



Modeling and simulation of neodymium oxide dissolution in molten fluorides

Xin-yu WU^{1,2}, Fei-fei LIU¹, Jia-hao LI³, Xin-yu CHEN³, Shu-mei CHEN⁴

1. School of Electrical Engineering and Automation,

Jiangxi University of Science and Technology, Ganzhou 341000, China;

2. Jiangxi Ionic Rare Earth Engineering Research Co., Ltd., Ganzhou 341000, China;

3. School of Mechanical and Electrical Engineering,

Jiangxi University of Science and Technology, Ganzhou 341000, China;

4. Faculty of Materials Metallurgy and Chemistry,

Jiangxi University of Science and Technology, Ganzhou 341000, China

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Abstract: By combining the mass transfer mechanism of neodymium oxide with dissolution kinetics, a solution strategy for neodymium oxide dissolution was proposed to predict the dissolved neodymium oxide concentration during the process under complex flow field conditions. The factors affecting neodymium oxide dissolution were analyzed in detail. Aiming at the pulse feeding and continuous feeding modes in industrial practice, the characteristics of the dissolution process under the two feeding modes were compared. Simulation results showed that pulse feeding took shorter time to distribute evenly than continuous feeding. Finally, the dissolution time of single-particle neodymium oxide under static flow field conditions was compared with the literature results. Except for only one set of data with a maximum error of about 10%, the errors of other data are all within 5%.

Key words: neodymium oxide; dissolution; simulation; mass transfer; multiphase flow; molten salt; electrolysis

1 Introduction

The rare-earth metal neodymium is an important raw material for preparing NdFeB magnets [1]. As one of the strongest permanent magnets known to date, neodymium is widely used in various applications, including electronics, electrical machinery, and medical equipment. In recent decades, the oxide–fluoride electrolysis system has replaced the traditional chloride electrolysis system as the dominant technique for the industrial production of neodymium metal and its alloys [2–4]. In the electrolysis process of neodymium production, neodymium oxide is the

main raw material feeding into the liquid $\text{NdF}_3\text{--LiF}$ electrolyte continuously or intermittently. The feeding strategy of the neodymium oxide powder is an important issue in the automatic control process of neodymium electrolysis. On the one hand, a deficiency of neodymium oxide in the electrolyte would lead to the occurrence of the anode effect, accompanied by large emissions of perfluorinated carbons (PFC) [5]. On the other hand, due to the low solubility of neodymium oxide in molten fluoride salt, undissolved neodymium oxide from overfeeding easily settles to the bottom of the electrolytic cell and forms agglomerated deposits, which increases production costs and shortens the facility life [6].

Corresponding author: Fei-fei LIU, Tel: +86-13607979162, E-mail: gzlff@126.com;

Shu-mei CHEN, Tel: +86-15083721063, E-mail: chenshumei8910@sina.cn

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Although several studies have appeared in the literature on the dissolution process of some solid particles in molten salts, such as alumina powder in cryolite, there have been few studies focused on the dissolution of neodymium oxide in fluorides, including oxides of other rare-earth elements. STEFANIDAKI et al [7] investigated the complexes in liquid $\text{NdF}_3\text{--LiF--MgF}_2$ melts by Raman spectroscopy and discovered that the solubility of Nd_2O_3 in the mixture increased with the increase of temperature, while it was less affected by the concentration of MgF_2 . HU et al [8,9] studied the ionic structure of $\text{NdF}_3\text{--LiF}$ melts and explored the influence of the temperature and electrolyte composition on the solubility of Nd_2O_3 . GUO et al [10–13] observed a single neodymium oxide particle in stationary molten fluorides with confocal scanning laser microscopy (CSLM) and identified the rate-limiting step of Nd_2O_3 dissolution in molten fluoride as a mass transfer based on experimental observations. HAAS et al [14] studied a conventional cell with vertical electrodes and compared it to an innovative cell concept with horizontal electrodes using CFD. LU et al [15] presented a 20 kA rare-earth reduction cell and studied the effects of the anode–cathode distance and electrolyte height on the thermo-electrical behavior of the cell. LIU et al [16] introduced a standard turbulence model and numerically simulated the anode bubble behavior in a rare-earth electrolysis cell using fluid dynamics calculations. The influence of the gas bubbles produced by the anode on the fluid velocity field was examined. To the best of our knowledge, there have been no systematic reports focused on a mass transfer approach for neodymium oxide dissolution in complex flow environments with CFD simulations yet.

In this work, a mass transfer solution strategy (MTSS) for neodymium oxide dissolution in multiphase flow was proposed to calculate the concentration of dissolved neodymium oxide theoretically at any time step during the dissolution process under complex flow field conditions. To visually show the dissolution process of neodymium oxide, the continuous and pulse feeding processes of a certain quantity of neodymium oxide were simulated. Finally, the dissolution of a single oxide particle in the static fluid was verified with the CSLM experimental

results by GUO et al [13]. In addition, to verify the neodymium oxide dissolution process in turbulent flow, a certain amount of neodymium oxide powder particles were artificially fed into an 8 kA commercial cell with an intermittent sampling of molten salt. The test results of the sample showed that the estimated concentration was rather close to the actual experimental value.

2 Dissolution mechanism and models of neodymium oxide

The solution strategy includes three parts: a fluid dynamics model, a mass transfer model, and a dissolution kinetics model. It started with a fluid dynamics model to describe the multiphase flow distribution in the electrolysis cell, which could be static, laminar, or turbulent flow. The mass transfer coefficient was able to be determined by equations from the mass transfer model. Based on that, the concentration of dissolved neodymium oxide and the dissolution rate at each time step could be calculated in the strategy of MTSS.

2.1 Dissolution mechanism of neodymium oxide

The dissolution of Nd_2O_3 in molten fluoride was proved to be a mass transfer-controlled process via in-situ observations with CSLM [12,13]. The driving force for dissolution is the difference between the concentration of the dissolved neodymium oxide surface and that of the bulk of the electrolyte. The neodymium oxide particles can be treated as smooth spheres with an initial diameter. It is also assumed that neodymium oxide particles should stay in a single dispersed state to allow the diffusion to occur continuously during the dissolution process. Thus, the effective diffusion area is the sum of the surface areas of all the particles. The assumption is reasonable because long-term observations in industrial neodymium electrolysis cells have shown that fed neodymium oxide powders disperse quickly in an electrolyte and do not agglomerate visibly.

2.2 Dissolution kinetics model

Assuming that the neodymium oxide particles are spherical, the basic equation for the mass transfer rate between the solid particles and the liquid electrolyte can be expressed as [17,18]

$$R = \frac{dc}{dt}V = k_1A(c_{\text{sat}} - c) \quad (1)$$

where R is the dissolution rate coefficient of mass transfer, c is the neodymium oxide concentration at time t , V is the volume of the electrolyte, k_1 is the mass transfer coefficient, A is the surface area of all the mono-sized spheres, and c_{sat} is the saturation concentration for neodymium oxide.

In the following discussion, the initial amount of neodymium oxide is considered. The surface areas of the particles would decrease as the mass of undissolved particles decreased, which is expressed by the following relationship:

$$A = A_0(M/M_0)^{2/3} \quad (2)$$

where A_0 is the initial total surface area of neodymium oxide particles, M is the mass of neodymium oxide remaining undissolved at time t , and M_0 is the initial mass added.

The mass of particles remaining undissolved can be related to the concentration of neodymium oxide in the electrolyte by the following relationship:

$$M = M_0 - (c - c_i)V \quad (3)$$

where c_i is the initial neodymium oxide concentration.

According to Eq. (3), the rate equation of neodymium oxide particle dissolution can be expressed as follows [19]:

$$R = \frac{dc}{dt}V = k_1A_0\left(1 - \frac{V}{M_0}c'\right)^{2/3}(c'_{\text{sat}} - c') \quad (4)$$

where c' is the difference between the concentration of neodymium oxide and the initial concentration, and c'_{sat} is the difference between the saturation concentration and the initial concentration.

After integrating the equation above and shifting the terms, the dissolution time t can be expressed as follows [19]:

$$t = \frac{Vb^2}{k_1A_0a^2} \left[\frac{1}{2} \ln \frac{(a+u)^2}{a^2 + au + u^2} + \sqrt{3} \tan^{-1} \frac{2u-a}{a\sqrt{3}} - \frac{1}{2} \ln \frac{(a+b)^2}{a^2 - ab + b^2} - \sqrt{3} \tan^{-1} \frac{2b-a}{a\sqrt{3}} \right] \quad (5)$$

where

$$u = \left(c' - \frac{M_0}{V} \right)^{1/3} \quad (6)$$

$$a = \left(\frac{M_0}{V} - c'_{\text{sat}} \right)^{1/3} \quad (7)$$

$$b = \left(-\frac{M_0}{V} \right)^{1/3} \quad (8)$$

2.3 Mass transfer equations

For the spherical neodymium oxide particles, equations describing the forced-convection mass transfer between a fluid and a solid body are usually described by the dimensionless Sherwood, Reynolds, and Schmidt numbers. These numbers are related as follows [20,21]:

$$Sh = \begin{cases} 2 + 0.52Re^{0.52}Sc^{1/3}, & Re > 0 \\ 2, & Re = 0 \end{cases} \quad (9)$$

where Sh , Re , and Sc are the Sherwood number, modified Reynolds number, and Schmidt number of neodymium oxide, respectively. They are defined as follows:

$$Sh = k_1L/D \quad (10)$$

$$Sc = \nu_L/D \quad (11)$$

$$Re = d^{4/3}\varepsilon^{1/3}/\nu_L \quad (12)$$

where d is the diameter of a neodymium oxide particle, D is the diffusion coefficient (mass transfer coefficient) of dissolved neodymium oxide in the electrolyte, ε is the turbulent dissipation rate, ν_L is the kinematic viscosity of the electrolyte, and L is the characteristic length of the solid particles. When the mass transport around a solid particle in a liquid is studied, L is typically the radius of the solid particle.

The only variable remaining to be determined in Eq. (10) is the mass transfer coefficient k_1 . Traditionally, once the type of dissolution kinetics model is selected, the data curve is fit to this model, and the coefficient in the model, assumed to be constant, is determined as a global optimal approximation by the least-squares method. The mass transfer coefficient is related to the fluid properties and the flow field distribution. In particular, for the case where the fluid and solid particles are relatively static, $Sh=2$. Through the numerical calculations, the mass transfer coefficient distribution in the dissolution models can be calculated directly with sufficient molten fluid movement information. In the present work, the neodymium oxide particle size, the dissolution rate,

and the dissolved neodymium oxide concentration over time were determined dynamically by numerical calculations. Thus, the mass transfer coefficient can be expressed as follows:

$$k_1 = D(2.0 + 0.52Re^{0.52}Sc^{1/3}) \quad (13)$$

It should be emphasized that k_1 is the rate constant related to the boundary layer thickness, which is invariant concerning the particle size. Equations (5) and (6) show that for given values of the initial mass, diameter, and diffusion coefficient of the particle, combined with quantities such as the saturation concentration, turbulent dissipation rate, and viscosity of the solvent, the neodymium oxide concentration in the dissolution process can be calculated.

2.4 Phase transport equations with turbulent flow

The flow field of electrolytes has a significant influence on the mass transfer rate, which is reflected by the Reynolds number of the fluid. To describe the movement of the multiphase substance in the neodymium electrolytic cell, the phase transport model was used to model the multiphase flow containing several dispersed phases, which showed good accuracy and convergence [22–24]. The phase transport model included two dispersed phases (oxide powder anode gas bubbles) and one continuous phase (molten salt). Because the mass of neodymium oxide added at a single time basically did not exceed 3 wt.% due to the low solubility, for simplicity and convergence, the slip between the dispersed phase and continuous phase was not considered here. As for the flow field, the k - ε turbulence model was adopted to calculate the Reynolds number of the turbulent flow coupled with the phase transport model [25]. In particular, the Reynolds number was set to be zero in the static fluid according to this definition.

2.4.1 Phase transport model

The model equations solved at the phase transport model interfaces are based on the mass conservation of each phase and conservation of momentum. It is assumed that the sum of the volume fractions of each immiscible phase $i=1, 2, \dots, N$, is given as follows [26]:

$$\sum_{i=1}^N s_i = 1 \quad (14)$$

where s_i represents the volume fraction.

The mass conservation equations for all phases yield the following continuity equation for the mixture:

$$\frac{\partial}{\partial t} \rho + \nabla(\rho \mathbf{j}) = \sum_{i=1}^N Q_i \quad (15)$$

where $\mathbf{j}$ and ρ denote the mass-averaged mixture velocity vector and the mixture density, respectively. They are defined as follows:

$$\mathbf{j} = \frac{1}{\rho} \sum_{i=1}^N s_i \rho_i \mathbf{u}_i \quad (16)$$

$$\rho = \sum_{i=1}^N s_i \rho_i \quad (17)$$

where ρ_i denotes the density of phase i , and $\mathbf{u}_i$ defines the velocity vector of phase i . In addition, the term Q_i denotes a mass source for phase i .

The phase transport model includes turbulent mixing via the gradient-diffusion hypothesis. In this case, it adds a diffusion term proportional to the turbulent kinematic viscosity to the phase transport Eq. (15), which then becomes the following equation:

$$\frac{\partial}{\partial t} (\rho_i s_i) + \nabla(\rho_i s_i \mathbf{u}_i) - \nabla(\rho_i \frac{\nu_T}{Sc_T} \nabla s_i) = Q_i \quad (18)$$

where ν_T is the turbulent kinematic viscosity, and Sc_T is the turbulent Schmidt number of neodymium oxide.

2.4.2 k - ε turbulence model

To determine the dissipation rate ε in Eq. (12), the standard k - ε turbulence model was used in this paper. This model introduces two additional transport equations and two dependent variables: the turbulent kinetic energy k and the turbulent dissipation rate ε . The following momentum conservation equation assumes that the fluid is incompressible and Newtonian, in which the Navier–Stokes equations take the form:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \nabla) \mathbf{u} = \nabla(\rho \mathbf{I} + \mathbf{K}) + \mathbf{F} + \rho \mathbf{g} \quad (19)$$

where $\mathbf{u}$ denotes the velocity field, $\mathbf{I}$ is the unit matrix, $\mathbf{F}$ is the volume force vector and the additional term, $\mathbf{g}$ is the gravity constant, and $\mathbf{K}$ is the viscous stress tensor, given as

$$\mathbf{K} = (\mu + \mu_T)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}(\mu + \mu_T)(\nabla \mathbf{u}) \mathbf{I} - \frac{2}{3} \rho k \mathbf{I} \quad (20)$$

where μ is the viscosity of the fluid, and μ_T is the turbulent viscosity in the k - ε turbulence model.

The transport equation for k is given as follows [27,28]:

$$\rho \frac{\partial k}{\partial t} + \rho \mathbf{u} \nabla k = \nabla \cdot \left(\left(\mu + \frac{\mu_T}{\sigma_k} \right) \nabla k \right) + P_k - \rho \varepsilon \quad (21)$$

where σ_k is a constant in the k - ε turbulence model, the turbulent viscosity μ_T and the production term P_k are modeled respectively as follows:

$$\mu_T = \rho C_\mu \frac{k^2}{\varepsilon} \quad (22)$$

where C_μ is a constant in k - ε turbulence model.

$$P_k = \mu_T (\nabla \mathbf{u} : (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) - \frac{2}{3} (\nabla \mathbf{u})^2 - \frac{2}{3} \rho k \nabla \mathbf{u} \quad (23)$$

The transport equation for ε is as follows:

$$\rho \frac{\partial \varepsilon}{\partial t} + \rho \mathbf{u} \nabla \varepsilon = \nabla \cdot \left(\left(\mu + \frac{\mu_T}{\sigma_\varepsilon} \right) \nabla \varepsilon \right) + C_{\varepsilon 1} \frac{\varepsilon}{k} P_k - C_{\varepsilon 2} \rho \frac{\varepsilon^2}{k} \quad (24)$$

where σ_ε , $C_{\varepsilon 1}$ and $C_{\varepsilon 2}$ are constants in the k - ε turbulence model.

The constants in Eqs. (22)–(24) were determined from experimental data, and the values are listed in Table 1.

Table 1 Constants in k - ε turbulence model and their values

C_μ	$C_{\varepsilon 1}$	$C_{\varepsilon 2}$	σ_k	σ_ε
0.09	1.44	1.92	1.0	1.3

2.5 Mass transfer solution strategy for neodymium oxide dissolution in multiphase flow

The entire dissolution process involved the dissolution of every single neodymium oxide particle [29–31]. The neodymium oxide particles were modeled as monodisperse smooth spheres, each with a specified initial diameter. In practice, the neodymium oxide particle size distribution had a normal distribution. For simplicity, the average particle diameter offered by the manufacturer was set to be the uniform initial diameter, and the initial surface area was the sum of the surface areas of all the spherical particles. In this work, a mass transfer solution strategy (MTSS) for neodymium oxide dissolution in multiphase flow was proposed to calculate dissolution rate and dissolution time. The

specific steps of the solution strategy of MTSS are described below.

Initially, only the phase transport model and the k - ε turbulence model were solved to obtain a quasi-steady-state flow field considering neodymium oxide as a dispersed phase, anode gas bubbles as a dispersed phase, and liquid molten salt as a continuous phase using the mesh-to-mesh solution interpolation. Then, based on the distribution of particle Reynolds numbers in the flow field and other basic thermodynamic properties of the electrolyte, the mass transfer coefficient of each neodymium oxide particle could be determined. When the particle diameter was very small, it could cause an abnormal surge of the mass transfer coefficient, so it was necessary to set a dead zone for the mass transfer coefficient. Given the mass transfer coefficient, the initial mass of added neodymium oxide, and the corresponding surface area, the concentration of dissolved neodymium oxide was determined by Eq. (5) with a continuously growing dissolution time. According to the concentration at each moment of the dissolution process, the dissolution rate of each time step could be solved based on Eq. (6). The current particle diameter d can be updated based on the current concentration as follows:

$$d = \left(d_0^3 - \frac{6Vc'}{N\pi\rho_{\text{liq}}} \right) \quad (25)$$

where d_0 is the initial diameter of neodymium oxide particles, N is the number of particles, and ρ_{liq} is the density of the electrolyte.

Finally, the calculation was ended when the neodymium oxide particles were completely dissolved, which was indicated by the dissolved concentration reaching the ratio of the initial neodymium oxide mass to the electrolyte volume. The flowchart of the MTSS computation procedure for one neodymium oxide particle dissolution process is shown in Fig. 1.

3 Physical model

The motion of the electrolyte fluid was induced mainly by rising anode gas bubbles, while the electromagnetic stirring force and temperature- or concentration-related convection were relatively negligible. The design of the neodymium electrolytic cell considered here is shown in Fig. 2. It is

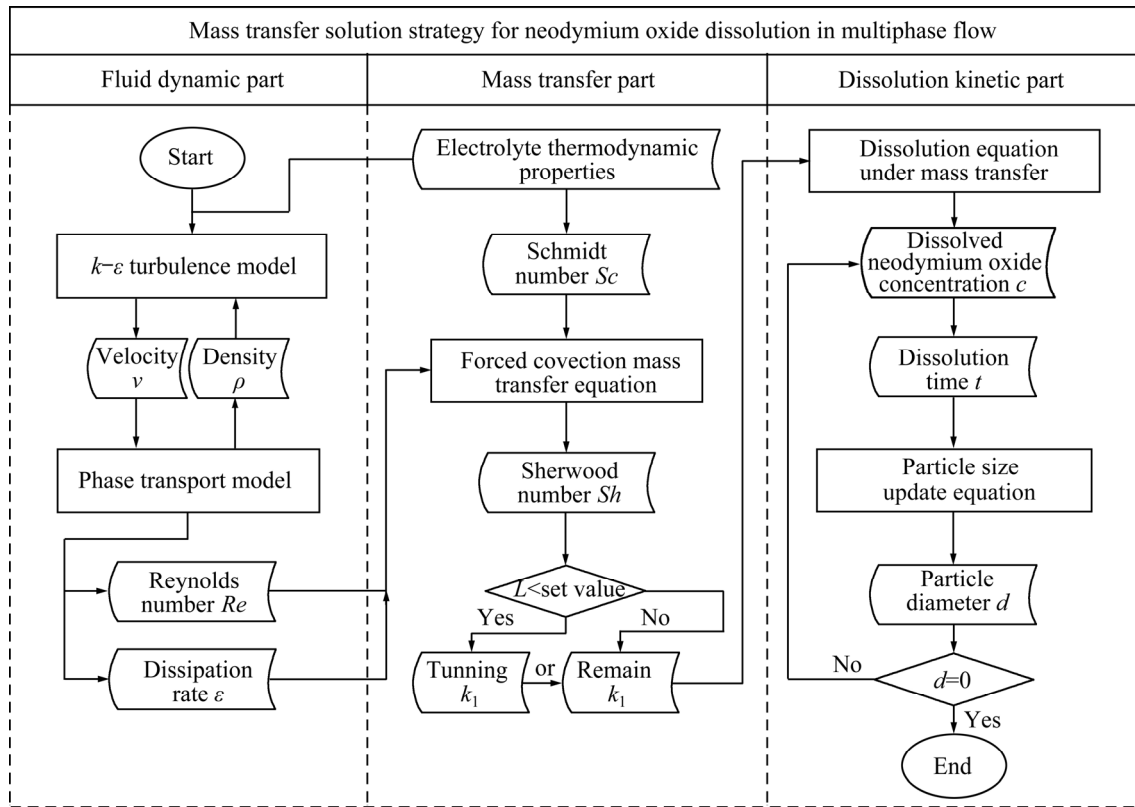


Fig. 1 Flowchart of mass transfer solution strategy (MTSS) computation

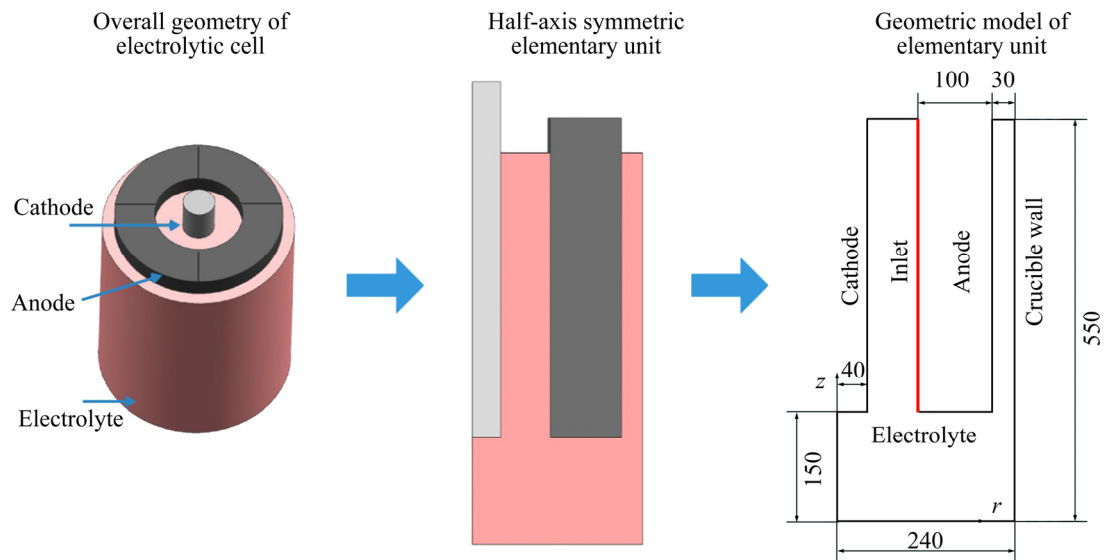


Fig. 2 Overall geometry of electrolytic cell with half-axis symmetric elementary unit and its geometric model (unit: mm)

made up of four 1/4-anode cylindrical sheets mounted in a circle around a central cathode rod. The electrodes are immersed in a molten-salt-based electrolyte containing the neodymium metal to be recovered at the cathode. There is a symmetry consideration to allow the implementation of

half-axis symmetry elementary unit without the loss of information, which significantly diminishes the number of degrees of freedom within the system. The overall geometry of the electrolytic cell and phase distribution is by the currently operated industrial electrolytic cell mentioned in previous

publications, which are presented in Fig. 2. The important thermodynamic and physical parameters used in the models are given in Table 2.

Table 2 Important physical parameters in simulation

Property	Value	Ref.
Electrolyte density/($\text{kg}\cdot\text{m}^{-3}$)	4060	[14]
Electrolyte viscosity/($\text{Pa}\cdot\text{s}$)	4.95×10^{-3}	[14]
Electrolyte surface tension/($\text{N}\cdot\text{m}^{-1}$)	0.27	[14]
Anode gas density/($\text{kg}\cdot\text{m}^{-3}$)	0.296	[14]
Anode gas viscosity/($\text{Pa}\cdot\text{s}$)	4.881×10^{-5}	[14]
Particle density/($\text{kg}\cdot\text{m}^{-3}$)	800	[14]
Bubble diameter/m	4×10^{-3}	[14]
Diffusion coefficient of particles/($\text{m}^2\cdot\text{s}^{-1}$)	26×10^{-10}	[13]
Diameter of particle/ μm	500	[8]
Saturated concentration/wt. %	4	[8]
Initial addition quantity/kg	0.01	Assumed

In the cell, a continuous molten salt electrolyte phase filled the space between the cathode and anode. In addition, a continuous air phase was considered as a wall on the surface above the free electrolyte. The first dispersed phase of the bubbles was generated from the surface of the anode and overflowed from the surface of the molten salt under the action of buoyancy.

The second dispersed phase was solid neodymium oxide particles, which were fed from the surface of the molten salt and gradually dissolved in it. On all surfaces, a no-slip boundary condition was applied, except for the wall on the surface of the electrolyte, at which a slip boundary condition was used.

4 Results and discussion

In general, the neodymium oxide dissolution process under the mass transfer mechanism could be influenced by the initial neodymium oxide concentration, the saturation concentration, and the dissolution rate. The initial and saturation neodymium oxide concentrations determined the starting and terminal points of the neodymium oxide dissolution process, respectively, while the dissolution rate determines the speed from starting to finishing. According to the mass transfer

equation (Eq. (4)), the dissolution rate was controlled by the mass transfer rate, which was jointly defined by the diffusion coefficient and Reynolds number according to Eq. (13). Specifically, the diffusion coefficient indicated that the diffusion behavior was dominated by temperature, and the Reynolds number characterized the behavior of convection. Furthermore, the temperature of the electrolyte determined not only the dissolution rate but also affected the saturation concentration of the particular electrolyte. Therefore, four factors influenced the transfer mechanism of the overall dissolution process of neodymium oxide: the initial solute concentration, the saturation concentration, the Reynolds number of the fluid, and the diffusion coefficient of the particles. In this study, the initial neodymium oxide concentration was set to be zero, and the composition of the molten salts was $34\text{NdF}_3\text{--}66\text{LiF}$ (molar fraction, %) unless stated specifically otherwise.

4.1 Flow field distribution of neodymium electrolytic cell

The flow field distribution is shown on the vertical section of the neodymium electrolytic cell in Fig. 3. The streamlines with arrows depicted the overall flow of electrolytes driven by the anode bubbles. Affected by the current distribution, the current density of the anode on the side close to the cathode was larger than that on the other side, so the gas generation rate on the anode surface on the side close to the cathode was also greater than that on the other side. Driven by the bubbles on the anode surface, the fluid on the surrounding anode

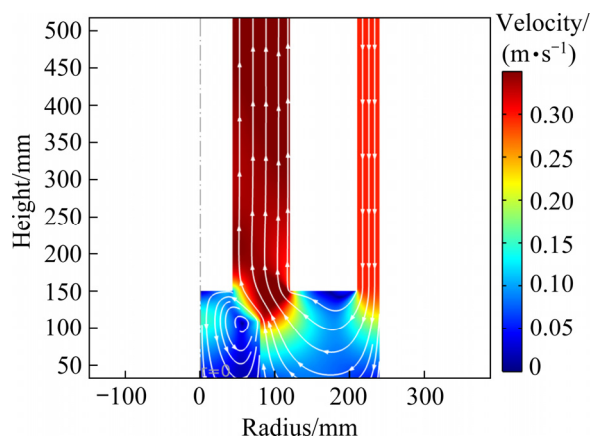


Fig. 3 Flow field distribution of electrolyte in half of neodymium electrolytic cell

surfaces flowed into the central cathode. The fluid on that anode surface moved upward with the fastest velocity in the cell, reaching about 0.30 m/s. There was a large symmetric vortex between the anode and cathode, which was mainly induced by the anode bubbles. As in the analysis below, the vortex had a significant effect on the dissolution of neodymium oxide since the fluid in the vortex had a higher dissipation rate. The flow velocity in the middle area of the electrolytic cell was significantly greater than that in other areas, such as in the boundary layer and at the bottom of the electrolytic cell.

4.2 Dissolution behavior of neodymium oxide under continuous feeding and pulse feeding conditions

Dissolution is a time-dependent process in which substances are gradually mixed in liquids uniformly. In the actual neodymium electrolysis industry, the feeding position is relatively fixed at the location where the neodymium oxides are fed from the upper part of the electrolytic cell between the cathode and anode. However, the feeding method, which includes continuous feeding and pulse feeding, usually has a significant impact on the dissolution of neodymium oxide. Pulse feeding means the addition of a certain amount of neodymium oxide to the electrolytic cell intermittently with a time separation Δt of 10–15 min, just like a sequence of pulses, while continuous feeding means that neodymium oxide is continuously added to the electrolytic cell over time. The total mass of the added oxide during continuous feeding was equal to that of the pulse

feeding, as shown in Fig. 4.

Figure 5 shows the simulated neodymium oxide concentration distribution on a vertical section during the dissolution process with the pulse feeding and continuous feeding strategies. The feeding point was fixed between the cathode and anode from the top of the cell, and the feeding amount was set to be 0.01 kg. More specifically, the continuous feeding was set to feed 0.01 kg of neodymium oxide within 50 s. In Fig. 5, a half-axis symmetry of the electrolytic cell is shown on the left, and the area in the red dashed frame is enlarged on the right. The distribution of dissolved neodymium oxide is shown in the upper row under continuous feeding, while that of pulse feeding is shown in the bottom row. There are eight images of each feeding strategy during the dissolution process, corresponding to the time of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 s, shown in (a), (b), (c), (d), (e), (f), (g), and (h) from upper and bottom rows of Fig. 5, respectively. Pulse feeding has better distribution characteristics than continuous feeding. Neodymium

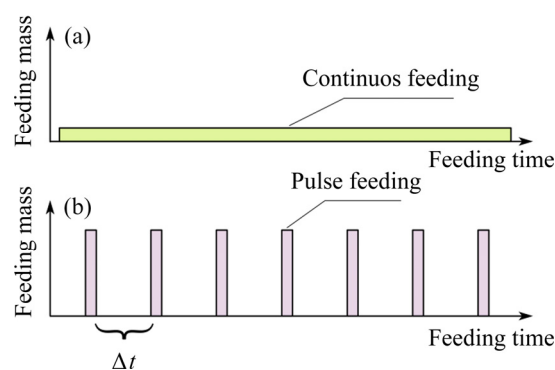


Fig. 4 Schematic diagram of continuous (a) and pulse (b) feeding

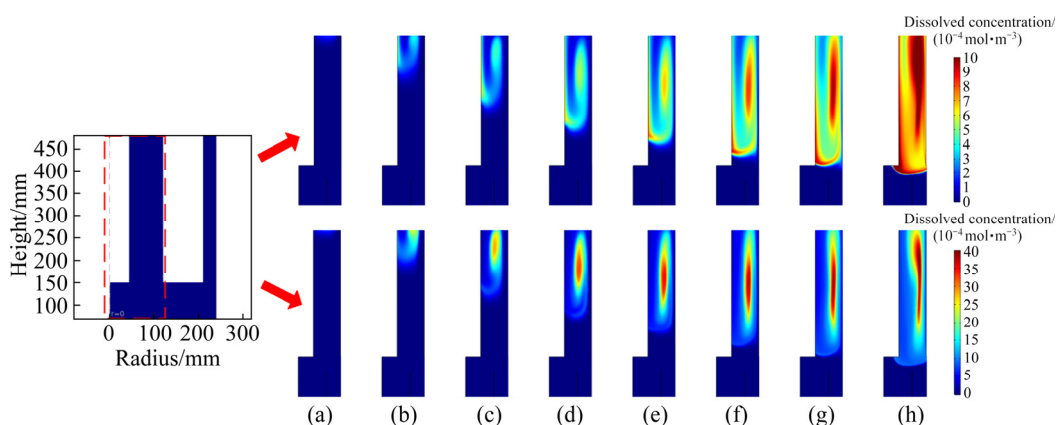


Fig. 5 Comparison of continuous and pulse feeding: Subfigures (a), (b), (c), (d), (e), (f), (g), and (h) from upper and bottom rows representing images of continuous feeding and pulse feeding during dissolution process, corresponding to time of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 s, respectively

oxide of pulse feeding can sink into the electrolyzer by its weight, while that of continuous feeding can only distribute through the flow field because the small amount of material floats on the surface of molten salt.

4.3 Factors affecting dissolution process of neodymium oxide

4.3.1 Reynolds number

Most previous studies mainly focused on the effects of the solute properties on the dissolution behavior, regardless of the fluid flow field. However, as shown by Eqs. (5) and (13), the Reynolds number of the fluid was related to the dissolution rate. In a high-Reynolds-number flow with dissipation, the dissolution rate of particles was significantly different from that of a low-Reynolds-number flow, which was also consistent with the experimental results under the condition of forced stirring and natural sedimentation. The dissolution behavior of neodymium oxide particles was investigated at the Reynolds numbers of 0, 1, 5, and 10. The particle size varied from 100 to 1000 μm , and the electrolyte temperature was fixed at 1291 K. To reduce the calculation cost, the dissolution behaviors of one neodymium oxide particle were discussed separately under different electrolyte fluid conditions. Figure 6 shows that with the increase in the particle size, the dissolution time of neodymium oxide particles increased accordingly in the fluid with the same Reynolds number. Under the same particle size, the dissolution time of neodymium oxide decreased as the Reynolds number of the electrolyte fluid increased. The reason may have been that the dissolved neodymium oxide in a stationary fluid could only achieve mass transfer by diffusion, while in the moving fluid, the dissolved neodymium oxide could be dispersed into the electrolyte not only by diffusion but also by convection. For larger Reynolds numbers, more violent convection occurred, as expected. This result indicated that accelerating the electrolyte by stirring or other means would help to dissolve the neodymium oxide particles.

4.3.2 Diffusion coefficient

Diffusion coefficients of 5.9×10^{-9} , 7.9×10^{-9} , 9.9×10^{-9} , and $1.9 \times 10^{-8} \text{ m}^2/\text{s}$ were investigated for the dissolution process of neodymium oxide. In this analysis, the saturation concentration was fixed to

be 110 g/L, and the results are shown in Fig. 7. With the increase in the particle size, the dissolution time of the neodymium oxide particles increased correspondingly at the same diffusion coefficient, as expected. For neodymium oxide particles of the same size, the dissolution time decreased when the diffusion coefficient increased. This indicated that the diffusion coefficient had significant effects on the dissolution process of neodymium oxide particles. Specifically, when the diffusion coefficient was $5.9 \times 10^{-9} \text{ m}^2/\text{s}$, the dissolution time of the neodymium oxide particles was 519 s for a diameter of 600 μm , which was three times more than that when the diffusion coefficient was $1.9 \times 10^{-8} \text{ m}^2/\text{s}$. Since the diffusion coefficient was mainly affected by the temperature and molten salt composition, increasing the temperature of the electrolyte and the proportion of neodymium fluoride could significantly increase its dissolution rate.

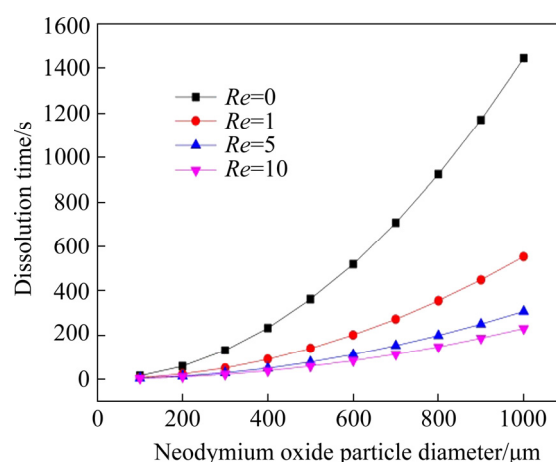


Fig. 6 Neodymium oxide dissolution at different Reynolds numbers

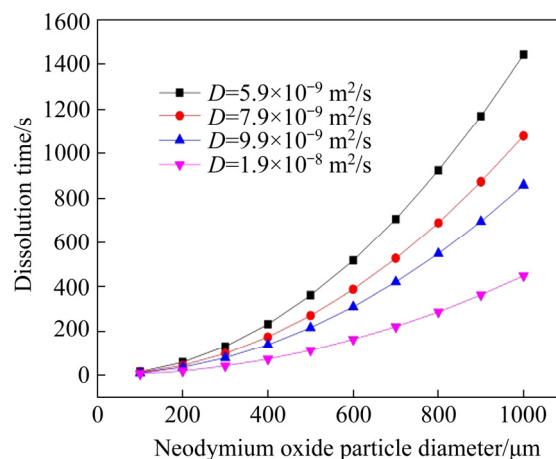


Fig. 7 Neodymium oxide dissolution at different diffusion coefficients

4.3.3 Difference between saturation and initial concentrations

A concentration difference is a driving force for dissolution controlled by mass transfer. Once the initial concentration was fixed, the dissolution process of neodymium oxide was then affected by the saturation concentration under the same other conditions. The influence of the concentration difference between the saturation and initial concentrations was investigated at saturation concentrations of 100, 110, 120, and 130 g/L when the initial concentration was fixed at 0. The result is illustrated in Fig. 8. As the concentration difference between the saturation concentration and initial concentration decreased, the dissolution time of neodymium oxide particles of each particle size increased correspondingly. More specifically, the dissolution time of neodymium oxide particles with a particle diameter of 1000 μm was 1111 s for an electrolyte concentration difference of 130 g/L, while the dissolution time for this particle size increased to 1445 s when the concentration difference was reduced to 100 g/L. However, compared to the diffusion coefficient and Reynolds number, the concentration difference seemed to have less effect on the dissolution time.

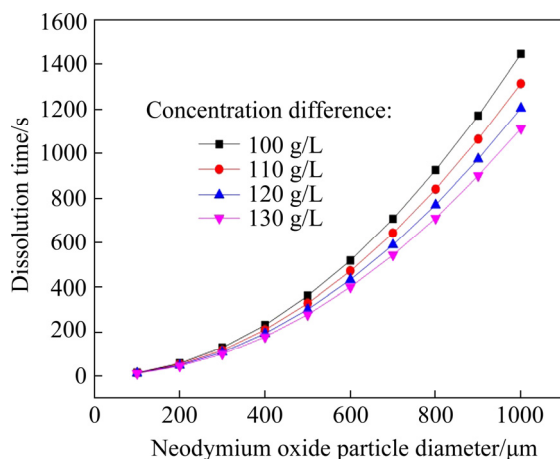


Fig. 8 Neodymium oxide dissolution at different concentration differences

4.3.4 Temperature

The influence of a single factor on the dissolution process of neodymium oxide was already discussed above. Environmental factors may comprehensively affect the dissolution process through multiple variables simultaneously. On the one hand, the temperature of the electrolyte affected the diffusion coefficient of neodymium oxide. On

the other hand, it also determined the saturation concentration of the electrolyte. Data on the solubility and corresponding diffusion coefficient of molten salt with a composition of 23NdF₃–77LiF (molar fraction, %) at temperatures of 1141, 1191, 1241, and 1291 K were obtained from a previous publication [13]. Based on these data, the dissolution time of neodymium oxide with different particle sizes is shown in Fig. 9. The dissolution time of neodymium oxide particles with a particle size of 600 μm at 1141 K was more than four times greater than that at 1291 K. The temperature of molten salt significantly influenced the dissolution time of neodymium oxide, which was consistent with the observed dissolution behavior. Thus, increasing the temperature would be effective to accelerate the dissolution of neodymium oxide in an industrial neodymium cell.

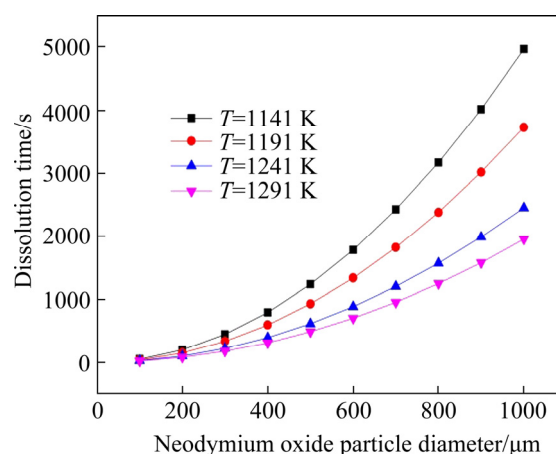


Fig. 9 Neodymium oxide dissolution at different temperatures

4.4 Validation

4.4.1 Single neodymium oxide particle dissolved in static fluid

In a recent study carried out by GUO et al [13], the dissolution behavior of Nd₂O₃ particles in molten fluorides was studied via in-situ CSLM observations. CSLM images of a single dissolving particle were recorded at a rate of 1 frame/s. Since the high-purity molten salt was gradually heated by an external device, the molten salt flow field was relatively stable, and it provided complete single-particle dissolution process data in an infinite stationary medium. The dissolution time of a single neodymium oxide particle at different temperatures and electrolyte compositions was obtained via simulation and compared with the CSLM

experiment results. The results are shown in Table 3. The number of data sets from 1 to 8 was obtained in the melt of $\text{NdF}_3\text{--LiF}$ at different temperatures and compositions, while the number of data sets from 9 to 12 was collected in the melt of $\text{NdF}_3\text{--CaF}_2$ at different temperatures. In the melt of $\text{NdF}_3\text{--LiF}$, the minimum relative error between the simulated results and the CSLM experimental data was 0.97%, and the maximum was 10.55% in data set 8. In the melt of $\text{NdF}_3\text{--CaF}_2$, the minimum relative error was 0.49%, and the maximum was 2.86%. Due to the lack of the diffusion coefficient values of the LiF--5NdF_3 melt at 1241 K, the reference values of LiF--23NdF_3 at 1241 K, which may be the reason for the relative error in data set 8. Nonetheless, the results were still within an acceptable range. Furthermore, most simulated dissolution time was longer than the experimental values. This may have been due to the tiny bubbles generated during the CSLM experiment reported by GUO et al [13], which caused the electrolyte to not be static. This accelerated the dissolution of the neodymium oxide particles. The result comparison proved that the mass transfer solution strategy for neodymium oxide dissolution was effective.

4.4.2 Mass of neodymium oxide particles dissolved in turbulent fluid

To verify the dissolution behavior of neodymium oxide particles in a turbulent molten

salt fluid, the dissolution process with a pulse feeding mass of 3.0 kg neodymium oxide particles was simulated and compared with the experimental results obtained from the commercial neodymium electrolytic cell under the same conditions. The neodymium electrolysis process was processed at 1323 K and the initial concentration of neodymium oxide in the electrolyte was 1.67%. The electrolytic cell structure and details of intermittent sampling are illustrated in Fig. 10 and the geometric size of the electrolytic cell is the same as shown in Fig. 2. The electrolyte was manually scooped out from the electrolytic cell every 20 s. After the electrolyte was cooled, it was crushed for sample preparation and chemical analysis. In this work, the prepared electrolyte samples were dissolved with hydrochloric acid, and the content of neodymium oxide was analyzed according to GB/T 14635—2008. Chemical analysis results and corresponding simulation results are shown in Fig. 11.

Similar to alumina particles, the dissolution process of neodymium oxide was also divided into a fast dissolution stage and a slow dissolution stage. In the simulation, a fast dissolution stage lasted for about 40 s, reaching a concentration of about 2.8%. Then, the concentration curve increased slowly and finally reached a steady-state concentration of 3.7%. According to the experiment curve, the concentration reached about 2.9% at 40 s, which

Table 3 Comparison of CSLM experimental data and simulation results (T is the temperature, c_{sat} is the saturation concentration, D is the diffusion coefficient, r_0 is the initial particle radius, t_{CSLM} is the CSLM-observed dissolution time, t_{simu} is the simulated dissolution time, and δ is the relative error)

No.	Electrolyte	T/K	$c_{\text{sat}}/(\text{mol}\cdot\text{L}^{-1})$	$D/(10^{-10}\text{ m}^2\cdot\text{s}^{-1})$	$r_0/10^{-16}\text{ m}$	t_{CSLM}/s	t_{simu}/s	$\delta/\%$	Ref.
1	LiF--23NdF_3	1141	0.18*	26	233	1210	1174	2.89	[12]
2	LiF--23NdF_3	1141	0.20*	34	312	1486	1449	2.49	[12]
3	LiF--23NdF_3	1191	0.21*	49	309	902	939	4.10	[12]
4	LiF--23NdF_3	1241	0.22*	59	338	851	891	4.70	[12]
5	LiF--20NdF_3	1291	0.20*	49 [▲]	279	772	804	4.14	[12]
6	LiF--15NdF_3	1241	0.15*	49 [▲]	258	900	917	1.89	[12]
7	LiF--10NdF_3	1241	0.14*	49 [▲]	265	1026	1036	0.97	[12]
8	LiF--5NdF_3	1241	0.03*	49 [▲]	235	3439	3802	10.55	[12]
9	LiF--24CaF_2	1241	0.076	15	292	7371	7582	2.86	[13]
10	LiF--24CaF_2	1191	0.075	21	297	5550	5667	2.11	[13]
11	LiF--24CaF_2	1241	0.074	48	169	810	814	0.49	[13]
12	LiF--24CaF_2	1291	0.073	63	323	2263	2296	1.46	[13]

* The solubility values were obtained from a previous publication [11]; [▲] The diffusion coefficient values were the same as those of LiF--23NdF_3 at 1241 K, assuming that they were independent of composition

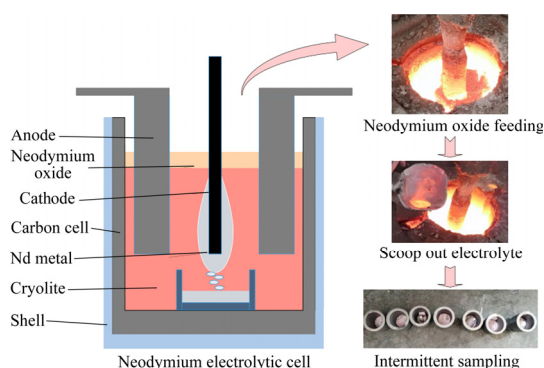


Fig. 10 Schematic diagram of electrolytic cell structure and details of intermittent sampling

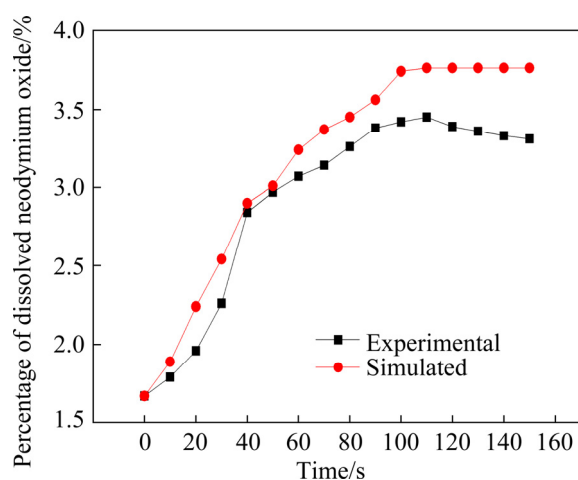


Fig. 11 Comparison between simulated and experimental dissolution curves

was consistent with simulation results. In the second half of the dissolution process, the concentration of neodymium oxide grew much more slowly and finally reached a maximum concentration of 3.3%. Then, it decreased slowly as the electrolysis process progressed. Finally, the time reaching the final concentration was about 120 s.

However, the steady concentration in the experiment was lower than that in the simulation. This might have been caused by the ongoing electrochemical reaction in the electrolytic cell and the neodymium oxide being continuously consumed. On the whole, the experimental data and simulated data were quite consistent, which proved the effectiveness of the MTSS algorithm.

In addition, it should be pointed out that the simulated concentration with small growth speed lasted for a long period at the end of one feeding cycle, because in the simulation, as the dissolution process progressed, the concentration difference

was continuously reduced, resulting in a decrease in the dissolution rate.

5 Conclusions

(1) The dissolution behavior of neodymium oxide was influenced by multiple factors, that is Reynolds number, diffusion coefficient, concentration difference, and temperature.

(2) The temperature of electrolyte comprehensively affects the dissolution process by changing the solubility and diffusion coefficient.

(3) The dissolution time of a single neodymium oxide particle dissolved in static fluid calculated by the algorithm was consistent with CSLM experimental results.

(4) A pulse feeding mass of 3.0 kg neodymium oxide took about 120 s to completely dissolve in a commercial 8 kA electrolytic cell.

(5) Theoretically, the mass transfer solution strategy can be applied to any particles of which dissolution process is controlled by mass transfer. However, further experimental verification will be required to identify whether the solution strategy can be extrapolated to other similar particles in general.

Acknowledgments

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氧化钹在熔融氟化物中溶解过程的建模与仿真

伍昕宇^{1,2}, 刘飞飞¹, 李嘉豪³, 陈鑫宇³, 陈淑梅⁴

1. 江西理工大学 电气工程与自动化学院, 赣州 341000;
2. 江西离子型稀土工程技术研究有限公司, 赣州 341000;
3. 江西理工大学 机电工程学院, 赣州 341000;
4. 江西理工大学 材料冶金与化学学部, 赣州 341000

摘 要: 结合氧化钹传质机制及其溶解动力学规律, 提出一种针对氧化钹溶解过程的求解策略, 以预测氧化钹在复杂流场条件下溶解过程中的浓度变化, 并对影响氧化钹溶解过程的各个因素进行详细分析。针对工业实际中的脉冲加料和连续加料方式对比研究两种给料方式下氧化钹溶解过程的特征。仿真结果表明, 与连续加料方式相比, 采用脉冲加料方式时氧化钹在电解槽内达到均匀分布的时间更快。最后, 将单颗粒氧化钹在静流场条件下的溶解时间与文献结果进行对比, 除仅一组数据的最大误差在 10% 左右外, 其他数据的误差均在 5% 以内。

关键词: 氧化钹; 溶解; 模拟; 传质; 多相流; 熔盐; 电解

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