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Experimental study by online measurement of the precipitation of nickel hydroxide: Effects of operating conditions[☆]

Weiwei E¹, Jingcai Cheng^{1,2,*}, Chao Yang^{1,2,*}, Zaisha Mao¹¹ Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China² Jiangsu Marine Resources Development Research Institute, Lianyungang 222005, China

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ABSTRACT

The objective of this work is using the online measurement method to study the process of precipitation of nickel hydroxide in a single-feed semi-batch stirred reactor with an internal diameter of $D = 240$ mm. The effects of impeller speed, impeller type, impeller diameter and feed location on the mean particle size d_{43} and particle size distribution (PSD) were investigated. d_{43} and PSD were measured online using a Malvern Insittec Liquid Process Sizer every 20 s. It was found that d_{43} varied between 13 μm and 26 μm under different operating conditions, and it decreased with increasing impeller diameter. When feeding at the off-bottom distance of $D/2$ under lower impeller speeds, d_{43} was significantly smaller than that at $D/3$. PSDs were slightly influenced by operating conditions.

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1. Introduction

As an important industrial unit operation, precipitation or reactive crystallization of sparingly soluble salts is widely used to produce fine and bulk chemicals, pharmaceuticals, biochemicals, catalysts, pigments, ceramics, etc. [1–5]. During the precipitation, a solution of reactant is mixed with another in a reactor [6], and the precipitation product is formed by a chemical reaction followed by nucleation and crystal growth [7,8]. In most cases, the chemical reaction is fast, or even quasi-instantaneous, and the particle size distribution (PSD) and the mean particle size (d_{43}) are influenced strongly by mixing conditions, which control the rate of instantaneous chemical reactions and influence the distribution of supersaturation in the system. Precipitation has been attracting much attention in research and development.

Barium sulfate precipitation from an aqueous solution is probably one of the most extensively researched test reactions. However, the results are not entirely consistent. In semi-batch tanks, Tosun [9] found that feeding two reactant solutions simultaneously produced larger crystals than feeding one reactant to a stirred solution of the other. In

double-feed semi-batch precipitation of BaSO_4 with a propeller agitator, Angehöfer [10] found that smaller particles were obtained when the feed pipes were near the impeller. By studying benzoic acid precipitation as the model system, Åslund and Rasmuson [11] found that under low impeller speeds, feeding near the free surface produced smaller particles compared to feeding near the impeller. However, under higher impeller speeds, this trend was reversed. They also investigated the effect of impeller type on d_{43} . Larger particles were produced with a three-blade marine-type propeller compared to those with a six-blade Rushton turbine. The reason was that at an equal stirring speed, the mean power input of the Rushton impeller was higher than that of the propeller.

However, few studies have been performed on the precipitation of nickel hydroxide. As the main active material for the positive electrode in rechargeable batteries [12–18], it is of great significance to investigate the relationship between electrical performances and the physical characteristics of nickel hydroxide particles, such as size, PSD and morphology. Now, most studies on nickel hydroxide are focused on using different synthetic methods, like using cobalt and other metals as the additive etc., to test its electrode performances [19–24]. For example, Guan and Deng [25] found that the charge–discharge process can take place more easily and more reversibly on the $\text{Ni}(\text{OH})_2$ electrodes prepared with nanometer spherical particles than that with micrometer ones. Nickel hydroxide with a small crystallite size shows a high proton diffusion coefficient, giving excellent electrochemical performance. A narrower PSD can improve the reversibility of electrode reaction [26].

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* Corresponding authors.

E-mail addresses: jcheng@ipe.ac.cn (J. Cheng), chaoyang@ipe.ac.cn (C. Yang).

Watanabe and Kikuoka [27] proposed that nickel hydroxide of small size showed better charge–discharge behavior due to its faster proton diffusion. 3D nanostructure with ravine-like surfaces provides an extremely large surface compared to the smooth crystalline surface, and thus promotes the electrical conductivity of the electrodes [28]. Sphere-like morphology has been proved to present better electronic behavior, such as higher capacities. Fish-like particles demonstrate improved electrochemical properties with the increase of cycling times [29]. From the literature survey, we can draw a conclusion that nickel hydroxide particles with small size, narrow distribution and sphere-like morphology behave better electronically. Effective charging of Ni(OH)₂ electrode to obtain maximum capacity depends on particle size, morphology and PSD. Although the precipitation process plays such an essential role in determining these characteristics, few works on nickel hydroxide investigate the effect of operation conditions on the precipitation process. Therefore, such a study is conducted to better understand the precipitation process of nickel hydroxide.

In view of the complicated complexation–precipitation system of Ni(OH)₂ (ammonium as a complexation reagent involved) with a high reagent concentration and therefore the extremely high particle number density in slurry, this work aims at investigating the effect of mixing conditions on the PSD and d_{43} in a single-feed semi-batch precipitation of nickel hydroxide using an online measurement technique. Online measurement is more accurate and reliable than by offline procedures, which take a long while so that considerable changes in the sample would occur, and may give misleading d_{43} and PSD information. Moreover, the measured transient PSD data could be used for determination of crystallization kinetics through some mathematical methods.

2. Experimental

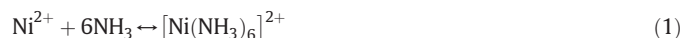
2.1. Experimental setup

A schematic of the experimental setup is shown in Fig. 1. Precipitation experiments were carried out in a 14 L, flat-bottomed, airtight, transparent cylindrical tank, which has a diameter of $D = 0.24$ m and height of $H = 1.3D$, equipped with four equally spaced wall baffles. A digital stirrer engine was used to drive the turbine. Two different types of turbine investigated are shown in Fig. 2. One is a standard Rushton turbine, and the other is a down-pumping 45° six-pitched-blade turbine (PBT). Both have the same diameter $D_i = D/3$ and impeller off-bottom clearance $C = D/3$. The feed of NaOH entered through a stainless steel tube with 4.8 mm ID inserted vertically into the tank from the top. The steel feeding nozzle was placed 50 mm off the tank

centerline, midway between two baffles, and its off-bottom distance is either $C_A = D/2$ or $C_B = D/3$.

2.2. Precipitation procedure

Ni(OH)₂ was synthesized via a complexation–precipitation route. The formation of Ni(OH)₂ in the present system can be expressed by the following reactions:



On one hand, NH_4^+ and Ni^{2+} form Ni–NH₃ complexes, as indicated by Eq. (1). This reaction consumes Ni^{2+} , reduces the supersaturation of the system, and therefore slows down the generating speed of Ni(OH)₂ [30]. When the molar ratio of NH_4^+ and Ni^{2+} is below 0.2, Ni^{2+} will combine with OH^- directly, making the nucleation rate speeded and the growth of crystal obstructed. This will produce particles of poor sphericity or even amorphous ones, which will further affect its electrochemical properties [31]. On the other hand, if the ratio of these two ions is too high, for instance, $\text{NH}_4^+ : \text{Ni}^{2+} > 3$, the rate of growth would be greater than the nucleation rate. This is the main reason for the formation of large particles and agglomeration, leading to the reduction in battery capacity [32]. From our former study, comparing the reaction systems with and without ammonia, the reaction was more stable and slower with ammonia. Therefore, in this study, the ratio of NH_4^+ and Ni^{2+} was 1.5. And the concentration of $[\text{OH}^-]$ was assumed to be constant due to the constant feeding of NaOH. $[\text{Ni}(\text{NH}_3)_6]^{2+}$ was assumed to be formed since pH was higher than 8.4 in this reaction system [33].

All chemical reagents used were of analytical grade. Distilled water was used throughout the experiment. A NiSO₄ solution (6464 ml, $0.1 \text{ mol} \cdot \text{L}^{-1}$) was mixed with a NH₃ solution (72 ml, 25%, by mass) in the tank at first to form the Ni-complex solution. The precipitation reaction was conducted at constant temperature controlled by a thermostat water bath within ± 0.1 °C. Then, 6464 ml of $0.2 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution was added into the tank under continuous stirring within 30 min through a peristaltic pump running at a speed of $215.5 \text{ ml} \cdot \text{min}^{-1}$ to avoid backmixing [34]. When the total feeding time of 30 min was over, the liquid level rose to $1.2D$. Since d_{43} and PSD had no further change after the feeding process, we mainly discussed the first 30 min after the NaOH feeding begins. The pH value of the system was closely monitored by an precise online digital pH meter with the accuracy of ± 0.01 . Table 1 gives the experimental operating conditions in this work.

The d_{43} and PSD in the suspension were measured online continuously by a Malvern Insittec Liquid Process Sizer (LPS). The LPS was based on the laser diffraction technique and the PSD was calculated by using the Mie theory. Furthermore, the focusing lens of the LPS-100 mm Fourier lens, which had the measurement range of d_{43} from $0.1 \mu\text{m}$ to $200 \mu\text{m}$, was precise enough for this experiment. One of the most significant advantages of the LPS was the fully automated sampling, dilution and measurement, all in one done automatically as preprogrammed. Moreover, when the small but sufficient amount of sample was taken into LPS, it will be immediately and consistently diluted by running water, which suppressed the further nucleation, growth and aggregation after sampling. This system was capable of measuring and displaying full particle size distribution every second, ensuring the accuracy of d_{43} and PSD. Each sample was measured continuously for 15 s with a very high rate of acquisition.

In this study, about 2.5 ml of the suspension sample was withdrawn from the reaction mixture every 20 s and instantly transported to the cascade diluter. A sampling valve was driven by compressed air. The suspension was diluted at a predefined ratio continuously and then the sample was conveyed to the flow cell for measurement. The effect of dilution can be controlled through the transmission level with higher

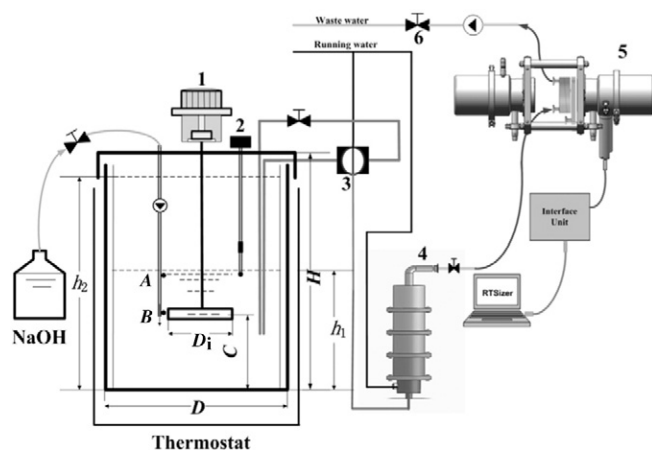


Fig. 1. Experimental setup. 1—stirrer; 2—pH meter; 3—sampling valve; 4—cascade dilution; 5—Malvern Insittec; 6—peristaltic pump; A,B—feeding positions; $D_i = 80$ or 96 mm, $D = 240$ mm, $H = 312$ mm, initial liquid level $h_1 = D/2$, final liquid level $h_2 = 1.2D$, $C = 80$ mm.

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