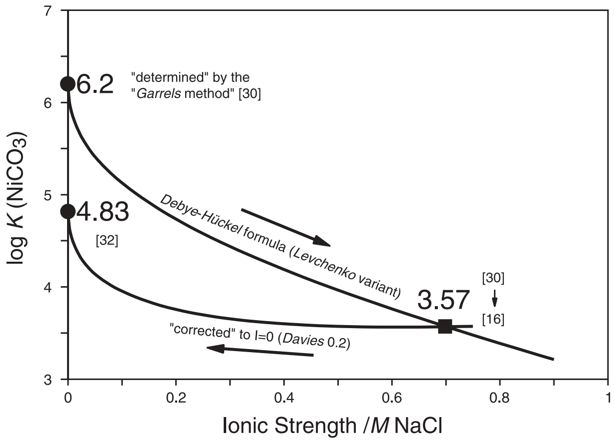

Fig. 3. An example of a data diagenesis process: An estimated complexation constant for $NiCO_3(aq)$ was mistaken for an experimental result and "corrected" back and forth by different ionic strength extrapolation methods

of $\log K^\circ = 1.40 \pm 0.02$ (the 2σ standard deviation stems from an average of three measurements).

$$Ni^{2+} + HCO_3^- \rightleftharpoons NiHCO_3^+ \qquad (7)$$

The authors do not provide much experimental detail. They state, "the absorbance of nickel bicarbonate, which is formed after mixing the $Ni(NO_3)_2$ with the $NaHCO_3$, was obtained by difference at 230 nm and the three different ionic strengths using NaCl solutions". The authors did not measure the *pH* after mixing the reagents and, therefore, calculated the concentration of HCO_3^- assuming that there is no acid excess/acid deficiency in the reagents.

However, the authors missed the concept of mass balance and calculated grossly erroneous results. They didn't even realise the contradiction in their own example given in the paper: "We started with concentration $6.18 \cdot 10^{-4} M$ $NaHCO_3$ to yield $2.5 \cdot 10^{-4} M$ HCO_3^-". According to their formula, this implies the formation of $3.68 \cdot 10^{-4} M$ H_2CO_3 by consumption of $3.68 \cdot 10^{-4} M$ H^+, not available in a pure $NaHCO_3$ solution. Applying the proper mass balance for a pure $NaHCO_3$ solution, *i.e.* $[H_2CO_3] + [H^+] = [CO_3^{2-}] + [OH^-]$, it can easily be calculated that in a closed system such a solution approaches a pH of about 8.5 for total carbonate concentrations above $10^{-4} M$. The errors in HCO_3^- concentration, and thus in the reported $\log K^\circ$ values, cannot be corrected as *Emara et al.* [33] do not provide any analytical data concerning their experiments, except the above mentioned example.

Moreover, there is no justification to assume a priori that the observed differences in nickel absorbance spectra are caused by the formation of $NiHCO_3^+$. The alkaline $NaHCO_3$ solutions of *Emara et al.* [33] contained a significant amount of CO_3^{2-}, and probably the much more stable $NiCO_3(aq)$ complex dominates in such solutions. But again, due to the complete lack of any analytical data in *Emara et al.* [33], no alternative interpretation of their data in terms of $NiCO_3(aq)$ complex formation is possible.

In summary, the stability constants reported by *Emara et al.* [33] cannot be included in any database due to computational errors and misinterpretations of their data. No reevaluation is possible due to a complete lack of experimental data in the paper.

More Guesswork

These are not the only numbers on nickel carbonate complexation appearing in thermodynamic data collections. A literature review reveals an entire series of numbers, reported in Table 2.

Shortly after the publication of the numbers "determined by the *Garrels* method" by *Zhorov et al.* [30], a data set was published by *Mattigod* and *Sposito* [34], which made its way into various thermodynamic data bases [35–37]. Thus, it seems worthwhile to have a closer look how these numbers were estimated.

Mattigod and *Sposito* [34] state that "there is a lack of data on carbonate and bicarbonate complexes, which therefore precludes the use of statistical methods". In order to estimate stability constants for metal carbonate and bicarbonate complexes they use a theoretical method based on electrostatics: the electrostatic model of ion-pairing of *Kester* and *Pytkowicz* [38]. The most sensitive parameter in this model is the radius of the ion-pair, *i.e.* the sum of the radii of the metal ion and the ligand forming the ion-pair. Several sets of radii are proposed in the literature and *Mattigod* and *Sposito* [34] tried to evaluate the most appropriate one by comparing calculated stability constants with experimental values. In the case of carbonate the only experimental value considered by *Mattigod* and *Sposito* [34] is $\log K^\circ = 6.73 \pm 0.05$ for $CuCO_3(aq)$ taken from *Schindler et al.* [41]. A first attempt using *Debye* radii (hydrated ionic radii) resulted in $\log K^\circ = 1.88$, five orders of magnitude off the experimental value. A second attempt using crystal radii gave $\log K^\circ = 3.63$, still three orders of magnitude off the experimental value. Therefore, *Mattigod* and *Sposito* [34] adjusted the radius of carbonate in such a way that the computed value for copper carbonate stability equals the experimental value. Using this "modified" carbonate radius and individual metal radii, $\log K^\circ$ values for carbonate complexes with Mn (6.31), Fe (6.57), Ni (6.87), and Zn (6.63) were calculated. The same procedure was used to estimate bicarbonate complexes. In

Table 2. Estimated nickel carbonate stability constants found in literature

$\log K_1^\circ$	$\log K_2^\circ$	$\log K^\circ$	Ref.	Method (for detailed discussion see text)
6.2		2.8	[30]	"determined by the *Garrels* method", electronegativity – $\log K$ correlation
6.87		2.14	[34]	electrostatic model, adjusted to $CuCO_3(aq)$ and $MnHCO_3^-$
	3.24		[34]	empirical relationship, adjusted to $CuCO_3(aq)/Cu(CO_3)_2^{2-}$
5.78		3.08	[42]	Q – $\log K$ correlation method, Q = f(electronegativity, ionic charge, ...)
5.36			[48]	oxalate–carbonate correlation
4.83		2.22	[32]	"corrected to $I = 0$ from *Zhorov et al.* [30]"
3.51		2.20	[32]	"simple" electrostatic model
2.56		0.96	[32]	electrostatic model of *Fuoss* [55]

Stability constants refer to the following equilibria at zero ionic strength, 25°C, and 1 bar: $\log K_1^\circ$: $Ni^{2+} + CO_3^{2-} \rightleftharpoons NiCO_3(aq)$, $\log K_2^\circ$: $NiCO_3(aq) + CO_3^{2-} \rightleftharpoons Ni(CO_3)_2^{2-}$ and $\log K^\circ$: $Ni^{2+} + HCO_3^- \rightleftharpoons NiHCO_3^+$

this case, the radius of HCO_3^- was adjusted to fit the stability constant of $\log K^\circ = 1.95$ for $MnHCO_3^+$ taken from *Morgan* [39]. Using this "modified" bicarbonate radius and individual metal radii, $\log K^\circ$ values for bicarbonate complexes with Fe (2.05), Ni (2.14), Cu (2.10), and Zn (2.07) were calculated. As the crystal radii for transition metals do not vary considerably, the stability constants estimated for a certain ligand are all within the same order of magnitude. Note, that in contradiction to well established features in complex chemistry the (estimated) nickel values are higher than the corresponding copper constants.

Stepwise stability constants were estimated by *Mattigod* and *Sposito* [34] using the empirical relationship proposed by *Van Panthaleon Van Eck* [40]: $\log K_2 = \log K_1 - 2\lambda$, where λ is an empirical constant characteristic of each metal-ligand system. As *Mattigod* and *Sposito* [34] state, "these constants are not available for the metal-ligand systems considered here, except for the Cu^{2+}–CO_3^{2-} system. Therefore, if it is assumed that the λ value for the Cu^{2+}–CO_3^{2-} system is typical for all systems of bivalent ions of the first transition metals and for ligands such as CO_3^{2-}, HCO_3^-, SO_4^{2-}, PO_4^{3-}, $H_2PO_4^-$, and HPO_4^{2-}, the association constants of higher complexes can be estimated." They used the copper data evaluated by *Schindler et al.* [41] to calculate $\lambda = 1.82$. This number was subsequently used to compute $\log \beta_2^\circ$ values for the entire range of metal-ligand systems mentioned above. For $Ni(CO_3)_2^{2-}$ the estimated value is $\log \beta_2^\circ = 10.11$.

In summary, all three values given by *Mattigod* and *Sposito* [34] for the nickel carbonate system were estimated by calibrating the respective estimation formula to a single experimental data point.

Two years later *Mattigod* and *Sposito* [42] published a revised data set. The authors state: "The association constants calculated in Ref. [34] with the method of *Kester* and *Pytkowicz* [38] for carbonate and phosphate complexes appear to be systematically different from those estimated recently with the correlation method of *Nieboer* and *McBryde* [43]. The latter method has a firmer empirical basis and, therefore, has been preferred." A table comprising the revised numbers is given in Ref. [42] but no further details are revealed by the authors on how they calculated these revised numbers. As this data set is not only included in the GEOCHEM thermodynamic data base [42] but also can be found in other data bases like the "Nagra Thermochemical Data Base" [44] we tried to reconstruct how these numbers were estimated.

The estimation method of *Nieboer* and *McBryde* [43] is based on correlating stability constants with a numerical index Q. The index Q is a multiple parameter quantity involving ionic charge, electronegativity, integral weighting factors, and a parameter calculated from atomic shielding constants. *Nieboer* and *McBryde* [43] provide a table of Q values for metal ions. The authors pretend to have used the electronegativity values of *Allred* [45] in all cases. However, *Allred* [45] does not provide any electronegativity value for Cu(II). A close inspection of the figures in *Nieboer* and *McBryde* [43] reveals that the authors used a Cu(II) value of 2.0 as given in *Pauling* [46]. All quantities necessary to compute Q are shown in Table 3.

A first, somewhat intriguing observation was made when we plotted the estimated values of *Mattigod* and *Sposito* [42] against their Q indices (Fig. 4): They do not plot on a straight line as they should do if they had been derived by the correlation method of *Nieboer* and *McBryde* [43]. At least a strong correlation can be

Table 3. Data used for the Q – $\log K$ correlation method of Fig. 4

Metal ion	Mg	Ca	Mn	Fe	Co	Ni	Cu(II)	Zn	Cd	Pb(II)
Q (def)	$2 \cdot X_M$	$2.6 \cdot X_M$	$2 \cdot X_M$	$X_M{}^2$	$X_M{}^2$	$X_M{}^2$	$X_M{}^2$	$2 \cdot X_M$	$2 \cdot X_M$	$X_M{}^2$
X_M	1.31	1.00	1.55	1.83	1.88	1.91	2.0	1.65	1.69	1.87
Q (value)	2.62	2.60	3.10	3.35	3.53	3.65	4.0	3.30	3.38	3.50
$\log K_1°$(exp)	2.88	3.15					6.73	4.76	4.3	7.0
$\log K_1°$(est)			4.52	5.31	5.53	5.78				
$\log K_1°$(old)			6.31	6.57	–	6.87		6.63		
$\log K°$(exp)	0.95	1.0	1.95							
$\log K°$(est)				2.72	2.89	3.08	4.29	2.79		
$\log K°$(old)				2.05	–	2.14	2.10	2.07		

Q (def): definition of Q according to Ref. [43] in terms of X_M; X_M: electronegativity, Cu(II) taken from Ref. [46], others from Ref. [45]; Q (value): numerical value of Q used in Q – $\log K$ correlation (Fig. 4); $\log K_1°$: $M^{2+} + CO_3{}^{2-} \rightleftharpoons MCO_3(aq)$, at zero ionic strength, 25°C, and 1 bar; $\log K°$: $M^{2+} + HCO_3{}^- \rightleftharpoons MHCO_3{}^+$, at zero ionic strength, 25°C, and 1 bar; (exp): experimental data, Ca, Mg: [15], Mn: [39], Cu(II): [41], Zn, Cd, Pb(II): [94] (black squares in Fig. 4); (est): estimated values, Q – $\log K$ correlation, taken from Ref. [42] (grey circles in Fig. 4); (old): estimated values, electrostatic model, taken from Ref. [34] (white circles in Fig. 4)

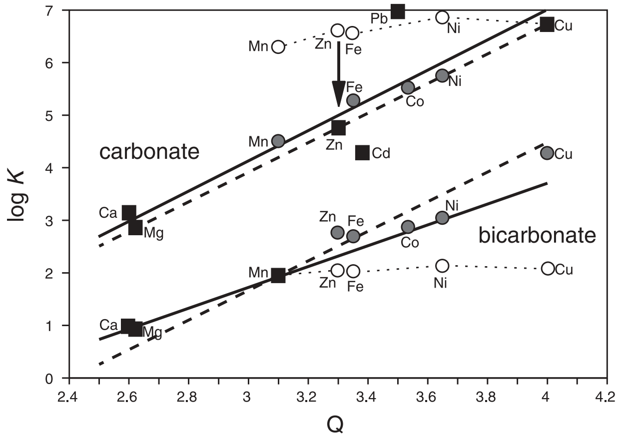

Fig. 4. Visualization of the estimation procedures used by *Mattigod* and *Sposito* [34] (open circles), and *Mattigod* and *Sposito* [42] (closed circles and squares, solid and dashed lines); numerical values for the Q indices are given in Table 3; for a detailed discussion see text

seen and thus, we reckon the scatter as due to rounding errors and/or other numerical deficiencies in the estimation procedure. The question remains how *Mattigod* and *Sposito* [42] established the regression lines for computing carbonate and bicarbonate values. We can only speculate about that, as they do not give any hints in their paper. Probably they derived a linear regression by using calcium and magnesium carbonate data from *Smith* and *Martell* [15] in addition to the copper data of *Schindler et al.* [41] and the new data set of *Bilinski et al.* [94] comprising zinc, cadmium, and lead data. The resulting regression line (upper solid line in Fig. 4) comes pretty close to the estimated values of *Mattigod* and *Sposito* [42].

However, repeating the same procedure for bicarbonate, using calcium and magnesium bicarbonate data from *Smith* and *Martell* [15] and in addition the manganese bicarbonate value from *Morgan* [39], results in a line at the lower end of the estimated values of *Mattigod* and *Sposito* [42]. Especially the estimated value for copper bicarbonate is quite off this regression line (lower solid line in Fig. 4). Possibly the solution of this puzzle is very simple. *Mattigod* and *Sposito* [42] might just have taken the data given in their paper, establishing a carbonate line by two points, namely copper and zinc carbonate, and generating a bicarbonate line by a parallel shift of the carbonate line through the single point for manganese bicarbonate (dashed lines in Fig. 4). Whatever they did, the new results differ quite considerably from their first estimates [34]. Contrary to their claim, they are not at all based on a ''a firmer empirical basis'' than their previous estimates (Fig. 4).

Again two years later, *Turner et al.* [48] published an extended compilation of thermodynamic data for 58 trace elements. Inspecting the carbonate subset of this data base reveals that 29 out of 38 stability constants are estimated. *Turner et al.* [48] comment on this observation: ''Few reliable values are available for carbonate complexation constants, but since stability constants are available for the formation of oxalate complexes with a wide range of cations [49] we have used a correlation between the stability constants of carbonate and oxalate complexes [50] to estimate carbonate stability constants using the equation $\log \beta_{M\mathrm{CO}_3} = -0.011 + 1.042 \log \beta_{M\mathrm{C}_2\mathrm{O}_4}$.'' The authors do not provide any further hint on how they determined their equation to compute carbonate constants from oxalate constants. As in all the cases discussed above, this is left as a puzzle to solve for the reader. Anyway, this time we solved it.

Initially, we assumed that they had used an equation derived by *Langmuir* [50] as they cite this paper. Indeed, we found a Fig. 6 in Ref. [50] showing the oxalate–carbonate correlation, and the figure caption reads as follows: ''Stability constants of some 1:1 divalent metal carbonate complexes plotted against stability constants for the corresponding oxalate complexes. Data are from literature and are for $I = 0$. The equation of the line is $\log K_{\mathrm{assoc}}(M\mathrm{CO}_3(\mathrm{aq})) = 1.11 \log K_{\mathrm{assoc}}(M\mathrm{C}_2\mathrm{O}_4(\mathrm{aq}))$.'' No clue is provided what ''literature'' means in detail and how the equation was derived. A close inspection of Fig. 6 in Ref. [50] revealed that a regression line was calculated by (arbitrarily) setting the intercept to zero and regarding Mg and Zn data as outliers, consequently excluding them from the regression analysis. Of course, there is no comment in Ref. [50] concerning the exclusion of these rather well established data from the regression analysis. The result of a recalculation with the remaining data points (Ca, Sr, Ba, Cu, Cd, Pb, and U(VI)) results in a slope of 1.11 ± 0.02. However, the origin of at least two of the seven data points used for regression analysis by *Langmuir* [50] remains dubious, namely the oxalate constants of Pb and U(VI). The other oxalate data apparently were taken from *Yatsimirskii* and *Vasil'ev* [51], the only reference cited. These oxalate data are basically the same as the values recommended by *Martell* and *Smith* [49], but the Pb and U(VI) oxalate constants shown by *Langmuir* [50] are one and two, respectively, orders of magnitude higher than the experimental values evaluated in Ref. [49] and, in the case of U(VI), later reevaluated by *Glaus et al.* [52]. Considering the exclusion of the rather well established Mg and Zn data on one hand and the inclusion of Pb and U(VI) oxalate data of dubious pedigree, the

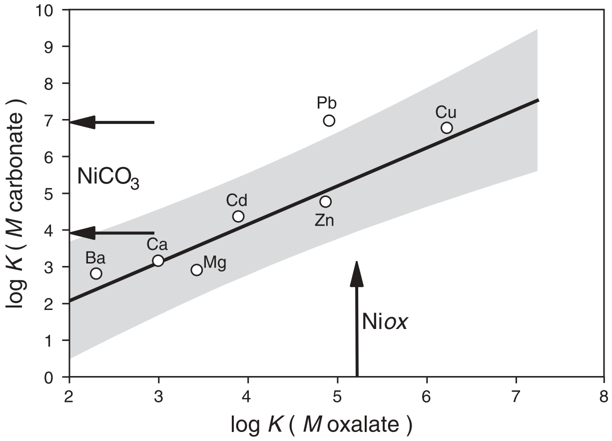

Fig. 5. Reconstruction of the oxalate–carbonate correlation used by *Turner et al.* [48] to estimate the complexation constant of $NiCO_3$(aq); for a detailed discussion see text

equation given by *Langmuir* [50] should be used with utmost care. Anyhow, it is not the equation proposed by *Turner et al.* [48].

Our next guess was that *Turner et al.* [48] had established their equation by linear regression analysis using experimental carbonate data as included in their data base, plus magnesium and calcium carbonate data from *Smith* and *Martell* [15], and oxalate data from *Martell* and *Smith* [49] as quoted above. A first attempt could not reproduce the above mentioned equation, but then we suspected that *Turner et al.* [48] excluded Pb from their regression analysis. This reduced data set (Mg, Ca, Ba, Cu, Zn, Cd) exactly reproduced the published equation (Fig. 5): $\log\beta_{MCO_3} = -0.011\ (\pm 0.6) + 1.042\ (\pm 0.15)\log\beta_{MC_2O_4}$. Note, that even excluding lead carbonate from the regression analysis (which is not mentioned in Ref. [48]) results in rather large statistical errors of the regression line and consequently in large errors of the estimated constants (which is also not mentioned in Ref. [48]). The prediction intervals [53] on the 95% confidence level for estimated carbonate constants are shown as grey area in Fig. 5. Hence, data for nickel carbonate should not be given as $\log K^\circ = 5.36$ [48] but rather as $\log K^\circ = 5.4 \pm 1.5$ (see Fig. 5). Nevertheless, *Turner et al.* [48] use their oxalate–carbonate correlation extensively to provide values at the border and even far beyond the borderlines of measured data, *e.g.* $\log K^\circ = 6.83$ for $EuCO_3^+$ (more than one order of magnitude off: $\log K^\circ = 8.1 \pm 0.2$ [4]), $\log K^\circ = 7.50$ for UO_2CO_3(aq) (more than two orders of magnitude off: $\log K^\circ = 9.67 \pm 0.05$ [54]), or $\log K^\circ = 11.03$ for $ThCO_3^{2+}$ (how many orders of magnitude off?).

Three years later, *Fouillac* and *Criaud* [32] published a "Critical reevaluation of stability constants" for carbonate and bicarbonate trace metal complexes. They applied two different versions of electrostatic models, named by the authors a "simple electrostatic model" and the "*Fuoss* model" [55]. The same difficulty arises as already discussed by *Mattigod* and *Sposito* [34]: Which is the appropriate set of ionic radii to be used in the electrostatic models? *Fouillac* and *Criaud* [32] discuss this problem at length and propose for nickel carbonate two sets of stability constants (see Table 2), but finally resort to the numbers of *Zhorov et al.* [30] which they mistook for experimental data and "corrected to $I = 0$". The cycle of guesswork is closed.

At the end of this adventure in the labyrinth of thermodynamic data collections we are left with the sobering fact that almost all nickel carbonate complexation constants published in literature are derived by dubious estimation procedures, and the only one actually measured [33] is useless. This results in variations of more than four orders of magnitude. This is no longer a surprise, as a close inspection of the individual estimation procedures revealed that the estimated values are based on shaky grounds, to say the least.

Can We Do Better Guesswork?

The question now arises, whether we can improve on the estimation procedures for nickel carbonate complexes. A review showed that the stability constants of nickel oxalate are rather well established [52]. In addition, a number of detailed studies of aqueous carbonate complexes were published within the last twenty years, implying that the oxalate–carbonate correlation of *Turner et al.* [48] can potentially be improved.

The alkali earth–carbonate systems were studied in detail and as a consequence, the carbonate constants of Ca, Mg, Sr, and Ba can now be regarded as well established (see Table 4). New data were derived for copper and zinc carbonate constants using various methods, and solubility studies of iron, cadmium and lead carbonates resulted in new stability constants (Table 4). A single publication reports cobalt carbonate complexation data, but the quality of these data is judged as

Table 4. Data used for the oxalate–carbonate correlation method (Fig. 6)

Cation	$\log K_1°$(carbonate)	Ref.	$\log K_1°$(oxalate)	Ref.
Mg	2.98 ± 0.06	[95]	3.4	[49] → [96]
Ca	3.22 ± 0.14	[61]	3.0	[49] → [96]
Sr	2.81 ± 0.13	[62]	2.5	[49] → [96]
Ba	2.71 ± 0.10	[63]	2.3	[49] → [96]
Fe(II)	5.5 ± 0.2	[65]	4.5	[49] → [97]
Co	$4 \ldots 5$	[57]	4.69 ± 0.12	[52]
Ni			5.2 ± 0.2	[52]
Cu(II)	6.8 ± 0.2	[66]	6.2	[49] → [98]
Zn	4.8 ± 0.2	[59]	4.9	[49] → [99]
Cd	4.7 ± 0.2	[70]	4.2	[49] → [100]
Pb	6.5 ± 0.2	[47]	5.6	[16] → [101]
Eu	8.0 ± 0.1	[52]	6.98 ± 0.14	[52]
U(VI)	9.68 ± 0.04	[54]	7.2 ± 0.2	[52]

Stability constants refer to the equilibrium $M + L \Leftrightarrow ML$, where M is the metal cation in the first column and L is CO_3^{2-} or $C_2O_4^{2-}$, respectively; uncertainties are $\pm 2\sigma$ standard deviations in all cases; note that *Smith* and *Martell* [16, 49] do not report any estimates of uncertainties for the values included in this table; however, the uncertainties most probably are not smaller than ±0.2 and thus, all values were rounded to the first decimal place in order to avoid the deceiving impression of too precise data

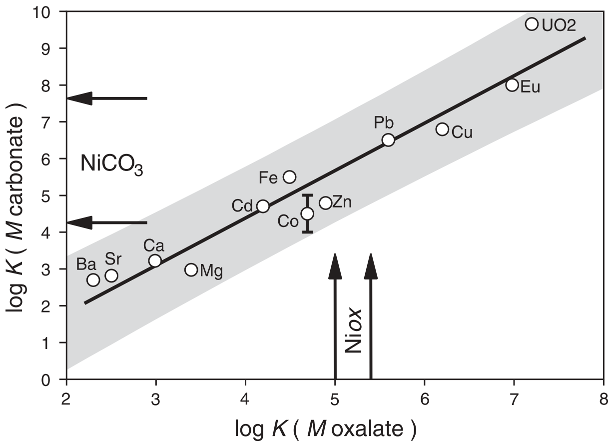

Fig. 6. New oxalate–carbonate correlation using an enlarged and improved data set for estimating the complexation constant of $NiCO_3(aq)$; for a detailed discussion see text

poor (see discussion below). The upper limit of carbonate complex stability is assured by detailed reviews for U(VI) [54] and Eu [4]. Oxalate data for Ni, Co, Eu, and U(VI) are also taken from a recent review [52] and all the other oxalate data originate from the tables of *Martell* and *Smith* [49] and *Smith* and *Martell* [16]. As in all their books, the authors do not report in detail the reasoning behind their recommendations, but in the case of oxalate data included in our regression analysis it was at least possible to trace back each value to a single reference (given in Table 4). Oxalate complexation constants for Fe, Cd, and Pb were given at 1 *M* $NaClO_4$ only. These constants were extrapolated to zero ionic strength using the SIT model [23] with a provisional ion interaction coefficient, $\varepsilon(\text{oxalate}^{2-}, \text{Na}^{+}) = -0.1$, estimated by *Glaus et al.* [52].

Using this enlarged and improved data set (Table 4) a new oxalate–carbonate linear regression was computed. However, the result is rather disappointing (Fig. 6). We considered twice the amount of data points than *Turner et al.* [48], which potentially decreases the statistical uncertainty of predicted values, but on the other hand, the overall scatter of the data increased. As a consequence, the prediction interval on the 95% confidence level (grey area in Fig. 6) spans about three orders of magnitude, almost the same as in the old correlation (Fig. 5). The new regression equation is: $\log K^{\circ}_{M\mathrm{CO}_3} = -0.8\ (\pm 0.5) + 1.29\ (\pm 0.11) \log K^{\circ}_{M\mathrm{C}_2\mathrm{O}_4}$. Inserting $\log K^{\circ}_{\mathrm{NiC}_2\mathrm{O}_4} = 5.2 \pm 0.2$ and considering the uncertainty interval (Fig. 6) yields $\log K^{\circ}_{\mathrm{NiCO}_3} = 5.9 \pm 1.7$. The regression parameters and the width of the prediction interval is rather sensitive to the U(VI) data. If we tentatively ignore U(VI) in the regression analysis, a considerably less steep line results $(\log K^{\circ}_{M\mathrm{CO}_3} = -0.3\ (\pm 0.5) + 1.15\ (\pm 0.10) \log K^{\circ}_{M\mathrm{C}_2\mathrm{O}_4})$ and the uncertainty in the predicted result decreases ($\log K^{\circ}_{\mathrm{NiCO}_3} = 5.7 \pm 1.3$), but what is the rationale behind excluding apparent “outliers” from the regression analysis?

As a detailed review of oxalate and carbonate data is outside the scope of this work, we are left with the statement that the oxalate–carbonate correlation is, in its present state, of little use for reliable predictions of stability constants. To make things worse, Eu and U(VI) data are already reviewed and judged as reliable data.

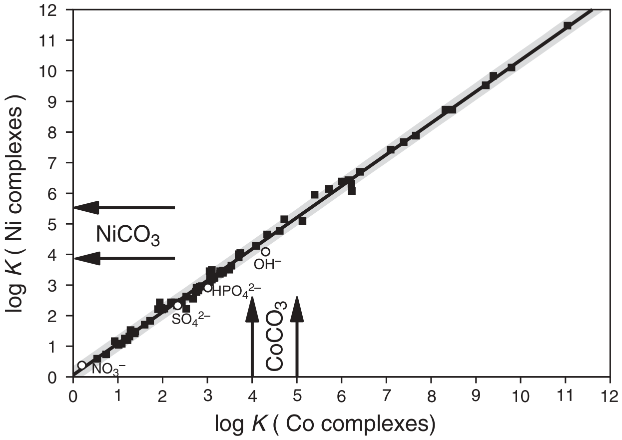

Fig. 7. Cobalt–nickel correlation for estimating the complexation constant of $NiCO_3(aq)$; for a detailed discussion see text

Hence, the considerable discrepancy between Eu and U(VI) is unlikely to turn out as a pure artefact due to bad experimental data. Therefore, it is not likely that future data reviews will result in a significantly improved oxalate–carbonate correlation.

Of course, there are other possible free energy correlations to predict stability constants. Instead of correlating two different ligands for a series of metal cations, we can correlate two metal cations for a series of ligands. The most promising correlation of this type is the cobalt–nickel correlation (Fig. 7). Cobalt and nickel are chemically similar, resulting in stability constants differing by one order of magnitude or less over more than ten orders of magnitude. The data for Fig. 7 were taken from *Smith* and *Martell* [15, 16, 49, 56]. Black squares represent organic ligands containing exclusively oxygen as chemically reactive sites (*i.e.* carboxyl, phenol, carbonyl groups, *etc.*). White circles represent inorganic ligands like OH^-, HPO_4^{2-}, SO_4^{2-}, and NO_3^-. The regression equation is: $\log K^\circ_{\mathrm{Ni}L} = 0.064\ (\pm 0.032) + 1.029\ (\pm 0.007) \log K^\circ_{\mathrm{Co}L}$. The prediction interval on the 95% confidence level (grey area in Fig. 7) has a width of only 0.6 log units. This excellent correlation allows reliable predictions, provided we have reliable data to use it.

In order to predict the complexation constant for $NiCO_3(aq)$, we need data on the formation of $CoCO_3(aq)$. Only one publication reporting measured data of cobalt carbonate complexation was discovered [57]. The measurements were made in $0.68\,M$ $NaClO_4$ by a polarographic method using the dropping mercury electrode. Unfortunately, the quality of this publication is poor, as no experimental details are reported and the results are given only in a small figure. As the data points in this figure seem to be inconsistent the stability constant reported by *Cosovic et al.* [57], $\log K_1 = 3.15 \pm 0.10$ at $I = 0.68\,M$, is questionable. The best we may derive from this study is a range within which we most probably expect the stability of cobalt carbonate: $\log K_1^\circ = 4 \ldots 5$ (at zero ionic strength). Inserting this range in our cobalt–nickel correlation (Fig. 7) we obtain a value for nickel carbonate of $\log K_1^\circ = 4.7 \pm 0.8$. This result is more precise than the results yielded by the oxalate–carbonate correlation, but nevertheless not quite satisfying, having used an excellent correlation with only poor input data.

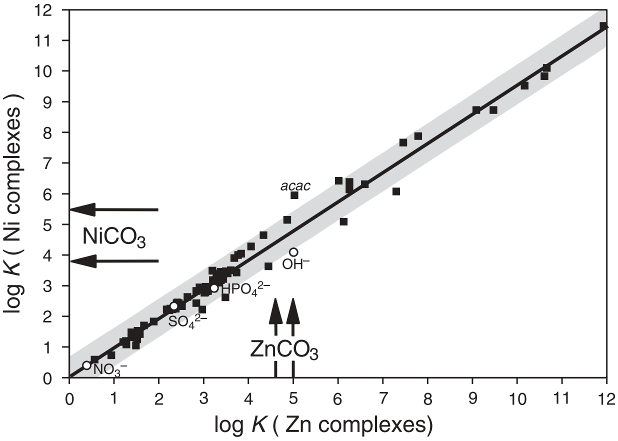

Fig. 8. Zinc–nickel correlation for estimating the complexation constant of $NiCO_3(aq)$; for a detailed discussion see text

Using the same sources of data (and the same graphic symbols) as in the case of the cobalt–nickel correlation, an analogous zinc–nickel correlation was established (Fig. 8). The regression equation is: $\log K^\circ_{\mathrm{Ni}L} = 0.05\ (\pm 0.07) + 0.952\ (\pm 0.015) \log K^\circ_{\mathrm{Zn}L}$. The prediction interval on the 95% confidence level (grey area in Fig. 8) has a width of 1.3 log units, reflecting the large statistical uncertainties of the zinc–nickel correlation. The significant scatter in the data seems to be caused by real differences in the chemical behaviour of zinc and nickel rather than by pure artefacts due to poor data. The most evident example is the behaviour of OH^- and acetylacetone (*acac* in Fig. 8). While complexation with zinc results in almost identical stability constants for both ligands, their complexation with nickel shows values differing by two orders of magnitude. Both data points originate from detailed reviews, the hydroxide data were taken from the monograph of *Baes* and *Mesmer* [14] and the acetylacetone data are recommended values from an IUPAC data review by *Stary* and *Liljenzin* [58]. This gives some confidence that the differences are not pure artefacts but at least to some degree reflect chemically different behaviour.

In the case of zinc we have reliable carbonate data from *Stanley* and *Byrne* [59] but a correlation with twice the predictive uncertainty as in the case of cobalt. Hence, using a zinc carbonate constant of $\log K_1^\circ = 4.8 \pm 0.2$ and our zinc–nickel correlation (Fig. 8) we end up with a value for nickel carbonate of $\log K_1^\circ = 4.6 \pm 0.8$, almost the same result as derived from the correlation with cobalt data.

To our present state of knowledge this is the end of the story. We are left with an uncertainty of a little less than two orders of magnitude and expect the stability constant of nickel carbonate in the range of 4 to 5.5 in log units.

Can We Estimate the Complexation Strength of Nickel Bicarbonate?

As in the case of carbonate complexes, studies concerning the alkali earth bicarbonate system are considered to be the most reliable ones and thus, association constants for Ca, Mg, Sr, and Ba with bicarbonate can be regarded as well established. The data are (with uncertainties of 2σ standard deviation):

$MgHCO_3^+$ 1.07 ± 0.06 [60], $CaHCO_3^+$ 1.11 ± 0.07 [61], $SrHCO_3^+$ 1.18 ± 0.14 [62], and $BaHCO_3^+$ 0.98 ± 0.12 [63]. The maximum difference in these constants is 0.2 log units, statistically insignificant considering the associated uncertainties.

The situation is less favourable in the case of transition metal bicarbonate complexes. For $MnHCO_3^+$, *Morgan* [39] reports a value of 1.95 with no uncertainty range. A decade later, *Lesht* and *Bauman* [64] derive 1.27 ± 0.02 from their experiments but fail to discuss the obvious discrepancy of their pretended very precise result with the number given by *Morgan* [39]. For Fe(II) we found only the study published by *Bruno et al.* [65], who state that including $FeHCO_3^+$ into their speciation model does not improve their fit of $FeCO_3$(cr) solubility data. This, of course, does not rule out the existence of a weak $FeHCO_3^+$ complex. For Co we also found only one study, published by *Cosovic et al.* [57]. As already discussed, the results of this study are judged as unreliable. *Byrne* and *Miller* [66] report a value of 1.8 ± 0.1 for the $CuHCO_3^+$ complex. The most studies were found for Zn, unfortunately accompanied by rather large discrepancies. *Ryan* and *Bauman* [67] report 1.40 ± 0.04, *Ferri et al.* [68] derive from measurements at high ionic strength ($3\,M$ $NaClO_4$) a value of 0.8 ± 0.2 at zero ionic strength, and most recently, *Stanley* and *Byrne* [59] published a constant of 1.64 ± 0.08 for $ZnHCO_3^+$.

This quick survey reveals differences of up to one log unit in the published transition metal bicarbonate constants. An attempt to resolve these discrepancies and to derive recommended values would require a detailed and time-consuming review of all these studies, which is outside the scope of this work. At least, we can assess provisional upper and lower bounds from these data. Considering the transition metal data we conclude that the nickel bicarbonate association constant will most probably have a value of less than 2 (in log units). On the other hand, we expect transition metal bicarbonate complexes to be stronger than alkali earth bicarbonate complexes. This provides our lower limit of about 1 (in log units).

A final step in our guesswork concerns a possible $Ni(CO_3)_2^{2-}$ complex. The stepwise stability constant of a 1:2 complex, $\log K_2°$, increases if $\log K_1°$ increases. If we have a sufficient number of experimental data, a $\log K_1° - \log K_2°$ correlation can be established. For example, such correlations are discussed for oxalate, citrate, and *NTA* (nitrilotriacetate) complexes in [69]. In the case of carbonate complexes, data are scarce and erratic preventing us from establishing a reliable correlation. However, some information can be gained from inspection of the difference of the stepwise stability constants $\Delta \log K = \log K_1° - \log K_2°$. The following $\Delta \log K$ values were derived from published constants: Fe(II) 3.9 [65], Cu(II) 2.0 [66], Zn 2.2 [59], Cd 2.9 [70], Pb 3.0 [47], Eu 3.2 [52] or 4.0 [4], and U(VI) 2.4 [54]. These numbers at least allow to assess an upper limit of $\log K_2°$ in relation to $\log K_1°$. Our survey of data suggests that we most probably can expect $\Delta \log K > 2$ for nickel carbonate implying that $\log K_2°$ of $Ni(CO_3)_2^{2-}$ should at least be two orders of magnitude lower than $\log K_1°$.

At the end, the results of so much guesswork are the following rough estimates of nickel carbonate complexation constants:

$NiCO_3(aq)$	$4 < \log K_1° < 5.5$
$Ni(CO_3)_2^{2-}$	$\log K_2° < \log K_1° - 2$
$NiHCO_3^+$	$1 < \log K° < 2$

Thermodynamic Data for Nickel Carbonate Solids

A detailed review of solubility products for metal(II) carbonates has been published by *Grauer* [71]. The information concerning nickel carbonate solids can be summarised as follows. For the reaction given in Eq. (8) *Smith* and *Martell* [16] report $\log K_{sp}{}^{\circ} = -6.87$, which differs by three to four orders of magnitude from the well established solubility of $FeCO_3$ and $ZnCO_3$.

$$NiCO_3(cr) \rightleftharpoons Ni^{2+} + CO_3{}^{2-} \tag{8}$$

This number can be traced back to very old solubility measurements performed by *Ageno* and *Valla* [72]. Their data seem suspicious, as pure anhydrous $NiCO_3$ can be synthesised only at temperatures above 220°C [73]. Since this compound is known to be virtually inert and acid resistant, attaining solubility equilibrium takes several weeks even at temperatures above 50°C. This indicates that the solid investigated by *Ageno* and *Valla* [72] did not consist of anhydrous nickel carbonate. Presumably their compound consisted of soluble carbonate hydrates. This objection is not new, but obviously has fallen into oblivion in the course of data diagenesis [71].

The only available solubility data for anhydrous $NiCO_3$ are the measurements of *Reiterer* [73] in the temperature range 50–90°C at ionic strength $1\,M$ $NaClO_4$. His data reveal negligible solubility differences between nickel and cobalt carbonates and show that their solubility constant is 0.4 log units below that of iron carbonate [65]. Presuming that this difference is also valid at 25°C, and using the same ionic strength correction procedure as applied for iron carbonate [65], a value of $\log K_{sp}{}^{\circ} = -11.2 \pm 0.2$ (Eq. 8) is recommended for both $CoCO_3$ and $NiCO_3$ by *Grauer* [71].

Recently, the experimental data of *Reiterer* [73] have been reevaluated and extrapolated to zero ionic strength and ambient temperature by *Wallner et al.* [74]. They recommend a value of $\log K^{\circ}_{sp} = -11.03 \pm 0.18$ at 25°C.

It must be pointed out that pure anhydrous nickel carbonate plays no role in natural environments. The mineral *gaspéite* is a solid solution with formula $(Ni, Fe, Mg)CO_3$ and it is a rare weathering product in massive sulphide deposits. Unlike the case of nickel hydroxide, the absence of anhydrous $NiCO_3$ in near-surface environments is not due to an exceedingly high solubility, but due to the high temperatures required to form this mineral.

The difficulty in forming anhydrous nickel(II) carbonates is related to the high hydration enthalpy of this ion. According to the data given by *Cotton* and *Wilkinson* [75], Ni^{2+} has the highest hydration enthalpy of all metals belonging to the first transition series ($\Delta H_{hydr} = -2105\,\text{kJ}\,\text{mol}^{-1}$). This means that the dehydration of the Ni^{2+} aqua ion, which is a necessary step on the way to form the anhydrous carbonate, requires a large amount of energy, and is thus inhibited at low temperatures. The high hydration energy also explains the weak Ni^{2+} sorption on calcite surfaces compared with other transition metals [76].

Recently, the solubility of *hellyerite*, $NiCO_3{\cdot}6H_2O$, has been studied as a function of temperature and ionic strength [74, 77]. Nickel hydroxide and nickel carbonate complexes are negligible in the *pH* ranges where these experiments were carried out. For the reaction given in Eq. (9) these authors determined a solubility product of $\log K_{sp}^{\circ} = -7.51 \pm 0.10$ at 25°C.

$$NiCO_3 \cdot 6H_2O(cr) \rightleftharpoons Ni^{2+} + CO_3^{2-} + 6H_2O \qquad (9)$$

A reevaluation of the experimental data of *Ageno* and *Valla* [72] by *Wallner et al.* [74] revealed a solubility product differing by only 0.1 log units from their new experimental results. This provides further evidence that *Ageno* and *Valla* [72] studied $NiCO_3 \cdot 6H_2O$ and not $NiCO_3$, confirming the argumentation of *Grauer* [71].

The solubility constants of *hellyerite*, $NiCO_3 \cdot 6H_2O$, and anhydrous $NiCO_3$ differ by 3.5 orders of magnitude. Due to its high solubility $NiCO_3 \cdot 6H_2O$ is of no importance as a solubility controlling solid phase in natural waters.

Geochemically Relevant Nickel Bearing Solids

Introductory Remarks

In sharp contrast to the restricted number and simple stoichiometry of nickel solids for which thermodynamic data exist, *i.e.* β-$Ni(OH)_2$ (*theophrastite*), NiO (*bunsenite*), $NiCO_3$ (*gaspéite*), and $NiCO_3 \cdot 6H_2O$ (*hellyerite*), stands the wide variety and complexity of nickel bearing solids found in nature. Mineralogy textbooks [78, 79] report a large number of solid phases containing nickel either as a major constituent or as a component of mixed phases. A search through a mineral catalogue published on the Internet (http://un2sg4.unige.ch/athena/mineral/mineral.html), for instance, returned a list of 167 nickel bearing minerals.

The large majority of these minerals are extremely rare and occur in nickel ores, often in association with other rare metals (typically Bi, Sb, As, Ag, Pt, Pd). Many of them are oxidative weathering products of primary Ni sulphides. These phases are formed under exceptional geochemical conditions, and are thus irrelevant in most polluted ground waters and radioactive waste repository environments. On the other hand, a number of low-temperature phases remains, which must be considered as potential solubility controlling phases in groundwater environments.

In an attempt to identify relevant nickel phases and distinguish them from solids that – due to their stability field – will not form at low temperatures, we prepared Table 5, where representative nickel solids are listed according to formation temperature and crystal-chemical and paragenetic criteria. On the base of these criteria minerals like *trevorite* and *pentlandite* can be readily excluded as solubility controlling phases since they form only under hydrothermal-magmatic or metamorphic conditions.

Six groups of low-temperature nickel minerals have been distinguished: sheet silicates, layered double hydroxides (*pyroaurite* group, including most hydrous carbonates), carbonates, phosphates, hydrous oxides, and sulphides. In view of the ubiquity of aluminum, silicium, and carbonate in repository environments, the former three groups will probably be preponderant. Most sheet silicates and carbonates listed in Table 5 are mixed phases, into which Ni^{2+} is incorporated as competitor to other transition metal ions. Typically, Ni is admixed as a dilute component in Fe, Mg dominated solids, further complicating nickel solubility calculations. Nickel phosphates (*cassidyite*, *reevesite*) have been found as weathering products of Fe–Ni meteorites [80], but the role of such phases in common ground

Table 5. Nickel minerals, with specification of their geological environment; low temperature phases include only solids that can demonstrably form at atmospheric pressure and temperature; italicised mineral names indicate the Ni-rich poles of solid solutions; the list is a small selection of representative phases and is forcefully incomplete, due to the very large number of known nickel minerals

Mineral	Formula	low – T environments				high – T environments	
		LAT	MTR	SOX	SRE	MHY	MET
sheet silicates							
lizardite – *népouite*	$(\mathrm{Mg}, \mathbf{Ni})_6[\mathrm{Si_4O_{10}}](\mathrm{OH})_8$	X					
berthierine – *brindleyite*	$(\mathrm{Fe, Mg}, \mathbf{Ni})_4(\mathrm{Al}, \mathrm{Fe}^{3+})_{1.8}[\mathrm{Al_{1.4}Si_{2.6}}]\mathrm{O_{10}(OH)_8}$	X					
kerolite – *pimelite*	$(\mathrm{Mg}, \mathbf{Ni})_3[\mathrm{Si_4O_{10}}](\mathrm{OH})_2 \cdot n\mathrm{H_2O}$	X					
chlinochlore – *nimite*	$(\mathrm{Mg}, \mathbf{Ni})_5\mathrm{Al}[\mathrm{AlSi_3O_{10}}](\mathrm{OH})_8$	X					
layered double hydroxides + anhydrous carbonates							
hydrotalcite – *takovite*	$(\mathrm{Mg}, \mathbf{Ni})_6\mathrm{Al_2(CO_3)(OH)_{16}} \cdot 4\mathrm{H_2O}$	X					
honessite	$\mathbf{Ni}_6\mathrm{Fe_2(SO_4)(OH)_{16}} \cdot 4\mathrm{H_2O}$			X			
nickelalumite	$\mathbf{Ni}\mathrm{Al_4(SO_4)(OH)_{12}} \cdot 3\mathrm{H_2O}$						
reevesite	$\mathbf{Ni}_6\mathrm{Fe_2(CO_3)(OH)_{16}} \cdot 4\mathrm{H_2O}$		X				
gaspéite	$(\mathbf{Ni}, \mathrm{Fe, Mg})\mathrm{CO_3}$			X			
phosphates							
cassidyite	$\mathrm{Ca_2}(\mathbf{Ni}, \mathrm{Mg})(\mathrm{PO_4})_2 \cdot 2\mathrm{H_2O}$		X				
hydrous oxides							
theophrastite	$\mathbf{Ni}(\mathrm{OH})_2$	X					
nickel goethite	$(\mathrm{Fe}, \mathbf{Ni})\mathrm{OOH}$	X		X			
sulphides							
violarite	$\mathrm{Fe}^{2+}\mathbf{Ni}^{3+}{}_2\mathrm{S}_4$			X			
millerite	$\mathbf{Ni}\mathrm{S}$				X	X	X
pyrite – *vaesite* (bravoite)	$(\mathrm{Fe}, \mathbf{Ni})\mathrm{S}_2$				X		X
pentlandite	$(\mathrm{Fe}, \mathbf{Ni})_9\mathrm{S}_8$					X	
oxides							
bunsenite	$\mathbf{Ni}\mathrm{O}$						X
magnetite – *trevorite*	$(\mathrm{Fe}^{2+}, \mathbf{Ni})\mathrm{Fe}^{3+}{}_2\mathrm{O}_4$						X

LAT = nickel laterites, MTR = weathering product of meteorites, SOX = oxidation zone of nickel sulphide ores, SRE = reduction zone of nickel sulphide ores, MHY = magmatic-hydrothermal origin, MET = metamorphic

waters is not clear. Pure nickel hydrous oxides, on the other hand, are very rare in nature (probably due to the high solubility at $pH < 9$) and can thus be neglected in most environmental systems (with the possible exception of cementitious systems). Sulphides may become important under reducing conditions, since there are nickel sulphides precipitating at low temperatures and which form solid solutions with common iron sulphides [81]. Examples are the *millerite – mackinawite* and *vaesite – pyrite* series.

Unfortunately, thermodynamic data for low-temperature nickel solids are scarce and have mostly no relevance to problems of surface geochemistry. This applies in particular to the already discussed soluble nickel hydroxide and carbonate phases. Moreover, the published solubility products of *millerite* (NiS), reviewed in detail by *Thoenen* [81], seem to be unreliable, since published values are found to vary by ten orders of magnitude.

The Role of Alumosilicates

Because of the abundance and ubiquity of Al and Si in surface rocks, it can be argued that a large fraction of Ni recycled in low-temperature environments will be fixed in alumosilicate minerals. In view of its similarity with Mg in terms of ionic radius and chemical properties nickel as a trace element is expected to concentrate in magnesium alumosilicates. This is confirmed by ample geological evidence. For instance, ore-grade Ni concentrations are typically found in clay minerals associated to laterites derived from ultramafic rocks.

In the following sections we summarise evidence (both from the field and from recent laboratory experiments) that alumosilicates and minerals of the *pyroaurite* group, rather than nickel hydroxides, generally control nickel concentrations in surface waters.

Ni Partitioning in Magnesian Rocks

The data compiled in Table 6 show typical Mg and Ni concentrations in marine clays and limestones. The data are taken from the ''Geostan'' database, a collection of chemical analyses carried out on internationally recognised geochemical standards [82]. These materials have been measured repeatedly in different laboratories and with various analytical methods, thus yielding accurate and precise concentrations. The numbers in Table 6 reveal a consistent picture, as the Ni concentrations

Table 6. Ni and Mg concentration data for marine clays and limestones; all but two of the listed data were selected from the ''GeoStan'' database, a collection of carefully cross-checked concentration data for geochemical standards [82]; data for the samples ATT-1 and CSB-1 are from *Hosterman* and *Flanagan* [102]; care was taken to select the most pure clay samples, *i.e.* those with a minimum amount of carbonates and organic matter; calculated partition coefficients (D) are given to a precision of 10 unities

Material	Identification label	Mg weight-%	Ni ppm	x_{Ni}/x_{Mg}	$D = \frac{x_{Ni}/x_{Mg}}{[\mathrm{Ni}]/[\mathrm{Mg}]}$
marine mud	MAG-1	3.0	53	0.0012	6550
shale	SGR-1	4.4	29	0.0005	2440
Cody shale	Sco-1	2.7	27	0.0007	3700
marine sedim.	PACS-1	2.4	44	0.0013	6800
clay shale	TB	1.9	40	0.0014	7810
clay shale	TB-2	1.9	39	0.0014	7610
shale	GSR-5	2.0	37	0.0013	6860
shale	AW-1	2.1	61	0.0020	10770
marine sedim.	GSMS-1	3.4	150	0.0030	16360
glauconite	GL-0	4.5	36	0.0005	2970
attapulgite	ATT-1	9.1	28	0.0002	1140
bentonite	CSB-1	1.9	9	0.0003	1760
median		*2.6*	*38*	*0.0010*	*5530*
limestone	KH	0.7	21	0.0021	11120
limestone	CCH-1	2.9	8	0.0002	1020
limestone	JLs-1	0.6	0.3	0.00003	190

in oceanic sediments are remarkably uniform, varying mostly between 10 and 100 ppm. This uniformity may reflect the constant Mg concentrations in seawater. From Table 2.2 in *Millero* [25] using a density of $1.023\,\mathrm{kg\,dm^{-3}}$, we calculated $[\mathrm{Mg}] = 0.054\,M$. Using this latter value and an average Ni concentration in seawater of $10^{-8}\,M$ [25] we estimated enrichment factors for Ni in the solid by computing empirical partition coefficients by Eq. (10), where x_{Ni}, x_{Mg} are mole fractions in the solid and [Ni], [Mg] the concentrations in solution.

$$D \equiv \frac{x_{Ni}/x_{Mg}}{[\mathrm{Ni}]/[\mathrm{Mg}]} \tag{10}$$

The results, listed in the rightmost column in Table 6, indicate a strong enrichment of Ni relative to Mg in the solid ($D = 10^3$ to 10^4). Nickel concentrations in limestones and other oceanic rocks appear to be more variable. Even if comparable to or even higher than in shales (*e.g.* several thousand ppm in manganese nodules), clays dominate the mass balance in marine sediments and are thus the main host phase for Ni. It is thus reasonable to assume that clay minerals control the aqueous concentration of Ni in the ocean through adsorption or solid equilibria [83].

Measured Partition Coefficients of Nickel in Magnesium Clays

Decarreau [84] measured the incorporation of Ni, Co, Zn, Fe(II), and Cu in synthesised trioctahedral magnesian smectites at temperatures between 25–75°C. The clays were precipitated from $0.1\,M$ $\mathrm{Na_2SiO_3}$ and $0.3\,M$ $\mathrm{MgCl_2}$ solutions at $pH \sim 9.5$–10.0, by adding the coprecipitating trace metal to obtain a desired magnesium:metal initial ratio in solution (ratios varied between 1 and 19).

Partition coefficients were then calculated from the final concentrations of Mg and Ni in solution and solid, according to the definition given in Eq. (10). The results indicate a strong partitioning of Cu, Ni, Co, and Fe in the solid, since partition coefficients always greatly exceed a value of 100. For $\mathrm{Mn^{2+}}$, on the other hand, a partition coefficient of only ~25 was determined. Thus, the laboratory data of *Decarreau* [84] confirm our finding, based on concentration data of seawater and marine sediments, that Ni is strongly enriched by clay minerals.

Evidence from X-Ray Spectroscopy

In recent years, a considerable amount of information on the interaction of dissolved nickel with alumosilicates has been gathered through spectroscopic studies, mainly X-ray absorption fine structure (XAFS) and optical absorption spectroscopy (OAS). Unlike preceding studies, these investigations focused on the atomic-scale binding mechanisms of Ni to the solid surface. Here, we try to summarise the findings and relate them to the perspective of the present review.

Manceau and *Calas* [85, 86] studied Ni–Mg clay minerals from New Caledonian laterites by XAFS and OAS. They selected samples of variable Ni content from both *lizardite – népouite* and *kerolite – pimelite* series. In every case they found evidence for six-fold coordination of Ni, independent of the Ni concentration in the clay minerals (which varied between about 5–50%). Moreover, they could establish the presence of 5–6 Ni neighbours at 3.05–3.07 Å in the second shell of the backscattering nickel atoms, even in the Mg dominated samples. This indicates that tiny discrete domains of the almost pure Ni end-members (*népouite* and *pimelite*) are segregated within a matrix of Mg end-member (*lizardite* and *kerolite*). Thus, Mg and Ni are not randomly mixed, as one would expect in ideal solid solutions. Therefore, these minerals must be regarded as intimately intermixed mechanical mixtures of pure Ni and Mg phases.

Later laboratory experiments [87, 88] revealed the formation of Ni–Al surface precipitates upon sorption of Ni on various alumosilicates (*pyrophyllite* and *gibbsite*). The experiments were carried out at *pH* 7.5 in 10 g dm^{-3} suspensions of 0.1 *M* $NaNO_3$, with high initial Ni concentrations (3 m*M*). Although the nucleation kinetics were quite variable (in the order of minutes for Ni on *pyrophyllite* and of months for Ni on *montmorillonite*), the precipitates yielded very similar XAFS spectra, all closely resembling those recorded for the reference compound *takovite*. Thus, these data provide evidence that minerals of the *pyroaurite* group may control the solution concentration of Ni in the presence of alumosilicate substrates. Note, that this Ni–Al double hydroxide forms despite the fact that the initial solutions are probably above saturation with respect to β-$Ni(OH)_2$. According to our data analysis the final concentrations, in the order $\sim 10^{-4}$ *M*, are still close to the saturation equilibrium curve of *Plyasunova et al.* [17] (see Fig. 1). Therefore, it cannot be excluded that the identified *takovite*-like phases are metastable. Similar results were obtained in an analogous study [89] conducted with cement pastes and *gibbsite* under completely different conditions (*pH* = 13.3, K–Ca–OH solution and initial Ni concentrations of 0.01 *M*). After 150 days reaction time, a Ni–Al compound similar to that identified by *Scheidegger et al.* [87] had formed as a secondary product, probably coexisting with minor amounts of nickel hydroxide.

More recently a polarised XAFS study of Ni uptake on sodium montmorillonite, carried out at 0.7 m*M* initial Ni concentration, revealed further details [90]. As in the previous studies, a discrete Ni phase is formed, but Ni–Al double hydroxides and $Ni(OH)_2$ phases had to be excluded on the base of the X-ray spectra. From a detailed analysis of their spectral data *Dähn et al.* [90] convincingly demonstrate that a separate nickel phyllosilicate formed in the presence of *montmorillonite*. This finding confirms the mentioned earlier results by *Manceau* and *Calas* [85], who observed formation of discrete nickel phyllosilicate domains within natural trioctahedral magnesium clays. If the initial concentration of Ni decreases below 10 μ*M*, however, no separate phase formation is observed, even after 1 year reaction time at 25°C [91, 92]. In this case, only specific sorption at the edges of the montmorillonite is identified as Ni retention mechanism, although there is some evidence for changes in the coordination shells of Ni at long reaction times.

Nickel(II) Stabilisation in Octahedral Coordination

From the data discussed above, the following facts emerge: 1) a specific affinity of Ni to concentrate in Mg-rich phases; 2) a tendency to form discrete nickel phases (as clay or *pyroaurite*-group minerals) rather than true solid solutions, even at low Ni/Mg ratios; 3) a prevalence of Ni to reside in octahedral sites.

These tendencies cannot be explained uniquely by the similar ionic radii of the divalent Mg and Ni cations. If this were the only reason leading to the formation of Mg–Ni solids, the partition coefficients for Ni^{2+} incorporation in Mg minerals would be close to one, indicating no selectivity between Ni^{2+} and Mg^{2+}, and true solid solutions would form (with random distribution of Ni^{2+} within a Mg dominated lattice). The high partition coefficients indicate, on the contrary, a strong preference for Ni incorporation (as for Cu, Co, Zn, Fe(II)) relative to Mg and the XAFS data point to the existence of miscibility gaps in Ni–Mg alumosilicates and double layer hydroxides at low temperatures.

These phenomena can be rationalised in terms of *crystal field theory*. As pointed out by *Burns* [93], cations with a *3d8* electronic configuration like Ni^{2+} are strongly stabilised in an octahedral environment as they have the highest stabilisation energy ($CFSE = 6/5\Delta_0$). Fe^{2+}, Cu^{2+}, Co^{2+}, and Zn^{2+} have also a positive CFSE, while Mn^{2+} (for which the smallest D-values were determined) has a $CFSE = 0$ in the normal low-spin configuration.

In conclusion, a consistent picture emerges indicating that, in most groundwaters, Ni concentrations will be limited by intermixed Ni–Mg alumosilicates or Ni–Al layered double hydroxides, not by simple nickel hydroxides. The formation of true solid solutions seems to be hindered at low temperatures and $[Ni] > 10^{-4} M$, but it is still unclear whether this finding can be extended to trace element concentrations ($[Ni] \leq 10^{-6} M$).

Conclusions

In contrast to the general opinion, a thorough review of thermodynamic data revealed that the aqueous speciation of nickel is poorly known. The first hydrolysis constant of Ni is the only thermodynamic constant of environmental relevance, which can be regarded as fairly well established. Polynuclear complexes are also known at high Ni concentrations but they are irrelevant in almost all natural environments. Although higher hydrolysis constants are crucial to determine the Ni speciation in alkaline groundwater and cement pore water, at present data are scarce and only poor estimates can be derived from the few published solubility studies of nickel hydroxide.

The situation is even worse in the case of aqueous carbonate complexes. No reliable experimental study has been published so far and almost all numbers reported in thermodynamic databases are unacceptable estimates based on shaky estimation procedures. Consequently, these values scatter over several orders of magnitude. The best we can do is to assess expectation ranges through correlation with other known thermodynamic constants. Careful experimental studies of the system $Ni–H_2O–CO_2$ are needed to remedy this unfortunate situation.

Solubility constants for a few simple nickel solids are known or have been estimated from thermochemical data. However, none of these simple solids is of geochemical relevance at ambient conditions. Nickel oxide is not a stable phase at ambient conditions in nature. Nickel hydroxide and $NiCO_3 \cdot 6H_2O$ are too soluble to be solubility limiting phases in natural groundwaters. Although the simple nickel sulphide, *millerite*, has been shown to form in low temperature systems, the enormous scatter in the solubility products published in literature (ten orders of magnitude) precludes any quantitative prediction. Other simple nickel solids will either not form at ambient temperature or they are highly soluble. Solids not formed at ambient temperature are, besides NiO, anhydrous $NiCO_3$, most nickel sulphides, and simple silicates like nickel olivine or nickel spinel. Highly soluble solids, like nickel chloride and nickel sulphate, are of no relevance in ground and surface waters.

Based on field evidence, we identified six classes of solids, which could theoretically limit Ni concentrations in groundwaters (either as pure nickel solids or as solid solutions): 1) sheet silicates, particularly Ni–Mg clay minerals; 2) layered double hydroxides (*pyroaurite* group minerals, including most hydrous carbonates); 3) anhydrous carbonates; 4) phosphates; 5) hydrous oxides; 6) sulphides. Recent spectroscopic data clearly indicate that the first two classes of solids play a major role. However, contrary to our expectation, in aqueous systems with $[\mathrm{Ni}] \geq 0.1\,\mathrm{m}M$ these minerals do not form solid solutions, but rather intermixed phases containing segregated Ni-rich domains. In aqueous systems with Ni at micromolar concentrations, specific sorption on alumosilicate surfaces seems to be the dominant uptake mechanism, at least on the timescale and temperatures of the experiments carried out (1 year at ~25°C). There is, however, some evidence that sorption is just a transient step towards formation of a new mineral structure.

Although thermodynamic data for these complex but geochemically relevant phases are lacking, there are at least measurements of empirical partition coefficients of Ni in some clay minerals, which indicate a strong enrichment of nickel in the solid phase. Since these partition coefficients are consistent with carefully selected data on Ni concentrations in the oceanic system and can be brought in relation with principles of crystal field theory, we think that they could be used as a preliminary modelling tool to determine Ni concentration limits in aqueous systems equilibrated with clay minerals. In any case, clay minerals and layered double hydroxides appear to be the most promising classes of solids for future investigations.

In summary, we need not only carefully designed solubility studies of nickel bearing phases at ambient conditions, but also precise measurements to decrease the uncertainty ranges of basic nickel hydrolysis and carbonate complexation constants.

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References

[1] OEHHA Office of Environmental Health Hazard Assessment (2001) Public Health Goals for Chemicals in Drinking Water: Nickel. California Environmental Protection Agency, http://www.oehha.ca.gov/water/phg/81701PHG.html

[2] Nagra (1994) Kristallin-I Safety Assessment Report. Nagra Technical Report NTB 93-22, Nagra, Wettingen, Switzerland

[3] Nagra (2002) The long-term safety of a repository for spent fuel, vitrified high-level waste and long-lived intermediate-level waste sited in the Opalinus Clay of the Zürcher Weinland. Nagra Technical Report NTB 02-05, Nagra, Wettingen, Switzerland

[4] Hummel W, Berner U, Curti E, Pearson FJ, Thoenen T (2002) Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra Technical Report NTB 02-16, Nagra, Wettingen, Switzerland; and Universal Publishers/uPublish.com, Parkland, Florida

[5] Berner U (1995) Kristallin-I Estimates of Solubility Limits for Safety Relevant Radionuclides. PSI Report Nr. 95-07, Paul Scherrer Institut, Villigen, Switzerland; Nagra Technical Report NTB 94-08, Nagra, Wettingen, Switzerland

[6] Berner U (2002) Project Opalinus Clay: Radionuclide Concentration Limits in the Near-Field of a Repository for Spent Fuel and Vitrified High-Level Waste. PSI Report Nr. 02-22, Paul Scherrer Institut, Villigen, Switzerland; Nagra Technical Report NTB 02-10, Nagra, Wettingen, Switzerland

[7] Bradbury MH, Baeyens B (1997) J Contam Hydrol **27**: 223

[8] Bradbury MH, Baeyens B (1997) Far-field sorption data bases for performance assessment of a L/ILW repository in an undisturbed Palfris Marl host rock. PSI Report Nr. 97-15, Paul Scherrer Institut, Villigen, Switzerland; Nagra Technical Report NTB 96-06, Nagra, Wettingen, Switzerland

[9] Bradbury MH, Baeyens B (2002) Near-field sorption data bases for compacted MX-80 bentonite for performance assessment of a high level radioactive waste repository in Opalinus Clay host rock. Nagra Technical Report NTB 02-18, Nagra, Wettingen, Switzerland

[10] Bradbury MH, Baeyens B (2002) Far-field sorption data bases for performance assessment of a high level radioactive repository in an undisturbed Opalinus Clay host rock. Nagra Technical Report NTB 02-19, Nagra, Wettingen, Switzerland

[11] NEA Nuclear Energy Agency (2001) Using Thermodynamic Sorption Models for Guiding Radioelement Distribution Coefficient (Kd) Investigations: A Status Report. OECD Publications, Paris, France

[12] Wieland E, Tits J, Spieler P, Dobler JP, Scheidegger AM (2000) Uptake of nickel and strontium by a sulphate-resisting Portland cement. In: Rammlmair D, Mederer J, Oberthür T, Heimann RB, Pentinghaus H (eds) Applied Mineralogy. Balkema, Rotterdam, p 705

[13] Wieland E, Van Loon LR (2002) Near-field sorption data base for performance assessment of an ILW repository in Opalinus clay. Nagra Technical Report NTB 02-20, Nagra, Wettingen, Switzerland

[14] Baes CF, Mesmer RE (1976) The Hydrolysis of Cations. Wiley, New York

[15] Smith RM, Martell AE (1976) Critical Stability Constants vol 4, Inorganic Complexes. Plenum Press, New York

[16] Smith RM, Martell AE (1989) Critical Stability Constants, vol 6, 2nd Suppl, Plenum Press, New York

[17] Plyasunova NV, Zhang Y, Muhammed M (1998) Hydrometallurgy **48**: 43

[18] Mattigod SV, Rai D, Felmy AR, Rao L (1997) J Solution Chem **26**: 391

[19] Gamsjäger H, Wallner H, Preis W (2002) Monatsh Chem **133**: 225

[20] Perrin DD (1964) J Chem Soc (London) 3644

[21] Gayer KH, Garrett AB (1949) J Amer Chem Soc **71**: 2973

[22] Ziemniak SE, Jones ME, Combs KES (1989) J Solution Chem **18**: 1133

[23] Grenthe I, Plyasunov AV, Spahiu K (1997) Estimation of medium effects on thermodynamic data. In: Grenthe I, Puigdomènech I (eds) Modelling in Aquatic Chemistry. OECD Nuclear Energy Agency, Paris, p 325

[24] Byrne RL, Yao W (2000) Geochim Cosmochim Acta **64**: 4153

[25] Millero FJ (1996) Chemical Oceanography, 2nd ed CRC Press, Boca Raton, Florida

[26] Pilkington NJ, Stone NS (1990) The solubility and sorption of nickel and niobium under high pH conditions. Report NSS/R186, AEA Technology, Harwell Laboratory, Oxfordshire, UK

[27] Kulmala S, Hakanen M (1993) The solubility of Zr, Nb and Ni in groundwater and concrete water, and sorption on crushed rock and cement. Report YJT-93-21, Nuclear Waste Commission of Finnish Power Companies, Helsinki, Finland

[28] Glasser FP, Kindness A, Smillie S, Altenhein-Haese C, Bischoff H, Marx G, Aggarwal S, Angus M, Hibbert R, Csetény L, Takács Z, Bagosi S (1996) Impact of additives and waste stream

constituents on the immobilization potential of cementitious materials. Final Report EUR 16942EN, European Commission, Luxembourg

[29] Ochs M, Hager D, Helfer S, Lothenbach B (1998) Solubility of radionuclides in fresh and leached cementitious systems at 22°C and 55°C. In: McKinley IG, McCombie C (eds) Scientific Basis for Nuclear Waste Management XXI. Mat Res Soc Symp Proc vol 506, p 773

[30] Zhorov VA, Bezborodov AA, Popov NI (1976) Oceanology **16**: 463

[31] Garrels RM, Christ CL (1965) Solutions, Minerals, and Equilibria. Harper & Row, New York

[32] Fouillac C, Criaud A (1984) Geochem J **18**: 297

[33] Emara MM, Farid NA, Shehata HA (1987) J Indian Chem Soc **64**: 119

[34] Mattigod SV, Sposito G (1977) Soil Sci Soc Amer **41**: 1092

[35] Benson LY, Teague LS (1980) A tabulation of thermodynamic data for chemical reactions involving 58 elements common to radioactive waste package systems. LBL-11448, Lawrence Berkley Lab

[36] Ball MA, Nordstrom DK, Jenne EA (1981) Additional and revised thermochemical data and computer code for WATEQ2 – a computerized chemical model for trace and major element speciation and mineral equilibria of natural waters. WRI 78-116, US Geol Survey Water Resources Invest

[37] Baeyens B, McKinley IG (1989) A PHREEQE Database for Pd, Ni and Se. PSI Report Nr. 34, Paul Scherrer Institut, Villigen, Switzerland; and Nagra Technical Report NTB 88-28, Nagra, Wettingen, Switzerland

[38] Kester DR, Pytkowicz RM (1975) Mar Chem **3**: 365

[39] Morgan JJ (1965) Chemical equilibria and kinetic properties of manganese in natural waters. In: Faust SD, Hunter JV (eds) Principles and Application of Water Chemistry. Wiley, New York, p 561

[40] Van Panthaleon Van Eck CL (1953) Rec Trav Chim Pays-Bas **72**: 529

[41] Schindler P, Reinert M, Gamsjäger H (1968) Helv Chim Acta **51**: 1845

[42] Mattigod SV, Sposito G (1979) Chemical modeling of trace metal equilibria in contaminated soil solutions using the computer program GEOCHEM. In: Jenne EA (ed) Chemical Modeling in Aqueous Systems. ACS Symposium Series 93, American Chemical Society, Washington DC, p 837

[43] Nieboer E, McBryde WAE (1973) Can J Chem **51**: 2512

[44] Pearson FJ, Berner U, Hummel W (1992) Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland

[45] Allred AL (1961) J Inorg Nucl Chem **17**: 215

[46] Pauling L (1960) The nature of the chemical bond, and the structure of molecules and crystals: An introduction to modern structural chemistry. Cornell University Press, Ithaca, New York

[47] Bilinski H, Schindler P (1982) Geochim Cosmochim Acta **46**: 921

[48] Turner DR, Whitfield M, Dickson AG (1981) Geochim Cosmochim Acta **45**: 855

[49] Martell AE, Smith RM (1977) Critical Stability Constants vol 3 Other Complexes. Plenum Press, New York

[50] Langmuir D (1979) Techniques of estimating thermodynamic properties for some aqueous complexes of geochemical interest. In: Jenne EA (ed) Chemical Modeling in Aqueous Systems. ACS Symposium Series 93, American Chemical Society, Washington DC, p 353

[51] Yatsimirskii KB, Vasil'ev VP (1960) Instability Constants of Complex Compounds. Pergamon Press, Oxford

[52] Glaus MA, Hummel W, Van Loon LR (1997) Experimental Determination and Modelling of Trace Metal – Humate Interactions: A Pragmatic Approach for Application in Groundwater. PSI Report Nr. 97-13, Paul Scherrer Institut, Villigen, Switzerland; and Nagra Technical Report NTB 97-03, Nagra, Wettingen, Switzerland, Appendix A, p 128

[53] Hahn GJ (1972) Technometrics **14**: 203

[54] Grenthe I, Fuger J, Konings RJM, Lemire RJ, Muller AB, Nguyen-Trung C, Wanner H (1992) Chemical Thermodynamics of Uranium. Elsevier, Amsterdam
[55] Fuoss RM (1958) J Amer Chem Soc **80**: 5059
[56] Martell AE, Smith RM (1982) Critical Stability Constants vol 5, 1st Suppl, Plenum Press, New York
[57] Cosovic B, Degobbis D, Bilinski H, Branica M (1982) Geochim Cosmochim Acta **46**: 151
[58] Stary J, Liljenzin JO (1982) Pure & Appl Chem **54**: 2557
[59] Stanley JK, Byrne RH (1990) Geochim Cosmochim Acta **54**: 753
[60] Siebert RM, Hostetler PB (1977) Amer J Sci **277**: 697
[61] Plummer LN, Busenberg E (1982) Geochim Cosmochim Acta **46**: 1011
[62] Busenberg E, Plummer LN (1984) Geochim Cosmochim Acta **48**: 2021
[63] Busenberg E, Plummer LN (1986) Geochim Cosmochim Acta **50**: 2225
[64] Lesht D, Bauman JE (1978) Inorg Chem **17**: 3332
[65] Bruno J, Wersin P, Stumm W (1992) Geochim Cosmochim Acta **56**: 1149
[66] Byrne RH, Miller WL (1985) Geochim Cosmochim Acta **49**: 1837
[67] Ryan MP, Bauman JE (1978) Inorg Chem **17**: 3329
[68] Ferri D, Grenthe I, Hietanen S, Néher-Neumann E, Salvatore F (1985) Acta Chem Scand **A39**: 347
[69] Grenthe I, Hummel W, Puigdomènech I (1997) Chemical background for the modelling of reactions in aqueous systems. In: Grenthe I, Puigdomènech I (eds) Modelling in Aquatic Chemistry. OECD Nuclear Energy Agency, Paris, p 69
[70] Rai D, Felmy AR, Moore DA (1991) J Solution Chem **20**: 1169
[71] Grauer R (1999) Solubility Products of M(II) – Carbonates. Edited and translated by U Berner. PSI Bericht Nr. 99-04, Paul Scherrer Institut, Villigen, Switzerland; and Nagra Technical Report NTB 99-03, Nagra, Wettingen, Switzerland
[72] Ageno F, Valla E (1911) Atti Accad naz lincei, Ren Classe Sci Fis mat nat **20**(2): 706
[73] Reiterer F (1980) Löslichkeitskonstanten und Freie Bildungsenthalpien neutraler Übergangsmetallcarbonate. PhD Thesis, Montanuniversität Leoben, Austria
[74] Wallner H, Preis W, Gamsjäger H (2002) Thermochim Acta **382**: 289
[75] Cotton FA, Wilkinson G (1982) Anorganische Chemie, 4 ed VCH Verlagsgesellschaft, Weinheim, Germany
[76] Zachara JA, Cowan CE, Resch CT (1991) Geochim Cosmochim Acta **55**: 1549
[77] Gamsjäger H, Preis W, Wallner H (2001) Monatsh Chem **132**: 411
[78] Betechtin AG (1974) Lehrbuch der speziellen Mineralogie. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig
[79] Ramdohr P (1980) The ore minerals and their intergrowths. Pergamon Press, Oxford
[80] White JS, Henderson EP, Mason B (1967) Am Mineral **52**: 1190
[81] Thoenen T (1999) Nuclear Technol **126**: 75
[82] Govindaraju K (1996) Geostandards Newsletter **20**: 3
[83] Li YH (1991) Geochim Cosmochim Acta **55**: 3223
[84] Decarreau A (1985) Geochim Cosmochim Acta **49**: 1537
[85] Manceau A, Calas G (1985) Am Mineral **70**: 549
[86] Manceau A, Calas G (1986) Clay Min **21**: 341
[87] Scheidegger AM, Strawn DG, Lamble GM, Sparks DL (1998) Geochim Cosmochim Acta **62**: 2233
[88] Roberts DR, Scheidegger AM, Sparks DL (1999) Environ Sci Technol **33**: 3749
[89] Scheidegger AM, Wieland E, Scheinost AC, Dähn R, Spieler P (2000) Environ Sci Technol **34**: 4545
[90] Dähn R, Scheidegger AM, Manceau A, Schlegel ML, Baeyens B, Bradbury MH, Morales M (2002) Geochim Cosmochim Acta **66**: 2335

[91] Dähn R (2001) Determination of Ni(II) and Th(IV) sorption mechanisms on clay mineral surfaces: a combined macroscopic, spectroscopic and microscopic approach. PhD Thesis, Swiss Federal Institute of Technology Zürich, Zürich, Switzerland

[92] Dähn R, Scheidegger AM, Manceau A, Schlegel ML, Baeyens B, Bradbury MH, Chateigner D (2002) Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals: A polarized EXAFS study. Geochim Cosmochim Acta (accepted for publication)

[93] Burns RG (1993) Mineralogical applications of crystal field theory. Cambridge University Press, Cambridge, Massachusetts

[94] Bilinski H, Huston R, Stumm W (1976) Anal Chim Acta **84**: 157

[95] Siebert RM, Hostetler PB (1977) Amer J Sci **277**: 716

[96] Money RW, Davies CW (1932) Trans Faraday Soc **28**: 609

[97] Bottari E, Ciavatta L (1965) Gazzetta Chimica Italiana **95**: 908

[98] McAuley A, Nancollas GH (1960) Trans Faraday Soc **56**: 1165

[99] Evans CE, Monk CB (1970) Trans Faraday Soc **66**: 1491

[100] Bottari E (1975) Monatsh Chem **106**: 451

[101] Ruiz-Cabrera G, Rodriquez-Placeres JC, Ramos-Steffens F, Arevalo A (1985) Polyhedron **4**: 221

[102] Hostermann JW, Flanagan FJ (1987) Geostandards Newsletter **11**: 1

[103] Allard B (1995) Groundwater. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC Press, Boca Raton, Florida, Table 8, p 172

[104] Borg H (1995) Trace elements in lakes. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC Press, Boca Raton, Florida, Table 6, p 189

[105] Hong J, Calmano W, Förstner U (1995) Interstitial waters. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC Press, Boca Raton, Florida, Table 4, p 137