Metastable Dissolution Regularity of Nd\textsuperscript{3+} in Na\textsubscript{2}CO\textsubscript{3} Solution and Mechanism

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ABSTRACT: The carbonate solution-dissolved rare earth showed some metastable chemical characteristics. In this paper, the systematic investigation of metastable dissolution regularity of Nd\textsuperscript{3+} in Na\textsubscript{2}CO\textsubscript{3} solution was carried out. The results showed that Nd\textsuperscript{3+} has an instantaneous saturated solubility in Na\textsubscript{2}CO\textsubscript{3} solution. When the amount of the dissolution Nd\textsuperscript{3+} did not reach the instantaneous saturated solubility, the solution was in a stable-state period. Once the concentration of Nd\textsuperscript{3+} exceeded the instantaneous saturated solubility, the solution was no longer in the metastable state and generated the neodymium double salt of carbonate precipitates rapidly. The molecular dynamics simulation of the solution in the metastable state was carried out. In high concentration Na\textsubscript{2}CO\textsubscript{3} solution, dissolved Nd\textsuperscript{3+} had a coordination reaction with the CO\textsubscript{3}\textsuperscript{2−}. Also, there was a stronger interaction between Na\textsuperscript{+} and CO\textsubscript{3}\textsuperscript{2−}, which caused the effective concentration of free CO\textsubscript{3}\textsuperscript{2−} which could react with Nd\textsuperscript{3+} to become lower. Thus, these reasons make the solution exhibit a metastable state. In that metastable period, the dissolved Nd\textsuperscript{3+} becomes steady and hard to generate the neodymium double salt of carbonate precipitates.

1. INTRODUCTION

A large amount of ammonia-nitrogen or high salinity wastewater is generated by using the traditional rare-earth separation methods, such as solvent extraction and ion exchange, which has been causing trouble to the healthy development of the rare-earth industry. Some new rare-earth separation methods, such as the nonsaponification, saponified, coordination extraction, and ionic liquid extraction, have some effects, but they are costly and difficult to resolve wastewater problems. Hence, it is necessary to develop a new, green, higher efficiency, and low-cost separation method for rare earth.

Rare-earth carbonate, the solubility of which is lower than 10\textsuperscript{-5} to 10\textsuperscript{-7} mol·L\textsuperscript{-1} in water, is a substance difficult to dissolve. However, when the rare-earth salt solution was added at the high concentrated carbonate solution, the rare earth could be dissolved in the carbonate solution. The solubility of the rare earth did not decrease with the increase of the concentration of carbonate but increased. During the precipitation process of rare-earth carbonate in industry, the dissolution of rare earth caused the higher rare-earth residual concentration and brought about the unnecessary waste of rare-earth resource. However, on the other hand, the concentration of rare earth in carbonate solution increased regularly with the increase of the rare-earth atomic number. This may provide an idea for a new rare-earth separation method.

Since 1963, the ability of rare earth to dissolve into potassium carbonate solution was noted and investigated first by Taketatsu.9,10 The rare-earth cations reacted with carbonate anions and generated rare-earth carbonate precipitates at first, but as the vibration and reaction time prolonged, it was dissolved again. In addition, the dissolution concentration of rare earth increased with the increase of potassium carbonate concentration and atomic number of the rare earth. Afterward, a series of studies confirmed the dissolution of rare earth obtained by Taketatsu, not only in potassium carbonate solution. For instance, De Vasconcellos et al. chose ammonium carbonate solution to dissolve rare earth and obtained the same fruitage with Taketatsu. The dissolution amount of rare earth also increased with the increase of the concentration of ammonium carbonate and rare-earth atomic number. Nevertheless, from the viewpoint of the precipitation yield of rare earth, it could be clearly known that the yield of rare earth decreased with the increase of the dosage of the carbonate precipitator. Thus, it was another piece of evidence that the dissolution amount of rare earth increased with the increase of the concentration of carbonate in solution.

Moreover, the ionic strength of the carbonate solution could also affect the dissolution process of the rare earth. Rao et al. investigated the chemical balance behaviors of Nd\textsuperscript{3+} in the solution system of Na\textsuperscript{+}−Cl\textsuperscript{−}−CO\textsubscript{3}\textsuperscript{2−}−HCO\textsubscript{3}− and found that at the same concentration of sodium carbonate, the dissolution amount of rare earth was enhanced with the existence of impurity salt sodium chloride, compared to without sodium chloride. The higher the concentration of sodium chloride, the more is the amount of rare earth dissolved. De Vasconcellos et al. also noted that the higher concentration of impurity...
ammonium anions increased the dissolution amount of rare earth. In addition, according to Tang et al.’s result from the research on rare-earth adsorption in water-bearing sand layer, it could be found that increased ionic strength of the solution could cause weakening of the adsorption behavior of rare earth on the sand layer because of the increase of the dissolution amount of rare earth. Therefore, the ionic strength of the solution was another important determinant in dissolving rare earth.

Nevertheless, we discovered that the sodium carbonate solution which dissolved rare earth exhibited some unique metastable properties. It had a metastable state period, in which rare earth could steadily be dissolved into a carbonate solution, and did not generate the precipitates of rare-earth carbonate. However, over the period, the precipitate of rare-earth carbonate still formed. Nevertheless, the period could be artificially controlled by changing the ionic strength of carbonate solution via adjusting the condition of the circumstance of the solution or enhancing the concentration of carbonate, which could affect the dissolution process of rare earth.

Inspired by the differential solubility in carbonate solution of different rare-earth elements previously introduced, the artificial domination of the metastable state period may have the potential application and was feasibly utilized in rare-earth separation.

However, existing reports of the dissolution of rare earth in carbonate solution are mostly aimed at the chemical balance and rarely involved in rare-earth separation. As for the metastable state, carbonate solution which dissolved rare earth was basically lacking. To investigate the regularity of the metastable state and provide a reference for the development of new rare-earth separation methods, in this paper, the neodymium was selected as the representative for rare-earth elements and metastable dissolution regularity of Nd³⁺ in Na₂CO₃ solution was systematically investigated. The research on the interaction between various ions in solution was performed using molecular dynamics (MD) simulation.

2. RESULTS AND DISCUSSIONS

2.1. Metastable Dissolution Regularity of Nd³⁺ in Na₂CO₃ Solution. 2.1.1. Determination of Instantaneous Saturated Solubility of Nd³⁺. The results showed that when the NdCl₃ solution was added into Na₂CO₃ solution, flocculent precipitates were formed first and were then dissolved again with vigorous shaking. At this time, the solution was in a clean state. It means that the Nd³⁺ completely dissolved in Na₂CO₃ solution.

From Figure 1, we can see that there existed the maximum solubility point, the solution was no longer clear, and a part of Nd³⁺ dissolved in the solution began to precipitate. Moreover, we also observed that the solubility of Nd³⁺ in Na₂CO₃ solution was not stable, and it would decrease within a few minutes. As shown in Figure 1, the maximum solubilities of Nd³⁺ in Na₂CO₃ solutions of 1, 1.5, and 2 mol·L⁻¹ are 1.868, 1.911, and 2.450 g·L⁻¹, respectively. Compared to the solubility we had measured, the deviation was quite huge. Obviously, it was not the equilibrium concentration from the dissolution process of NaNd(CO₃)₂. Hence, the maximum solubility point was defined as instantaneous saturated solubility.

Furthermore, from the fitted result of the instantaneous saturated solubility of Nd³⁺ with Na₂CO₃ concentration in Figure 2, we could see that the solubility of Nd³⁺ increased with the increase of Na₂CO₃ concentration in the solution, and it approached a significant linear relationship $y = -1.18877 + 2.38043x$ because the $R^2$ was 0.99992.

2.1.2. Dissolution of Nd³⁺ with Time. In order to evaluate the dissolution of Nd³⁺ with time in Na₂CO₃ solution, two

Figure 1. Instantaneous saturated solubility of Nd³⁺ under the experimental condition, the concentration of sodium carbonate was 1, 1.5, and 2 mol·L⁻¹ and the activity coefficient of sodium carbonate was calculated to be 0.236, 0.205, and 0.188 via Pitzer theory, respectively. Then, the corresponding concentration of Nd³⁺ in equilibrium was evaluated, and it should be $1.563 \times 10^{-19}$, $1.911 \times 10^{-19}$, and $2.450 \times 10^{-19}$ g·L⁻¹.

2.2. Potential of Metastable State in Rare-Earth Separation. In addition, according to Tang et al. research on rare-earth adsorption in water-bearing sand layer, the carbonate solution which dissolved rare earth exhibited some unique metastable properties. It had a metastable state period, in which rare earth could steadily be dissolved into a carbonate solution, and did not generate the precipitates of rare-earth carbonate. However, over the period, the precipitate of rare-earth carbonate still formed.

Thus, the period could be artificially controlled by changing the ionic strength of carbonate solution via adjusting the condition of the circumstance of the solution or enhancing the concentration of carbonate, which could affect the dissolution process of rare earth.

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The generated precipitate was confirmed to be NaNd(CO₃)₂ (see Section 2.1.4 and the FTIR result in Figure 6). According to the solubility product of NaNd(CO₃)₂ ($\log K_{sp}$ was $-21.39$), for the reaction

$$NaNd(CO_3)_2 \rightarrow Na^+ + Nd^{3+} + 2CO_3^{2-}$$

Figure 2. Instantaneous saturated solubility variance with the concentration of CO₃²⁻.
experiments were carried out. In the first one, the initial dissolution concentration of Nd$^{3+}$ in Na$_2$CO$_3$ solution was controlled to be equal to the instantaneous saturated solubility of Nd$^{3+}$, which was 1.186, 2.394, and 3.566 g L$^{-1}$ in 1, 1.5, and 2 mol L$^{-1}$ Na$_2$CO$_3$ solution, respectively (the experiments are named “Nd$^{3+}$ saturated”). In the other one, the initial dissolution concentration of Nd$^{3+}$ was controlled to be lower than the solubility, which was 0.734, 1.362, and 2.621 g L$^{-1}$ in 1, 1.5, and 2 mol L$^{-1}$ Na$_2$CO$_3$ solution, respectively (the experiments are named “Nd$^{3+}$ unsaturated”).

As for Nd$^{3+}$ saturated dissolved in Na$_2$CO$_3$ solution, in the beginning, all the Na$_2$CO$_3$ solution dissolved Nd$^{3+}$ was in a clarification state, but the clarification period was truly short. The solution precipitated gradually at the bottom of the conical bottle as the standing time went on. From Figure 3, all the results illustrate that the Nd$^{3+}$ concentration of Na$_2$CO$_3$ solution of various concentrations showed a downward trend in the former 0–10 min stage. In addition, the decrease of the concentration of Nd$^{3+}$ was slightly slower in the first 0–120 min but became faster later. The reason may be that the precipitation and crystallization need a crystal core, and the core was under the forming and growing process initially. Later, the precipitation became faster because abundant cores had been generated in the static process.

The consequence concluded that the Nd$^{3+}$ saturated dissolved in Na$_2$CO$_3$ solution was not stable. However, it could also be admitted that the solution was basically not in the metastable state. Hence, the situation under this condition ought not to be investigated in the following studies.

As for the experiment of Nd$^{3+}$ unsaturated dissolved in Na$_2$CO$_3$ solution, the solution exhibited some metastable characteristics. The solution was clean, and the Nd$^{3+}$ was stable dissolved and did not precipitate with a period. As shown in Figure 4, in the first 90 min, the solution was in the period of the metastable state and the dissolution concentration of Nd$^{3+}$ was almost unchanged.

However, this metastable state still had a time limit that is called the metastable period. The solution began to precipitate slowly after the metastable period. For example, when the aging time was 120 min, the concentration of Nd$^{3+}$ in 1, 1.5, and 2 mol L$^{-1}$ Na$_2$CO$_3$ solution was 0.708, 1.329, and 2.610 g L$^{-1}$, respectively. Compared to the initial concentration, it was decreased slightly by only 3.47, 2.43, and 0.42%, but it was still a reduction, which indicates that in the solution over the metastable period, the self-precipitation occurred.

In addition, with the prolongation of the settling time, the concentration of Nd$^{3+}$ in the solution reduced increasingly. For instance, when the aging time reached 360 min, the corresponding concentration of Nd$^{3+}$ in 1, 1.5, and 2 mol L$^{-1}$ Na$_2$CO$_3$ solution was 0.580, 1.220, and 2.501 g L$^{-1}$, respectively. The decrease of the concentration of Nd$^{3+}$ was significant, and the reduction ratios were about 20.92, 10.43, and 4.58% approximately than the initial.

Compared with the previous instantaneous saturated data (see in Figure 3), it can be viewed in Figure 4 that when the dissolution Nd$^{3+}$ did not reach the corresponding instantaneous saturated solubility, the solutions with various concentrations of Na$_2$CO$_3$ all possessed a metastable period. At the same time, with the higher concentration of Na$_2$CO$_3$ solution, a longer metastable period was obtained. The solution metastable period in 1 mol L$^{-1}$ Na$_2$CO$_3$ solution was 90 min, but in 1.5 and 2 mol L$^{-1}$ Na$_2$CO$_3$ solution was 120 min. Moreover, the results could suggest that a higher concentration of Na$_2$CO$_3$ solution makes the dissolution concentration of Nd$^{3+}$ become higher. As shown in Figure 4, the dissolution concentration of Nd$^{3+}$ in 2 mol L$^{-1}$ Na$_2$CO$_3$ solution could reach 2.621 g L$^{-1}$ in the metastable period, but in 1.5 mol L$^{-1}$, the dissolution concentration of Nd$^{3+}$ in Na$_2$CO$_3$ solution was only 2.394 g L$^{-1}$.

2.1.3. Coordination Behavior of Nd$^{3+}$ in the Metastable Solution
The UV–vis full-wavelength scanning for the solution in a better metastable state, with 2.621 g L$^{-1}$ Nd$^{3+}$ in 2 mol L$^{-1}$ Na$_2$CO$_3$ solution, which did not reach instantaneous saturated solubility, was carried out. To provide experimental contrast, the solution not in the metastable state, with 3.566 g L$^{-1}$ Nd$^{3+}$ in 2 mol L$^{-1}$ Na$_2$CO$_3$ solution, which was equal to instantaneous saturated solubility, was also scanned. The results are presented in Figure 5.

From Figure 5, we could know whether the dissolution concentration of Nd$^{3+}$ in Na$_2$CO$_3$ solution was equal to or did not reach instantaneous saturated solubility; there were two
characteristic peaks of neodymium\textsuperscript{20} found in the spectra of samples at 340−370 nm, which were located at 349 and 357 nm. It is worth noting that the characteristic peaks of neodymium, which was obtained from those Na\textsubscript{2}CO\textsubscript{3} solutions that dissolved Nd\textsuperscript{3+}, were slightly red-shifted from 347 and 354 to 349 and 357 nm than the blank NdCl\textsubscript{3} solution. The reason was that the alkalinity of the solution dissolved Nd\textsuperscript{3+} was more than that of the blank NdCl\textsubscript{3} solution.

Also, there were two characteristic peaks of neodymium\textsuperscript{20} at the wavelengths 524 and 575 nm in all the samples. It should be noticed that the spectra of the samples of solution dissolved Nd\textsuperscript{3+} showed a new stronger characteristic peak at 583 nm, but it could not be found in the spectra of the blank sample. Thus, the dissolution Nd\textsuperscript{3+} in Na\textsubscript{2}CO\textsubscript{3} solution has a significant coordination reaction with CO\textsubscript{3}\textsuperscript{2−}.

By referring to the results of Vercouter and Vitorge's\textsuperscript{21} studies on the equilibrium steady-state dissolution of rare earth in carbonate solution, we can know that Nd\textsuperscript{3+} could dissolve in high concentration Na\textsubscript{2}CO\textsubscript{3} solution because the coordination reaction occurred between neodymium and CO\textsubscript{3}\textsuperscript{2−} forms of the complex ions like Nd\textsubscript{n}(CO\textsubscript{3})\textsubscript{m}\textsuperscript{3n−2m}. Therefore, it can be further guessed that the existence of a metastable state in Na\textsubscript{2}CO\textsubscript{3} solution was probably due to the complex coordination between neodymium and CO\textsubscript{3}\textsuperscript{2−}, which causes the dissolution Nd\textsuperscript{3+} to not precipitate immediately.

2.1.4. Characterization of Precipitates. During the typical aging period, the precipitates formed from a metastable state, in which 2.621 g·L\textsuperscript{−1} Nd\textsuperscript{3+} (not reached instantaneously saturated) dissolved in 2 mol·L\textsuperscript{−1} Na\textsubscript{2}CO\textsubscript{3} solution, were collected as samples and detected by Fourier transform infrared (FTIR). To provide experimental contrast, the precipitates, that were generated from the solution with 3.566 g·L\textsuperscript{−1} Nd\textsuperscript{3+} (was equaled instantaneously saturated) dissolved in 2 mol·L\textsuperscript{−1} Na\textsubscript{2}CO\textsubscript{3} solution, were also collected and detected. The results are presented in Figure 6.

Figure 5. UV−vis spectrum of the solution (a) saturated and (b) unsaturated.

Figure 6. FTIR results of solid precipitates of neodymium (a) saturated and (b) unsaturated.

From Figure 6, the FTIR spectra of precipitates show that the characteristic infrared peaks were consistent with the solid phase of blank sample NaNd(CO\textsubscript{3})\textsubscript{2}, regardless of whether the initial dissolution concentration of Nd\textsuperscript{3+} in the solution was equal to or did not reach instantaneous saturated solubility.

The results were also in agreement with the study of the equilibrium steady-state solubility of rare earth in carbonate solution by Rao\textsuperscript{15,22} et al.; that is, under the high concentration of CO\textsubscript{3}\textsuperscript{2−} solution environment, the stable solid phase in the solution was only the complex salt NaNd(CO\textsubscript{3})\textsubscript{2} and Nd\textsubscript{2}(CO\textsubscript{3})\textsubscript{3} almost did not exist.
2.2. Simulation of the Mechanism of the Metastable State. 2.2.1. Establishment and Optimization of Metastable Solution Models. Although the UV–vis full-wavelength scanning results of the above solution samples can qualitatively explain the dissolution behavior of Nd$^{3+}$ in Na$_2$CO$_3$ solution, and combined with the previous literature, it can also prove that Nd$^{3+}$ in metastable solution did coordinate with CO$_3^{2−}$, the results cannot fully explain the essence of the existence of a metastable state.

To explore the mechanism of the metastable state, the simulation processes of the solution in a better metastable state, with 2.621 g·L$^{-1}$ Nd$^{3+}$ in 2 mol·L$^{-1}$ Na$_2$CO$_3$ solution, which did not reach instantaneous saturated solubility, were carried out by MD calculation using the software Materials Studio. The blank Na$_2$CO$_3$ solution only added water, and the solution that is not in the metastable state, with 3.566 g·L$^{-1}$ Nd$^{3+}$ in 2 mol·L$^{-1}$ Na$_2$CO$_3$ solution, which was equal to instantaneous saturated solubility, was also simulated. All the solution establishment parameters are listed in Table 1.

The established solution model after geometry optimization is shown in Figure 7.

The energy changing of the solution model is shown in Figure 8. According to that, we could know that in the optimization process, the overall energy of each model decreased gradually with the increase of the optimization steps, there was no large-scale energy disturbance, and the energy tended to be stable at a low level in the end. This means that the optimized solution model was at the lowest local energy level, and the model could be considered to be in a relatively stable state.

2.2.2. MD Calculation Process. The temperature changes of each solution model during the MD calculation are shown in Figure 9. The temperature of each solution model was raised first and then decreased steadily, but the temperature of each solution model was all stable at 298 K (±10%) at the end of calculation, and there was no significant disturbance. It should be focused that the credibility of the solution model dynamic is closely related to the corresponding termination temperature.

![Figure 7](image1.png)  
**Figure 7.** Constructed solution model after geometry optimization (a) saturated, (b) blank solution relates to saturated solution (c) unsaturated, and (d) blank solution relates to unsaturated solution.

![Figure 8](image2.png)  
**Figure 8.** Energy change of the modes during the geometry optimization (a) saturated and (b) unsaturated.

![Figure 9](image3.png)  
**Figure 9.** Temperature changes of each solution model during the MD calculation (a) saturated and (b) unsaturated.

Table 1. Solution Establishment Parameters

| components | the solution, dissolution Nd$^{3+}$ saturated | the blank solution | the solution, dissolution Nd$^{3+}$ unsaturated | the blank solution |
|------------|---------------------------------|-------------------|---------------------------------|-------------------|
| number     | number                          | number            | number                          | number            |
| mass fraction (%) | mass fraction (%)               | mass fraction (%) | mass fraction (%)               | mass fraction (%) |
| H$_2$O     | 10 590                          | 10 590            | 10 590                          | 10 590            |
| Na$^+$     | 488                             | 488               | 560                             | 560               |
| CO$_3^{2−}$| 244                             | 244               | 280                             | 280               |
| Nd$^{3+}$  | 4                               | 0                 | 3                               | 0                 |
| Cl$^−$     | 12                              | 0                 | 9                               | 0                 |
The result is credible while the temperature of the model is within ±10% range of the initial at the end of the calculation. Hence, the results were credible.

The solution models after the MD calculation are shown in Figure 10.

As shown in Figure 10, the solution was homogeneous in general after dynamic calculation. However, in the local region, each component was not randomly and evenly distributed in the solution. The interaction between ions (molecules) result in varying degrees of agglomeration phenomenon at the local level.

Among them, no matter what the dissolution level (saturated or unsaturated) of Nd³⁺ in Na₂CO₃ solution is, the Nd³⁺ was all surrounded by CO₃²⁻, and it was coordinated by about 2−4 CO₃²⁻; the specific coordination situation is shown in Figure 11. This was consistent with the results obtained from the full-wavelength UV−vis scan of the solution sample before.

It was also confirmed with Vercouter and Vitorge’s conclusion,²¹ which was that rare-earth elements and CO₃²⁻ coordination in high concentration CO₃²⁻ solution and all kinds of complex ions in the form of Ndₙ(CO₃)ₘ³⁻−₂ₘ (ₘ ≥ 2) existed but in different proportions.

In addition, all the solution models, including corresponding blank solutions, showed local agglomeration of CO₃²⁻ distribution and a large number of Na⁺ distributed around them. It could surmise that Na⁺ and CO₃²⁻ did not dissociate completely in the circumstance of the high concentration Na₂CO₃ solution, which means that the free CO₃²⁻ concentration in the solution was at a low level.

2.2.3. Radial Distribution Function and Coordination Behaviors. The coordination behavior of neodymium with CO₃²⁻ in high concentration Na₂CO₃ solution could be visually expressed by the solution model after the MD calculation. To further quantify the interaction between components in the solution model at the micro level, for the main ion pairs in the solution, such as Nd³⁺−CO₃²⁻, Na⁺−CO₃²⁻, and Nd³⁺−Cl⁻, the analyses of radial distribution function (RDF) were conducted using the Forcite.

As shown in Figure 12, the peak positions of RDF of Nd³⁺−CO₃²⁻ in the solution were almost the same, regardless of whether the dissolution concentration of Nd³⁺ was equal to the instantaneous saturated solubility or unsaturated, but there are still some strong differences. The first RDF peak of Nd³⁺−CO₃²⁻ in saturated situation was stronger than that in the unsaturated situation. This phenomenon indicated that Nd³⁺ could bind more closely with CO₃²⁻ at a closer microscopic distance.

However, in the overall chemical bond range (r < 2.6 Å),²³ the average coordination number of Nd³⁺ with CO₃²⁻ at the solution with Nd³⁺ saturated was about 2.37. It was lower than the number 2.50, in which, the dissolution of Nd³⁺ in the solution was unsaturated. However, when Nd³⁺ saturated dissolved in the solution, some of the dissolution Nd³⁺ precipitated and form NaNd(CO₃)₂ in a short time, and the average coordination number of Nd³⁺ and CO₃²⁻ in NaNd(CO₃)₂ is 2.0. Thus, the average coordination number of Nd³⁺ and CO₃²⁻ was lower. Correspondingly, when the dissolution Nd³⁺ was unsaturated, the solution was in a better metastable state, and the dissolution Nd³⁺ can be stable in the solution for a long time; thus, the coordination number was slightly higher.

From Figure 13, it could be found that there was no interaction between Nd³⁺ and Cl⁻ because the RDF strength was zero. In this case, no matter whether dissolution Nd³⁺ was saturated or not, there was no coordination behavior between Nd³⁺ and Cl⁻.
This phenomenon indicated that the dissociation of CO$_3^{2-}$ in the solution was strongly related to the excess water added to the solution. When dissolution concentration Nd$^{3+}$ reaches instantaneous saturated solubility (3.566 g L$^{-1}$), the required volume of 10 g L$^{-1}$ NdCl$_3$ was 14 mL, but the solution when unsaturated (2.621 g L$^{-1}$) was only 9 mL. The excess water diluted the high concentration Na$_2$CO$_3$ solution, resulting in more CO$_3^{2-}$ being dissociated into the solution. That is to say, the concentration of free CO$_3^{2-}$, which could react with Nd$^{3+}$ to generate precipitates in the solution, was further increased. The interaction between Na$^+$ and CO$_3^{2-}$ in the corresponding blank solution we had calculated could also provide an evidence.

In other words, the total concentration of CO$_3^{2-}$ in the solution was slightly lower when the dissolution Nd$^{3+}$ was saturated than when the dissolution Nd$^{3+}$ was unsaturated, but the corresponding concentration of free CO$_3^{2-}$ that could react with Nd$^{3+}$ to generate precipitates was higher and causes the solution to become unstable. Therefore, the higher concentration of CO$_3^{2-}$, but the lower concentration of free CO$_3^{2-}$ in the Na$_2$CO$_3$ solution, was also one of the important reasons for the existence of the solution metastable period.

3. CONCLUSIONS

In this work, the instantaneous saturated solubility of Nd$^{3+}$ in 1–2 mol L$^{-1}$ Na$_2$CO$_3$ solution, metastable dissolution regularity of Nd$^{3+}$, and metastable mechanism were investigated in detail. The main conclusions are reproduced below.

First, instantaneous saturation solubility of Nd$^{3+}$ was positively correlated with the concentration of Na$_2$CO$_3$ solution. In 1.0, 1.5, and 2.0 mol L$^{-1}$ Na$_2$CO$_3$ solution, the solubility was 1.186, 2.394, and 3.566 g L$^{-1}$, respectively.

Second, when the initial dissolution concentration of Nd$^{3+}$ in the solution was equal to the instantaneous saturated solubility, the solution was not in the metastable period and the dissolved Nd$^{3+}$ precipitated quickly. However, when the initial dissolution concentration of Nd$^{3+}$ in the solution did not reach the instantaneous saturated solubility, the solution had a metastable period, and in that period, the dissolution of Nd$^{3+}$ was stable, but it still had the precipitation behavior, while beyond the period. Moreover, the precipitants obtained were all in the form of NaNd(CO$_3$)$_2$.

And the last, the coordination reaction between Nd$^{3+}$ and CO$_3^{2-}$ occurred, and all kinds of complex ions in the form Nd$_m$(CO$_3$)$_{3n-2m}$ (m ≥ 2) existed, and the interaction between Nd$^{3+}$ and Cl$^{-}$ was not found in the solution. The higher concentration of CO$_3^{2-}$ in the solution, but the lower concentration of free CO$_3^{2-}$ that could react with neodymium to generate precipitate, was an important reason for the existence of the solution metastable state.

4. EXPERIMENTS

4.1. Materials and Equipment. In the experiment, the rare-earth raw material was 1.3568 mol L$^{-1}$ high purity NdCl$_3$.

Table 2. Composition Content of the High Purity NdCl$_3$ Solution

| concentration of Nd$^{3+}$ (mol L$^{-1}$) | concentration of H$^+$ (mol L$^{-1}$) | specific gravity (g mL$^{-1}$) | rare-earth impurities/REO (μg mL$^{-1}$) |
|----------------------------------------|-------------------------------------|-----------------------------|---------------------------------------|
| 1.3568                                 | <0.10                               | 1.326                       | La$_2$O$_3$                            |
|                                        | non-rare-earth impurities (μg mL$^{-1}$) |                              | Ce$_2$O$_3$                          |
|                                        | Fe$_2$O$_3$                           |                              | Pr$_2$O$_3$                           |
|                                        | SiO$_2$                              |                              | Sm$_2$O$_3$                           |
|                                        | CaO                                 |                              | Eu$_2$O$_3$                           |
|                                        | 2.49                                 |                              | Gd$_2$O$_3$                           |
|                                        | 7.3                                  |                              | Tb$_2$O$_3$                           |
|                                        |                                      |                              |                                       |
|                                        |                                      |                              |                                       |
|                                        |                                      |                              |                                       |
solution and is produced by rare-earth separating factory in Longnan, Jiangxi Province. The composition content of the high purity NdCl₃ solution is shown in Table 2.

NdCl₃ feed solution (10 g L⁻¹) was prepared by diluting the high purity solution with deionized water. The analytical pure (AR) Na₂CO₃ was used for the preparation of 1, 1.5, and 2 mol L⁻¹ solution by using deionized water. The purity of other chemical reagents, such as HCl, ethylenediaminetetraacetic acid (EDTA), and so on, was also of AR grade. The information on experimental equipment is given in Table 3.

### 4.2. Metastable Dissolution Regularity of Nd³⁺ in Na₂CO₃ Solution

4.2.1. Determination of Instantaneous Saturated Solubility of Nd³⁺. Na₂CO₃ solutions (1, 1.5, and 2 mol L⁻¹) were selected as a basal solution for dissolving Nd³⁺. Na₂CO₃ solution (25 mL) was put into a conical flask, and then, 10 g L⁻¹ NdCl₃ solution was dropwise added into it by shaking the flask via an oscillator at 20–25 °C. First, the white precipitates of basic rare-earth carbonate were formed and then dissolved with vigorous shaking. However, the precipitates were generated again while the dissolution concentration of Nd³⁺ in Na₂CO₃ solution attained the instantaneous saturated solubility. At this time, the solution was muddy and the addition of NdCl₃ solution was stopped, and then, a known amount of muddy solution was centrifuged with 6000 rpm for 5 min. After that, 5 mL of liquor was transferred and the carbonate system was completely destroyed by using diluted HCl. Subsequently, the dissolution concentration of Nd³⁺ in Na₂CO₃ solution was measured by EDTA titration or inductively coupled plasma–optical emission spectroscopy (ICP–OES).

4.2.2. Dissolution of Nd³⁺ with Time. In order to control whether the dissolution concentration of Nd³⁺ was equal to or lower than the instantaneous saturated solubility, a known volume of 10 g L⁻¹ NdCl₃ solutions was dropwise added into Na₂CO₃ solution with shaking, at 20–25 °C. After adding dropwise, the static aging process was carried out and the time was set between 0 and 480 min. At the end of each aging time, a known amount of the solution was transferred and centrifuged to get the liquor; subsequently, 5 mL of liquor was acidized completely by diluted HCl. The dissolution concentration of Nd³⁺ in Na₂CO₃ solution was titrated with EDTA or analyzed by ICP–OES.

4.2.3. Coordination Behavior of Nd³⁺ in the Metastable Solution. To monitor the coordination behavior of Nd³⁺ quickly in the metastable solution, aqueous samples in different aging time were collected and full-wavelength scanned by using UV–vis. The blank solution, such as single Na₂CO₃ and NdCl₃ solution, was also scanned.

4.2.4. Characterization of Precipitates. To investigate the formation of precipitates of basic rare-earth carbonate generated from the metastable solution, precipitate samples in different aging times were collected and detected by FTIR. It should be noticed that the precipitates samples were prestored in deionized water to prevent them from decomposition. Before analyzing, the water was completely removed by sucking filtration, and the samples were analyzed immediately.

### 4.3. Simulation of the Mechanism of the Metastable State

4.3.1. Establishment and Optimization of Metastable Solution Models. Materials Studio 8.0 is powerful software for material simulation and modeling and is developed by Accelrys. In this section, all the components of the metastable solution, such as H₂O, CO₃⁻, Nd³⁺, Na⁺, and Cl⁻, were established by the Visualizer and optimized under the universal force field by Forcite in software Materials Studio 8.0. After the establishment and optimization process of the components, the solution box model was built, and the well-optimized components were added into the box via an amorphous cell. The values of density and the concentration of each component were settled by following the actual metastable solution. Subsequently, the geometry optimization of the solution model was performed. Also, the blank solutions, which were the Na₂CO₃ solution with only added water, were also established and optimized. During the optimization step, it was necessary to check whether the energy of the system was converted smoothly to a lower energy state.

4.3.2. MD Calculation Process. The MD calculation was conducted by Forcite after the optimization of the solution models. The calculation ensemble was NVT. The simulation temperature was 298 K, and the time was set at 20 ps and calculated once per 1 fs. The parameters of the initial heating rate and temperature control sets were selected at Random and Andersen. To save experimental time, the accuracy of calculation was chosen as a middle. At the end of the calculation, it was necessary to verify whether the result of the dynamic calculation is credible. When the temperature is stable at the range of 298 ± 29.8 K in the end and there is no large temperature disturbance, the calculation result is credible; otherwise, it needs to be recalculated.

4.3.3. RDF and Coordination Behaviors. The schematic diagram of the RDF is presented in Figure 15. After the MD
calculation, the RDF analysis was carried out. Utilizing the formula 1 to establish the relationship between the results of RDF analysis and the coordination behaviors, the average coordination number between each component was obtained. The entire simulation flowchart is shown in Figure 16.

\[ N(L) = \int_{0}^{L} g(r) \rho 4\pi r^2 \, dr \]  

Figure 16. Simulation flowchart.

\( N(L) \) refers to the number of coordination atoms (molecules) in the 0–L spherical shell around the target atom. \( \rho \) refers to the number density of coordination atoms (molecules), and the value is the ratio of the number of atoms (molecules) to the volume of space. \( g(r) \) refers to the RDF value, and it indicates the probability of the occurrence of coordination atoms (molecules) within a certain distance. \( r \) refers to the cutoff radius.

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**Notes**
The authors declare no competing financial interest.

- **ACKNOWLEDGMENTS**
The authors gratefully acknowledge the financial supports of the Program of National Natural Science Foundation of China (51774155).

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