

Solubility of Nickel Oxide and Hydroxide in Water

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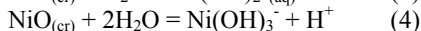
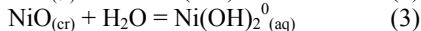
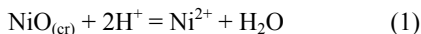
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The solubility of NiO_(cr) was measured using flow techniques and a potentiometric method from *ca.* 0 to 350°C in aqueous solutions as a function of pH. A more limited study of the solubility of β-Ni(OH)_{2(cr)} was conducted by both techniques to 200°C. These results indicate that the transition temperature at which nickel hydroxide dehydrates to form the oxide is *ca.* 75°C, much lower than previously reported. However, β-Ni(OH)_{2(cr)} can persist as a metastable phase to 200°C for a sufficient period of time to conduct solubility measurements. The oxide was also found to persist metastably below ambient temperatures, at least in acidic solutions. Independent calculations of the thermodynamic properties of these two nickel phases support the claim of a 75°C transition temperature. Only two aqueous nickel(II) species were identified over the entire pH range studied, in contrast to the results reported previously. However, in general, excellent agreement was found with previous investigations for the solubility constant of NiO in acidic solutions where Ni²⁺ is stable. At higher pH, the stable solution species is Ni(OH)₂⁰ and reasonable agreement was obtained with one previous study for the thermodynamic stability of this species. The first comprehensive set of results of the solubility of β-Ni(OH)_{2(cr)} is reported here.

1. Introduction

The study of the solubility of nickel oxides and hydroxides was undertaken in order to understand and quantify corrosion phenomena with the primary circuit of a PWR. The principal solubility equilibria considered previously for the example of NiO_(cr) are:



There were two major studies of the solubility of bunsenite, NiO_(cr), to high temperatures (≤ 300°C) in the 1980's [1,2]. These results tend to diverge at near neutral pH values where mainly Ni(OH)₂⁰_(aq) is dominant in solution above 150°C, which was also thought to be near the lower thermal stability limit of NiO_(cr). Tremaine and LeBlanc [1] reported solubility constants for equilibria (1-4), whereas the experiments of Ziemniak *et al.* [2] dealt with the pH region where equilibria (3,4) were believed to dominate. In the current study, despite the wide

range of pH investigated, only solubility constants for equilibria (1) and (3) could be extracted from the data. Nevertheless, the values for K_{s0} , Eq. (1), are in excellent agreement with those presented previously [1], whereas the values of K_{s2} , Eq. (3), are intermediate between those reported earlier [1,2]. However, the absence of any anionic Ni(II) species leads to markedly different predicted solubilities at high pH. There is a huge disparity of almost three orders of magnitude in the solubilities of β-Ni(OH)_{2(aq)} reported at 25°C over the last 77 years [3]. The most recent solubility study by Gamjäger *et al.* [3] provides some support for the present results. However, it will be shown that the results reported here for the first time in basic solutions provide an internally consistent model for the thermodynamic behavior of both nickel(II) phases as a function of temperature and pH.

2. Experimental Methods

Two flow-through cells and a hydrogen-electrode concentration cell (HECC) were used in this study as described sequentially in the following sub-section.

2.1. Experimental Apparatus For solubility measurements at temperatures of 25 and 50°C the NiO or Ni(OH)₂ crystals were contained in three PEEK (polyether ether ketone) chromatography columns (25 cm long x 7.5 mm in diameter) connected in series (total volume of oxide bed is 33 mL). The columns rested in a water bath at 25.0 or 50.0 (± 0.1)°C. All inlet, outlet and connecting lines were made of PEEK tubing. The outlet stream was received into a weighed polypropylene syringe into which, in most cases, a weighed amount of 0.2% ultrapure nitric acid had been added. The flow rate was varied in the initial series of experiments, but thereafter it was maintained at 0.02 mL·min⁻¹. The approximate residence time for the feed solution in the oxide bed was *ca.* 10 h at this flow rate. In those cases where the pH of the feed solution increased significantly in consecutive series of experiments, many days of flushing the columns, even at enhanced flow rates, were necessary to re-establish equilibrium at the lower nickel concentration. Note that due to the strong complexation of nickel(II) ions by ammonia at 25°C, other pH buffer systems were introduced in these experiments, namely, boric acid and monosodium/disodium phosphate.

The high-temperature flow-through apparatus was described previously [4] and essentially consisted of a packed cylindrical titanium reaction tube: internal diameter, 1.2 cm; length, 36 cm; internal volume, 41 mL. All wetted surfaces were platinum, titanium or PEEK. A preheater of platinum tubing was wound in a spiral around the reaction tube. Downstream from the outlet closure nut, a short section of 0.318 and 0.635 cm OD platinum/rhodium tubing was used to make a mixing chamber, which is located within the furnace. Dilute acid (nitric or hydrochloric) was pumped from a second HPLC pump through a 0.16 cm OD platinum outlet tube gold-welded into the side of chamber, thus acidifying the outlet stream at the experimental temperature and pressure and preventing precipitation of nickel(II) hydroxides as the saturated solution cools in the sampling line. Temperature stability was on the order of ± 0.2°C. Pressure stability was maintained at better than 0.1 MPa, at pressures ranging to at least 26 MPa. Feed solution flow rates of 0.3 mL·min⁻¹ were generally used after initial tests were made to establish the optimum flow rate. The differential pressure across the reactor was typically, 40 to 88 kPa under these conditions. The flow rate of 0.2% nitric acid was usually kept constant at 0.01 mL·min⁻¹, but was

increased when stronger basic feed solutions were used.

The use of a hydrogen-electrode concentration cell (HECC) obviates the need to control pH either by addition of excess acid or base, or through the use of pH buffering agents that might interact with the nickel species in solution to form nickel complexes which thereby enhance the solubility of NiO or Ni(OH)₂. Indeed, for this study at low temperatures especially, the former approach cannot be applied in acidic solutions as the solubility was too high, *i.e.*, virtually all the free acid is consumed by reaction (1). However, at high pH were hydrolysis ensues, reduction of the dissolved nickel by the prevailing hydrogen atmosphere became so acute as to render this method useless.

The design and function of the HECC have been recently described in Palmer *et al.* [5]. The test solution contained a suspension of NiO or Ni(OH)₂ (*ca.* 1 g of solid in *ca.* 65 mL of solution). The HECC was purged with a hydrogen/argon mixture (2,000 ppm H₂) at ambient temperature prior to placing the vessel in the thermostat filled with silicon oil for equilibration at temperature. After the purging process, the hydrogen/argon pressure was regulated to *ca.* 1 MPa at 25°C with higher initial pressures being employed for the low temperature equilibrations involving Ni(OH)₂. Temperature control was generally better than ± 0.05°C. Aliquots of the test solution were withdrawn through a platinum dip tube gold-welded to a porous platinum frit to prohibit particles entering the dip tube, as their presence may serve as seeds promoting precipitation during the sampling process. Samples were collected through a 0.2 µm PVDF syringe filter into preweighed polypropylene syringes containing a known mass of high purity 0.2% HNO₃. Due primarily to the relatively low partial pressure of hydrogen, experiments required several days to reach a stable potential reading. Two or sometimes more readings were taken at each starting temperature, usually about eight hours apart, whereupon the temperature was adjusted for overnight equilibration with samples then being taken each morning and evening at this new temperature. Note that for those experiments conducted later in the program at 100°C or less, the cell was first equilibrated at 100°C then cooled in subsequent steps, rather than initiating the experiments at lower temperatures, because this initial equilibration was found to be very slow

below 100°C, requiring additional purging with the H₂/Ar mixture. For experiments at 50°C or less, the cell was transferred to a water bath on a magnetic stirrer plate. The water bath was equipped with an immersion cooler that allowed the temperature to reach about 4°C when the temperature controller was turned off. In order to reach 0.3°C, the bath was filled with a water and ice slurry.

2.2. NiO and Ni(OH)₂ solids Well-crystallized nickel oxide was obtained commercially (Alfa Aesar, 99.998%, Aldrich Chemical Co., 99.99%) and in some experiments this material was used without further treatment, but in most cases it was first heated overnight twice in an air oven to 1,000°C to increase the average size of the crystals. The XRD pattern and SEM image of this recrystallized NiO clearly showed it to be pure, crystalline NiO. The surface area of the treated NiO as determined by BET (nitrogen) analysis was $(0.26 \pm 0.02) \text{ m}^2\cdot\text{g}^{-1}$. The nickel oxide recovered from the exit end of the high-temperature flow cell after the entire sampling series was completed was found to have a surface area of $(0.74 \pm 0.04) \text{ m}^2\cdot\text{g}^{-1}$. The XRD pattern of this material showed only NiO. This unusual increase in surface area could be attributable to the de-aggregation of the NiO crystal clusters over time. On the other hand, after washing the solid material recovered from the HECC experiments with water and drying under vacuum, the SEM images showed no appreciable de-aggregation, but did show clear evidence of dissolution pits on the crystal surfaces. The XRD pattern of the washed solid material reclaimed from the HECC experiment that was terminated at 0.3°C, which is well below the thermal stability range of the NiO starting material, showed that the major peaks corresponded to crystalline NiO with possibly a small occurrence of Ni(OH)₂. The measured solubility at this low temperature was substantially higher than that of Ni(OH)₂ obtained from independent HECC experiments, indicating quite logically that the NiO higher energy phase still controlled the equilibrium solubility. This is further evidence that the kinetics of transformation of the oxide and hydroxide phases are very sluggish at low temperatures.

Nickel hydroxide was obtained in very pure form commercially (Johnson Mathey, 99.995%), but only as ultra-fine, irregular-shaped particulates that exhibited characteristic broad XRD peaks. A method for the direct preparation of well-defined crystalline β-Ni(OH)₂ recently became available

from Gamsjäger *et al.* [3]. The SEM images of these crystals indicated that some fine-grained Ni(OH)₂ was present in the freshly prepared material. Therefore after packing it into the flow-through columns, acidic feed solutions were pumped in the reverse direction for many days to dissolve the fine particles at the exit end of the reactor in particular, before the flow was reversed and samples were taken. The BET (nitrogen) surface area was $(2.27 \pm 0.07) \text{ m}^2\cdot\text{g}^{-1}$.

The XRD pattern of solid Ni(OH)₂ recovered from the HECC after completion of an experiment begun at 100°C and completed at 0.5°C, over a period of eight days, including the initial 48 h at 100°C required for a stable potential reading indicated pure, crystalline β-Ni(OH)₂ with no phase changes having occurred during the experiment.

Based on private communication from Malcolm Rand (consultant, UK) using thermodynamic data for NiO [6] and older, less precise data for β-Ni(OH)₂ [7], a plot of the dehydration of β-Ni(OH)_{2(cr)} to yield NiO_(cr) and H₂O_(g) *versus* temperature in Kelvin gives a temperature for a zero energy change of 350K, or 77°C, which is considerably below the temperatures cited previously [1,2]. Despite the fact that the line in such a plot is steep, thereby compounding the uncertainties in the thermodynamic data for β-Ni(OH)₂, this is the preferred thermodynamic method for determining this transition temperature.

Nickel analyses were performed by the following techniques depending on the nickel concentration in the sample: atomic absorption in a graphite furnace (Perkin Elmer 4110ZL) or flame (Perkin Elmer 3110) spectrophotometer, an ICP (Thermo Jarrell Ash IRIS), or ICP-MS (Finnigan MAT ELEMENT two double focusing sector field (SF)-ICP-MS).

3. Results and Discussion

3.1. Solubility Results for NiO_(cr) In this work, pH_m refers to the log(*m*_H) values. For the HECC measurements in particular where a supporting electrolyte must be employed and hence the ionic strengths of the solutions are significant (typically 0.03 mol·kg⁻¹, but also 1.0 and 0.3 mol·kg⁻¹, sodium trifluoromethanesulfonate, NaF₃CSO₃) the water activities, *a*_w, and the activity coefficients of the aqueous species in Eqs. (1-4) must be estimated. As these activity coefficients are not known, the

standard substance approach based on $\text{NaCl}_{(\text{aq})}$ was used [8] with single ion activity coefficients, $\gamma_{\pm(\text{NaCl})}$, and a_w being calculated according to Archer [9]. For example, where Ni^{2+} is the dominant nickel-containing species in solution, the logarithm of the nickel molality at infinite dilution, $\log(m_{\text{Ni}}^\circ)$, is $\log(m_{\text{Ni}} \cdot \gamma_{\pm(\text{NaCl})}^4)$. The corresponding pH_m° value at infinite dilution is given by: $-\log(m_{\text{H}^+} \cdot \gamma_{\pm(\text{NaCl})})$. The activity coefficient of $\text{Ni}(\text{OH})_2^0_{(\text{aq})}$ is assumed to be unity.

The combined results for NiO solubility at 250°C are shown in Fig. 1 in terms of the logarithm of the infinite dilution m_{Ni}° values versus pH_m° . The three sets of independent data obtained with the HECC at different ionic strengths are in good agreement despite the simplicity of the activity coefficient model. Note that there is residual complexing of Ni^{2+} by ammonia that leads to higher solubilities. At all temperatures investigated in this study, there was no evidence for increased solubility at high pH_m (the highest m_{OH^-} employed was $0.1 \text{ mol}\cdot\text{kg}^{-1}$). Therefore, **inclusion of the $\text{Ni}(\text{OH})_3^-$ species was not justified based on the results of this study.** Moreover, given the precision of all the results collected in this study, **inclusion of the $\text{Ni}(\text{OH})^+$ species could also not be justified.** Therefore, the solid curve in Fig. 1, referred to as “our fit”, is based only on Eqs. (1) and (3). However, agreement between this solubility curve and those of Tremaine and LeBlanc [1] and Ziemiak *et al.* [2] at 250°C is very good to pH_m° (250°C) *ca.* 9, noting that pK_w is 11.196 at 250°C [10].

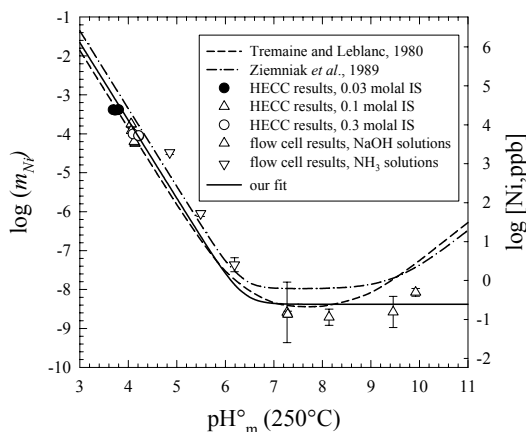


Fig. 1. Solubility of $\text{NiO}_{(\text{cr})}$ at infinite dilution versus pH_m° at 250°C.

The corresponding solubility data at 350°C are presented in Fig. 2 where only the high-temperature flow cell could be employed. Despite the three sets of data at $\text{pH} > 5.2$ obtained with ammonia as the pH buffer where the nickel concentration was abnormally low, the remaining results fit the aqueous speciation scheme described above for 250°C. Note that at 350°C the solubility of NiO in acidic solution is sufficiently low so as to allow excess $\text{F}_3\text{CSO}_3\text{H}$ to control the pH.

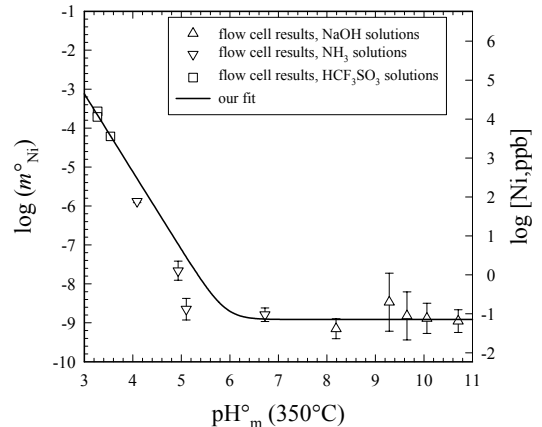


Fig. 2. Solubility of $\text{NiO}_{(\text{cr})}$ at infinite dilution versus pH_m° at 350°C.

3.2. Solubility Results for $\beta\text{-Ni}(\text{OH})_2(\text{cr})$ Although there are numerous studies reported in the literature of the solubility of this phase near ambient temperature in acidic solutions, there is only one recent report of the solubility of a well characterized, crystalline solid as a function of temperature (35 to 80°C) [3], and there are no reports of data at moderate to high pH.

Flow cell measurements were conducted in $\text{F}_3\text{CSO}_3\text{H}$, NaOH, borate and phosphate buffer solutions, whereas the HECC measurements were made in solutions containing $\text{F}_3\text{CSO}_3\text{H}$ in NaF_3CSO_3 at an ionic strength of $0.03 \text{ mol}\cdot\text{kg}^{-1}$, as described above for the analogous NiO solubility experiments.

Figure 3 shows the solubility profile at 25°C. It is clear from Fig. 3 that as dictated by thermodynamics, the same two aqueous species, Ni^{2+} and $\text{Ni}(\text{OH})_2^0$, are sufficient to fit the experimental data at 25°C. Figure 3 also shows that the fitted solubility curve, which is derived from a global fit of all the data as a function of temperature and pH_m , is higher than reported by Gamsjäger *et al.* [3], who worked at higher ionic strengths (1.0

mol·kg⁻¹, NaClO₄) and only down to 35°C, and Tremaine and LeBlanc [1] whose experimental results are extrapolated from 150°C and who, like Ziemiak *et al.* [2], did not isolate and characterize the solid phase.

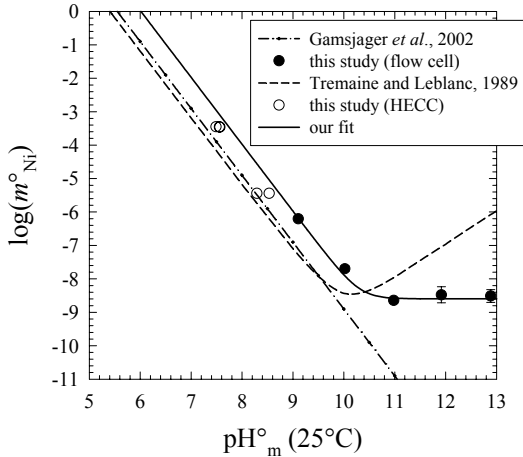


Fig. 3. Solubility of Ni(OH)_{2(cr)} at infinite dilution versus pH^o_m at 25°C.

Measurements of β-Ni(OH)_{2(cr)} solubility in acidic solution using mainly the HECC at low temperatures (due to far more rapid equilibration in this cell as compared to the flow cell) extended from 0.4 to 200°C. Some measurements were also made with a sample of β-Ni(OH)_{2(cr)} obtained from Gamsjäger and his co-workers. In dilute NaOH solutions, the low-temperature, flow-cell was used for solubility measurements from 25 to 80°C.

3.3. Combined Solubility Results for NiO_(cr) and β-Ni(OH)_{2(cr)} The solubility constant for the equilibrium represented in Eq. (1), K_{s0} , is illustrated in Fig. 4 for both nickel solid phases, although the experimental points for NiO_(cr) are not shown in order to provide a better visual image. Also the temperature range shown is limited to that investigated for the hydroxide solid, to provide better resolution. The dependence of $\log K_{s0}$ on reciprocal temperature (kelvin) for both phases is linear over this temperature range. The intersection point of these two lines is 75°C, in near perfect agreement with the calculated transition temperature (77°C). The results in Fig. 4 show that NiO_(cr) can exist metastably to 0°C for several days, which is the time required for equilibration in the HECC. Conversely, also in acidic solutions, β-

Ni(OH)_{2(cr)} can persist up to 200°C in the HECC for ca. 24 h.

The transition or dehydration temperature of β-Ni(OH)_{2(cr)} to NiO_(cr) must be independent of pH, so that the intersection of the curves for $\log K_{s2}$ (corresponding to the solubility constant for the equilibrium in Eq. (3)) should also be at 75°C. This final affirmation is provided in Fig. 5.

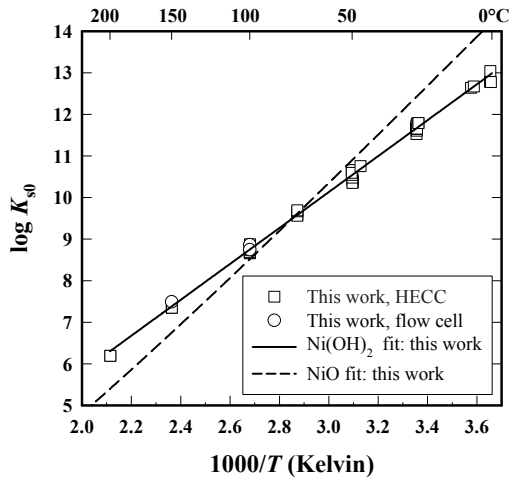


Fig. 4. Dependence $\log K_{s0}$ on reciprocal temperature (Kelvin) for NiO_(cr) and β-Ni(OH)_{2(cr)}.

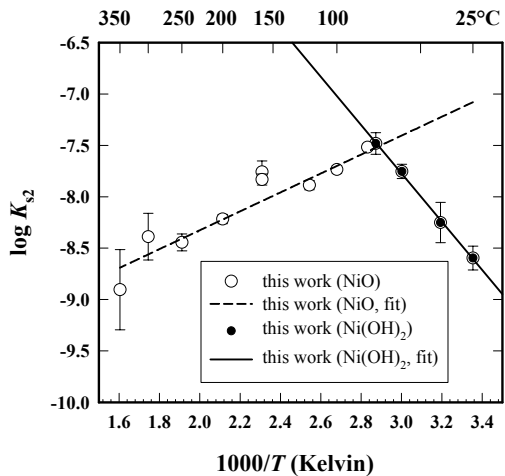


Fig. 5. Dependence $\log K_{s2}$ on reciprocal temperature (Kelvin) for NiO_(cr) and β-Ni(OH)_{2(cr)}.

Therefore, this broad-based experimental study which extends to higher temperatures than previously attained, with applications to

dissolution/precipitation processes near the fuel rods in the primary circuit of a PWR, provides a consistent thermodynamic model of nickel(II) behavior. Moreover, the results for NiO_(cr) are consistent with those obtained in the two previous pioneering studies to 300°C up to moderately high pH.

Acknowledgements

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