

Nickel hydroxide ageing time influence on its solubility in water acidified with sulphuric acid

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Abstract

Nickel hydroxide samples freshly settled as well as stored over 1 month, 2 months and 6.5 years were examined for their solubility rate in diluted H₂SO₄ solutions of pH 1.9 and 2.8 as a function of time. Samples with a longer ageing history dissolved less readily than freshly settled ones. It was determined that the resistance to dissolving rose with sample ageing time and the solubility of the 6.5 years stored sample was particularly low. X-ray examination evidenced that during storage the crystallinity of Ni(OH)₂ subsequently rose. The parallelity of both time-dependent phenomena allows the conclusion that with nickel hydroxide ageing the transformation of disordered nickel hydroxide species into crystalline Ni(OH)₂ (without phase changes) is responsible for increasing nickel hydroxide resistance to dissolving in acidic solutions. Such decrease of nickel hydroxide solubility with ageing in case of waste nickel hydroxide, is worth to notice in a view of environment protection against pollution with electroplating waste.

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1. Introduction

Waste electroplating sludge due to high concentrations of heavy metals is highly dangerous to dispose of in landfills without careful protection against metals leaching into the ground. Usually, stabilization and solidification [1–3] are considered as effective methods in such protection. Sometimes electroplating sludge, which contains mainly metal hydroxides, is utilised by admixing it to ceramic building materials, e.g. to roof tiles [4] and bricks [5] or to concrete used in the production of foundation blocks, wall and floor tiles, pavement slabs and other wares for building purposes [6–8]. Such admixture to building wares is permitted in Poland (excluding buildings for human habitation) under the condition that the total concentration of heavy metals in water leachate obtained during 48 h stirring at a water-to-sample mass ratio 10:1 does not exceed 10 mg/dm³ [9].

Having in mind the eventual ecological consequences of such electroplating waste sludge admixing to building materials, a number of metal leaching examinations were

performed with ceramics which were prepared with admixtures of metal hydroxides, such as copper [10], chromium [11,12], iron [13] and nickel hydroxides [14] as well as with their mixtures [15]. As the environmental pollution danger from such admixtures greatly depends on their leaching, the examination of particular metal hydroxides solubility is the important factor worth examining due to ecological views. The metal hydroxide ageing time influence on its solubility and the eventual reasons of such influence are of particular interest.

Recent investigations were conducted with nickel hydroxide precipitate. Its solubility in neutral water is highly dependent on a solution pH with a minimum value of pH 10, at which it falls to 10⁻³ mg/dm³ [16]. In order to obtain more precise measurable nickel ion concentrations, the solubility measurements undertaken in this work, were performed in an acidic medium, using stoichiometric amounts of Ni(OH)₂ and H₂SO₄, where the initial pH of the acid solution in one series was diluted to provide pH 1.9 and in the second – 2.8.¹ The presented investigations were carried out with

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¹ Such moderate pH values were chosen to provide the limited dissolving rate and to disclose the related differences as a function of time.

nickel hydroxide samples: freshly settled, stored over 1 and 2 months as well as 6.5 years.

Among the nickel(II) hydroxide forms, two types of layered-structure forms are distinguished: α and β . Disordered α -Ni(OH)₂ with a variable excess of intersheet water represent a primary precipitate product of poor crystallinity with amorphous phase features. It covers a great variety of hydroxide species ranging from hydrated turbostratic hydroxide proposed by Le Bihan et al. [17] to a wide set of non-stoichiometric intermediate compounds. The “well crystallised” β -Ni(OH)₂ consists of hexagonal plate-like structures with adsorbed foreign ions and water [18] and is isostructural with brucite. It can be obtained by ageing α -type hydroxides [19].

2. Experimental

2.1. Analytical methods

Nickel concentration in leachate was determined with the atomic absorption spectrometry method (AAS) at a wavelength $\lambda = 232.0$ nm. The method was experimentally evaluated to be of a confidence interval of two standard deviations ($\alpha = 0.95$) for the midpoint of the calibration curve $\pm 1.1\%$ of the measured value 10 mg/dm^3 and $\pm 2.3\%$ for a maximum point of 20 mg/dm^3 . The detectable level of nickel by this method was 0.025 mg/dm^3 .

3. Wide angle X-ray diffraction scattering (WAXS) examination

To determine the crystallinity of particular nickel hydroxide samples, the investigations were performed by X-ray pattern evaluation, using horizontal diffractometer TUR M-62 mated with a computer control. The examinations were performed by the WAXS method with the CuK α radiation at a wavelength of 1.5418 \AA and nickel filtering. The following measurement parameters were used: tension 30 kV; anodic current 25 mA; angle range 2θ : 3° – 60° ; counting step (2θ): 0.04° ; counting time: 6 s; with remaining standard parameters. The identification was performed by a comparative method, using standard X-ray patterns and the computer program X-RAYAN [20].

3.1. Sample preparation

Nickel hydroxide samples were prepared in separate flasks by dissolving 12.8182 g (first series) or 1.2818 g (second series) of nickel chloride (NiCl₂·6H₂O) in 150 cm^3 of distilled water and by adding dropwise 10% solution of NaOH until pH 11 was attained. Hence, each flask of the first series contained 5 g, while each one of the second series contained 0.5 g of nickel hydroxide.

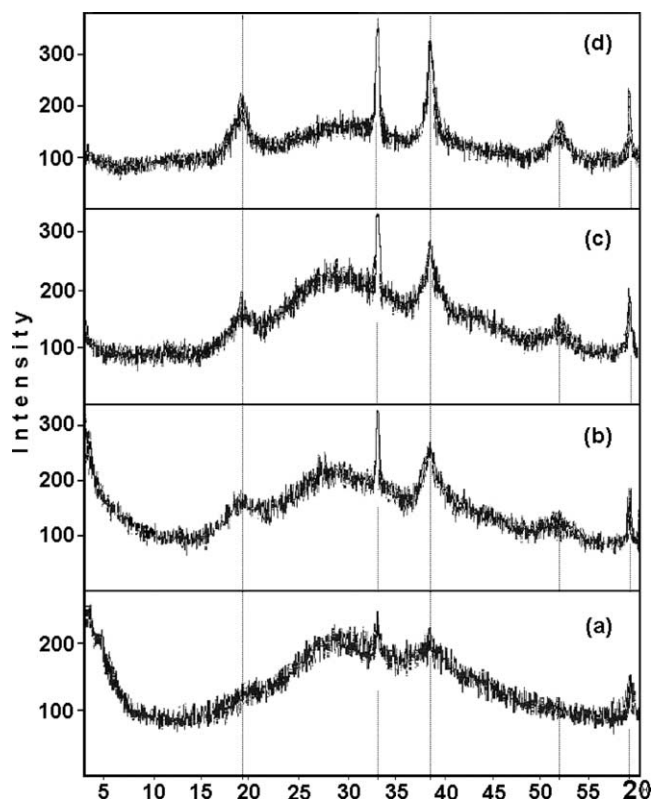


Fig. 1. X-ray patterns of Ni(OH)₂: (a) freshly settled; (b) after 1 month storage; (c) after 2 months storage; (d) after 3.3 years storage.

Samples with such prepared nickel hydroxide suspensions were used for further examinations either at once (freshly settled nickel hydroxide) or after storage over the mentioned time periods.

The resultant samples were examined for crystallinity² and solubility: (a) freshly settled and investigated the same day (without storage); (b) after 1 month; (c) after 2 months; (d) after 3.3 years storage (for X-ray examinations) and (e) after 6.5 years storage (for solubility examinations).

4. Results

4.1. X-ray examinations

The X-ray patterns of each sample are presented in Fig. 1. The examination of freshly settled and wet Ni(OH)₂ (sample a) evidenced that apart from an disordered Ni(OH)₂ form, already some hours following precipitation, the X-ray pattern facilitates the detection of diffraction maxima which originate from the crystalline structure of Ni(OH)₂. Especially distinct maxima appeared at the angles $2\theta = 33.0^\circ$, 38.5° and 59.0° . After one month storage (at ambient temperature) the share of the crystalline Ni(OH)₂ phase increased as

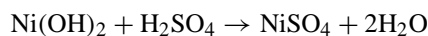
² X-ray examinations were performed with nickel hydroxide samples stored in a wet state.

all said characteristic maxima of crystalline form of nickel hydroxide were shaped more distinctly and additional characteristic reflexes occurred at the angles 2θ : 19.3° and 52.0° (sample b). After 2 months storage in similar conditions the share of crystalline $\text{Ni}(\text{OH})_2$ forms increased even more significantly (sample c), especially if compared with the X-ray pattern of sample a. The examination of sample d, stored wet over 3.3 years (40 months), revealed a further increase in distinctly shaped reflexes pertinent to crystalline form of $\text{Ni}(\text{OH})_2$. It was evidenced that during ageing, water molecules housed between layered sheets of freshly settled $\text{Ni}(\text{OH})_2$ [18] leave the intersheet layer, resulting in more compact structure. This in turn implies the secondary consequences, such as increase of nickel hydroxide specific gravity and decrease of its specific surface. It should be emphasised however that particular X-ray patterns demonstrate the increasing crystallinity, while the polymorphic changes were not observed (phase remains the same, i.e. the theoprasite [20]).

To determine what influence such changes of crystallinity exert on nickel hydroxide leaching, the solubility trials with differently aged $\text{Ni}(\text{OH})_2$ were undertaken. For a more distinct differentiation of solubility results, the leaching trials were performed in water acidified with sulphuric acid in the first series to pH 1.9 and in the second one to pH 2.8.

5. Leaching trials

Trials were performed with two series of differently stored nickel hydroxide samples. The sulphuric acid amount used for dissolving trials was stoichiometric to each nickel hydroxide sample according to the reaction:



however, being diluted in the first series to pH 1.9 and in the second one to pH 2.8. The initially adjusted portions of nickel hydroxide (5.0 and 0.5 g) and adequate stoichiometric amounts of sulphuric acid, allowed to prepare sufficient volumes of solutions to provide a greater number of analytical samples to be withdrawn as a function of time.

Before nickel hydroxide samples were mixed with acidified dissolving water, the surplus amount of storage-water was drained off through filter paper. Then each sample was introduced into a diluted H_2SO_4 solution volume together with a drain-off filter. The suspension was intensively stirred with a magnetic stirrer taking pH readouts during first half hour every 2 min, during the second half hour every 5 min and next every 10 and 30 min. The simultaneously withdrawn suspension aliquots were centrifuged during 1 min. at 6000 rpm and concentration of dissolved Ni^{2+} was determined in supernatant solution after additional filtration through the paper filter (the experimental points of solubility trials shown in figures represent the mean values obtained with five identically stored samples). Besides samples stored over 1 and 2 months, the solubility of samples stored over 78 months (6.5 years) was also examined within both series of solubility trials. Solubility decrease with sample ageing time is distinctly seen when compared to shortly aged samples with those aged over 6.5 years.

The nickel hydroxide dissolving course in diluted H_2SO_4 solution of pH 1.9 was displayed in percents of dissolved Ni^{2+} amount with respect to total nickel content introduced with nickel hydroxide precipitate (Fig. 2). In parallel the pH readouts of suspension during 300 min are shown in Fig. 3.

Similarly, the share (%) of dissolved Ni^{2+} in diluted H_2SO_4 solution of pH 2.8 was displayed in Fig. 4 and changes of pH in Fig. 5.

As follows from Fig. 2, the freshly settled nickel hydroxide dissolved thoroughly in sulphuric acid solution of pH 1.9 after 50 min, the sample stored over one month, after 90 min

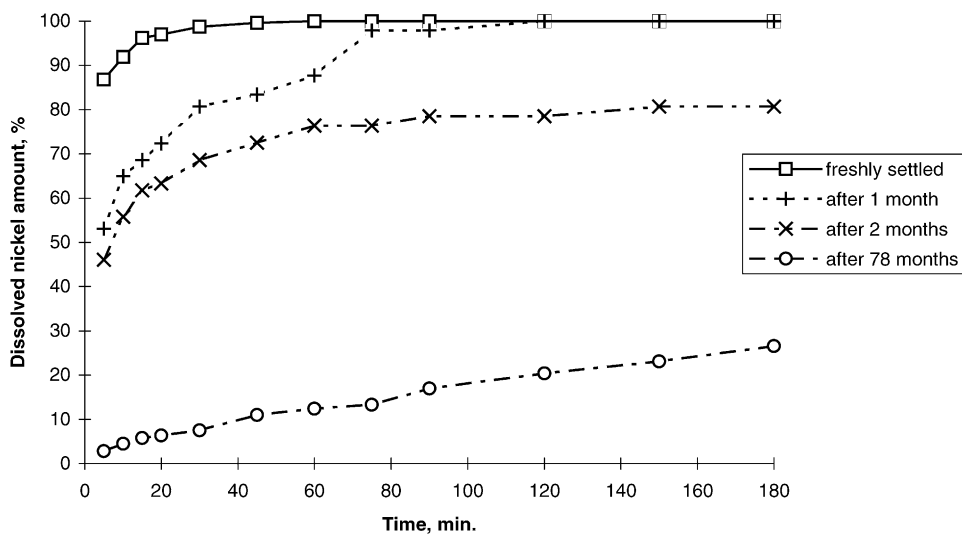


Fig. 2. The share of dissolved Ni^{2+} (%) in $\text{Ni}(\text{OH})_2$ suspension in water acidified to pH 1.9 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

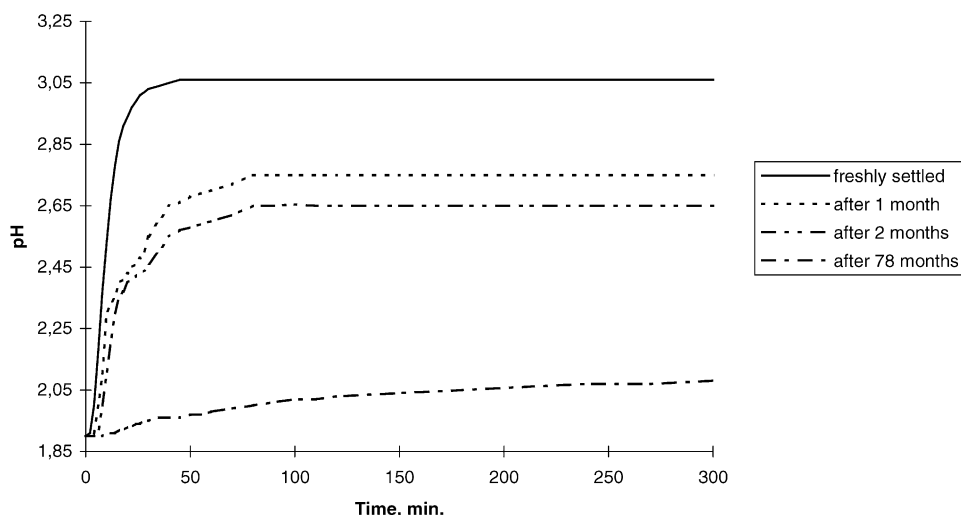


Fig. 3. pH changes in $\text{Ni}(\text{OH})_2$ suspension in water acidified to pH 1.9 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

and the sample stored over 2 months dissolved as much as approximately 81% after 180 min. The sample stored over 6.5 years dissolved as much as 27% after 180 min (and nearly thoroughly after 8 days). As follows from the pH changes (Fig. 3), the dissolving speed was greatest during the first 20 min (excluding the 6.5-year-old sample, where pH change was permanently slow).

The second series examination performed in a sulphuric acid solution of initial pH 2.8 displayed less steeply, however at the same sequence laid dissolving curves (Fig. 4). The freshly settled nickel hydroxide after 300 min dissolved as much as approximately 82%, the sample after 1 month storage—approximately 64% and the sample after 2 months storage—approximately 23%. The sample stored over 6.5 years after 300 min dissolved not more than 0.1%. Changes of pH were also much slower and its value remained nearly at

the same value for the sample stored over 6.5 years (Fig. 5). It is natural to expect that depending on nickel hydroxide storage time (as a matter of fact—its crystallinity), its dissolving rate (at the constant temperature) is controlled by pH and by nickel ions concentration in surrounding solution, i.e. by its unsaturation level with respect to nickel hydroxide of particular development of crystallinity. The comparison of Fig. 2 and Fig. 3 (as well as Fig. 4 and Fig. 5) shows the mutual relation between the both said parameters, especially with respect to nickel hydroxide samples of the shorter age of storage. Nevertheless, considering said figures it is worth to notice that dissolving rate of the higher crystallinity 6.5 years aged $\text{Ni}(\text{OH})_2$ sample is extremely low and pH influence seems to be significantly limited. It is logical to expect that decreased specific surface of aged nickel hydroxide additionally contributes to decreasing of its dissolving rate.

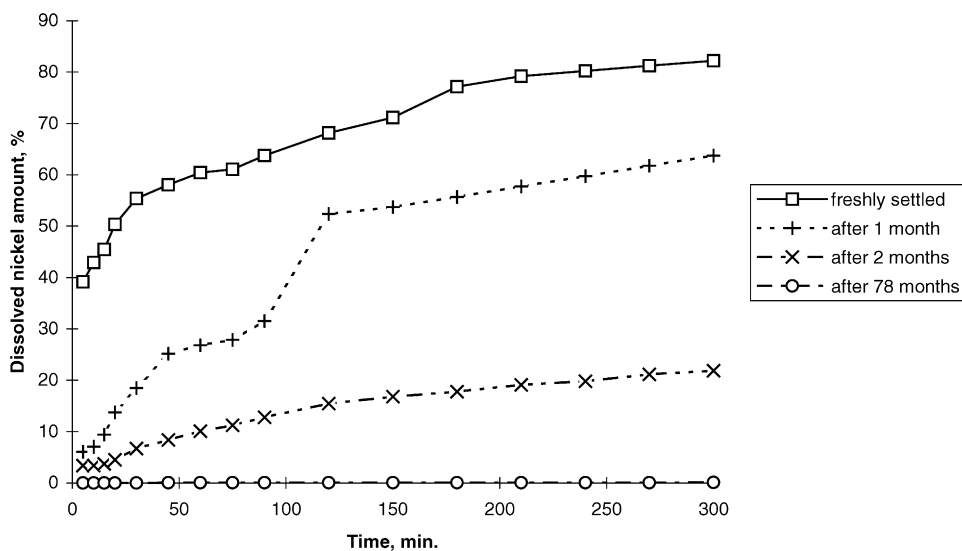


Fig. 4. The share of dissolved Ni^{2+} (%) in $\text{Ni}(\text{OH})_2$ suspension in water acidified to pH 2.8 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

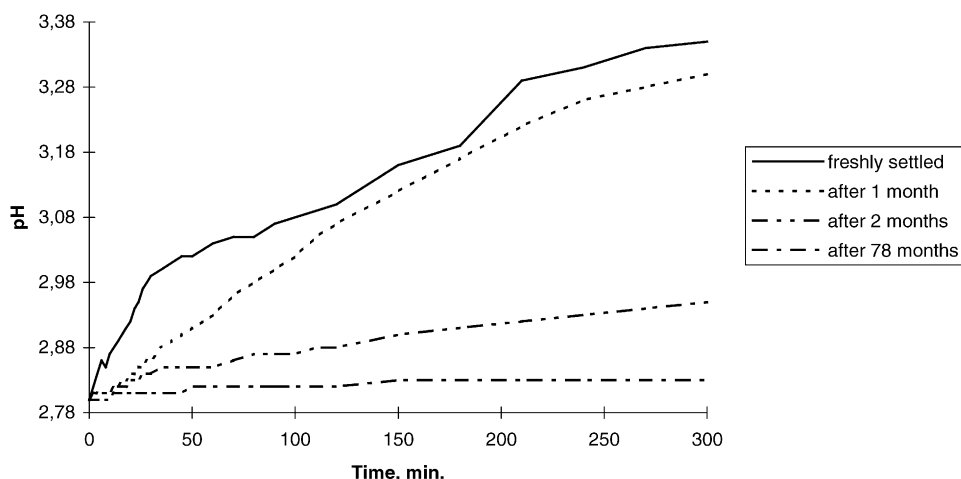


Fig. 5. pH changes in $\text{Ni}(\text{OH})_2$ suspension in water acidified to pH 2.8 as a function of time for nickel hydroxide species: freshly settled, stored during 1, 2 and 78 months (6.5 years).

However, the decrease in specific surface is only a secondary cause for reduction in the observed dissolution rate, while the main cause is the increase in $\text{Ni}(\text{OH})_2$ crystallinity.

6. Conclusions

If the dissolving results are compared with the X-ray pattern data, the conclusion follows that high solubility of freshly settled $\text{Ni}(\text{OH})_2$ is caused by its low crystallinity which favours the easy access of acid solution to irregularly arranged nickel hydroxide molecules. With $\text{Ni}(\text{OH})_2$ crystallinity rising during storage, the dissolving readiness decreases and this is in line with the known dependence between the crystallinity of the substance and its solubility. The leaching trials performed in acidic media (pH 1.9 and pH 2.8) demonstrated the significant decrease of aged $\text{Ni}(\text{OH})_2$ solubility rate and the conclusion can be drawn that the rate of dissolving in neutral water (ground and rain water) and even in mildly acidic acid-rain water conditions will be of even lesser value. As during ageing the nickel hydroxide crystallinity rises and its solubility decreases, it follows that long-term storage of waste nickel hydroxide (e.g. of electroplating origin) should reduce the danger of environment pollution with nickel ions.

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