**ABSTRACT:** Reducing chlorine corrosion to metals at high temperatures is a big problem for many industrial processes. Some high Ni alloys such as Hastelloy C-276 (Ni > 50 wt %) have been widely used for this purpose. Chlorine and chlorides often coexisted in many industrial processes at high temperatures, such as some industrial incinerators and metallurgical furnaces. Thus, a comprehensive experimental investigation regarding the effect of NaCl on the chlorination corrosion of metallic nickel powder by chlorine at a high temperature was performed. It was more convenient to investigate the intrinsic chlorination mechanisms and kinetics of metallic Ni if Ni powder was used instead of a Ni plate. It was found that there existed a critical chlorination temperature of 450 °C for relative safe use of Ni-based alloy in the presence NaCl. The Ni chlorination in the presence of NaCl was increased with increasing temperature and reached a maximum of 97% at 700 °C, which was about 21% higher than that in the absence of NaCl. An anhydrous NiCl$_2$ was initially formed at about 700 °C during the chlorination process and then immediately reacted with NaCl to form a novel eutectic complex with a flaky shape, a melting point of 585 °C, and a simplified molecular formula of NiNa$_{0.33}$Cl$_{2.33}$ based on X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electronic microscopy (SEM), and chemical analysis with inductively coupled plasma atomic emission spectroscopy (ICP-AES). As a result, only the complex of NiNa$_{0.33}$Cl$_{2.33}$ and NaCl was left in the chlorinated product. At 700 °C, the chlorinated product evaporated only in the form of complex NiNa$_{0.33}$Cl$_{2.33}$ instead of individual NiCl$_2$ or NaCl. The chlorination mechanisms of metallic Ni at a high temperature, for example, 700 °C, in the presence of NaCl were as follows. Step 1: Formation of initial chlorinated solid product NiCl$_2$ (mp 1001 °C) at a high temperature; step 2: The NiCl$_2$ reacted with solid additive NaCl (mp 801 °C) to form a final liquid product NiNa$_{0.33}$Cl$_{2.33}$ (mp 585 °C); step 3: External Cl$_2$(g) was dissolved in the liquid product layer; step 4: The chlorine dissolved in the liquid product of NiNa$_{0.33}$Cl$_{2.33}$ reacted with the unreacted Ni core. The external Cl$_2$(g) passed through the liquid product NiNa$_{0.33}$Cl$_{2.33}$ layer faster than the solid product NiCl$_2$ layer formed in the absence of NaCl. This resulted in 21% more chlorination corrosion of metallic Ni powder with NaCl addition than that without NaCl addition.

**1. INTRODUCTION**

Chlorides and chlorine-containing high-temperature environments are common in metallurgical industry, petrochemical industry, incinerators, gas turbines, and marine equipment.1–3 For example, chlorine is widely used in the metallurgical industry to produce TiCl$_4$ and ZrCl$_4$, which are the precursors to manufacture metallic Ti and Zr, respectively. The industrial metallic tubes and furnaces used to produce TiCl$_4$ and ZrCl$_4$ are required to be able to resist chlorine corrosion at high temperatures. In addition, many industries involving high temperatures are located near seashore because they need large amounts of seawater to remove the heat generated during the production processes. Studies have indicated that in the above processes, the chlorine generated by the oxychlorination of NaCl and oxygen at high temperatures is the main source of NaCl-induced hot corrosion.4 Chlorine and chlorides often coexisted in many industrial processes at high temperatures such as industrial incinerators and metallurgical furnaces. It is generally thought that a high nickel content in alloys has a positive influence on the chlorine corrosion resistance at high temperatures, while a high iron content favors the corrosion of alloys.5 Thus, many Ni-based alloys with a high content of nickel (Ni > 50 wt %) such as Hastelloy C-276 have been widely used as transporting tubes in the metallurgical furnaces to extract precious metals such as Au, V, Cu, and rare earth elements from the minerals.5,6 Chlorine and chlorides often coexisted in many industrial processes at high temperatures such as industrial incinerators and metallurgical furnaces. It is generally thought that a high nickel content in alloys has a positive influence on the chlorine corrosion resistance at high temperatures, while a high iron content favors the corrosion of alloys.7 Thus, many Ni-based alloys with a high content of nickel (Ni > 50 wt %) such as Hastelloy C-276 have been widely used as transporting tubes.
in industrial processes such as the manufacture of TiCl4, where hot chlorine and chlorides pass through them. These issues have stimulated the metallurgists to explore the appropriate alloying elements in the Ni-based alloys, which can lead to alloy property improvements in chemical resistance to chlorine corrosion in the presence of chlorides at high temperatures. However, a few studies were performed to investigate the influence of coexisting chlorides on the chlorine corrosion of Ni-based alloys. Thus, this effect was studied in this work.Actually, it was found that the coexisting chloride such as NaCl catalyzed and accelerated the hot chlorination corrosion of metallic nickel and thus enhanced the chlorination percentage significantly based on this work. To exclude the synergistic effect of alloyed elements such as Cr, Mo, V, and Ti on the chlorine corrosion resistance of Ni-based alloys, only pure metallic nickel was used to study its ability to resist chlorine corrosion. The effect of sodium chloride on the chlorine corrosion to pure metallic nickel at high temperatures was studied in this work. To investigate the possible chlorination complex formed due to the interaction between the corrosion product of nickel chloride and sodium chloride and chlorination kinetics more conveniently, nickel powder instead of nickel plate was used in this work. In reality, hot NaCl powder (dust) suspended in the gas phase impacted the Ni plate during hot Cl2 chlorination and thus affected Ni chloride by Cl2. However, such a process cannot be simulated in a laboratory. If a Ni plate was used instead of Ni powder in the laboratory, it was difficult to study the interaction between the chlorinated product NiCl2 of Ni plate and NaCl powder because there was only loose contact between the two. Also, it was very difficult to set up a kinetic model if a Ni plate was used instead of Ni powder. The chlorination kinetics of Ni plate is related to the Ni plate area; thus, the laboratory results regarding the chlorination kinetics might not be applied in industry even if this model can be set up. However, if Ni powder was used instead of a Ni plate, the interaction between the chlorinated product NiCl2 of Ni powder and NaCl powder can occur effectively because the both mixed sufficiently and thus had a good contact. Also, a unconstrained core model in kinetics for gas–solid reaction can be applied. Thus, it was more convenient to investigate the intrinsic chlorination mechanisms and kinetics of metallic Ni if Ni powder was used instead of a Ni plate.

In this work, the anhydrous nickel chloride was initially generated and then reacted with NaCl very quickly to produce a eutectic complex during the hot chlorination of metallic nickel by chlorine in the presence of NaCl at 300−800 °C. Thus, this work also involved the preparation of anhydrous nickel chloride by chlorinating metallic Ni in the absence of NaCl for better understanding the role of NaCl during the chlorination process. The anhydrous nickel chloride has been widely used in producing superfine metallic nickel powder to make the Ni electrode used in manufacturing multilayer ceramic capacitor (MLCC), hard alloys, catalysts, and magnetic materials. The eutectic complex of nickel chloride and sodium chloride has been used to synthesize micro- and nanoparticles of metallic nickel particles of single crystalline structure.

2. EXPERIMENTAL SECTION

2.1. Materials. A commercial nickel powder with a purity of about 99.9% from Beijing General Research Institute of Nonferrous Metals was used as the raw material of metallic Ni. Unless otherwise specified, nickel powder with a particle size of 200−500 ASTM mesh (28−74 μm) was used in this work. Before use, it was placed in a tightly closed glass desiccator filled with some anhydrous calcium chloride. The chemical composition of the powder was analyzed with XRF (XRF-1800, X-ray fluorescence spectrocope, Shimadzu) and a classic chemical analysis method. Both argon (Beijing Haipu Gas Co., Ltd., China) and chlorine (Tianjin Simeite Special Gas Co., Ltd., China) with purities of over 99.99% (v/v) were used in this work. The analytical-grade sodium chloride powder from Sinopharm Chemical Reagent Co., Ltd. was used in this work, whose particle size ranged from 106 to 149 μm. Before use, it was dried at 500 °C for 2 h and then preserved in a tightly closed desiccator filled with some anhydrous calcium chloride.

2.2. Chlorination of Nickel Powder. Chlorination of the nickel powder was carried out in a horizontal tube furnace with split hinge (Figure 1).

Both upper and lower parts of the furnace can be split to observe the chlorinated products through the transparent quartz tube, where the nickel powder was placed. The length of the heating zone of the furnace is 60 cm. About 0.5000−1.5000 g of weighed nickel powder was mechanically mixed with a weighed sodium chloride powder. The solid mixture was then loaded on a quartz boat (position 6 of Figure 1), and the quartz boat was then placed inside the quartz tube with an outer diameter of 48 cm. Then, the quartz tube was inserted into the furnace. The quartz boat was located in the center of the furnace (position 6 of Figure 1). Before heating, argon gas with a flow rate of 50 mL/min was passed through the quartz tube for 30 min to purge the air in the system. Then, the furnace temperature was increased, while the argon gas was maintained at a flow rate of 50 mL/min. When the furnace temperature was increased to a preset temperature and maintained at this temperature for 30 min, the argon gas was switched to dry chlorine for a preset time, which varied according to the requirements of different experiments. After that, the power of the furnace was shut down and the boat was cooled down to room temperature under an atmosphere of argon. The nickel chlorides thus obtained were divided into two parts. One was located inside the quartz boat (position A of Figure 2A), which was referred to as “not evaporated product”. The other was located outside the quartz boat (position B of Figure 2A), which was called as “evaporated product”. Most of the evaporated product was present at the outlet of the quartz tube close to the heating zone and existed in the form of flocus (Figure 2B). These two parts of products were collected, stored in the plastic bags, respectively, and then characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA), X-ray
fluorescence spectrometry (XRF), and chemical analysis, which are described in Section 2.3.

These plastic bags were preserved in a tightly closed desiccator filled with some anhydrous calcium chloride.

2.3. Characterization of Chlorinated Products. To calculate the weight percentage of chlorinated nickel powder, a typical chemical analysis was performed as follows. After one chlorination experiment, the quartz boat was taken out of the tube. The aqueous solution in the first gas-adsorbing bottle (position 7 of Figure 1) and some fresh deionized water were sequentially used to flush the soluble nickel ions sticking on the whole inner walls of the quartz tube (position 4 of Figure 1). The washing solution thus collected was transferred to an Erlenmeyer flask A. The quartz boat was put in a glass beaker B filled with some fresh deionized water. Both the flask A and the beaker B with glass covers were put on an electric heating plate and heated to dissolve the solids composed of the nickel chlorides and the sodium chlorides. After that, the solutions in the flask A and the beaker B were filtered through some Whatmann GF-A membranes, respectively. The filtrates thus obtained were used to determine the concentrations of the dissolved nickel ions using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH). According to the volumes and the Ni\(^{2+}\) concentrations of the filtrates, the weights of Ni ions in the flask A and the beaker B could be calculated, respectively. The nickel ions thus collected in the flask A and the beaker B were referred to as "evaporated chlorinated Ni" and "not evaporated chlorinated Ni", respectively. The totality of both was called as "total chlorinated Ni". The weight percentages of evaporated chlorinated Ni and not evaporated chlorinated Ni can be calculated using the following eqs 1 and 2.

\[
evaporated \text{ chlorinated Ni (wt %)} = \frac{\text{weight of Ni in flask A}}{\text{weight of Ni powder used}} \times 100 \tag{1}
\]

\[
\text{not evaporated chlorinated Ni (wt %)} = \frac{\text{weight of Ni in beaker B}}{\text{weight of Ni powder used}} \times 100 \tag{2}
\]
X-ray diffraction (XRD) patterns of both the evaporated and not evaporated chlorinated products were recorded with a Siemens D5000 X-ray diffractometer equipped with a Cu Kα radiation source (λ = 0.15405 nm). The diffraction patterns of XRD were analyzed using Crystallographica Search-Match software version 2.1.1.0.

The evaporated chlorinated product was observed for the morphology with an SEM (Zeiss EVO 18, special edition) and analyzed for the elemental distribution in the product with the affiliated X-ray energy-dispersive microanalysis (EDX).

The differential thermal analysis (DTA) experiments were conducted in a flowing N₂ atmosphere to measure the melting points of the not evaporated chlorinated products using a DTA instrument (ZCR-1, JMGK, Beijing, China). The temperatures for the DTA experiments ranged from 25 to 1000 °C. The heating rates were all 5 °C/min.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of NaCl Addition on Ni Chlorination

The variations of the evaporated chlorinated Ni, the not evaporated chlorinated Ni, and the total chlorinated Ni with the molar ratio of NaCl to Ni at 700 °C are presented in Figure 3A.

The total chlorinated Ni was 74.5 wt % in the absence of NaCl (Figure 3A). This value was increased with increasing molar ratio of NaCl to Ni in the range of 0–2.0 and reached a maximum of 97.1 wt % at the ratio of 2.0 (Figure 3A). This phenomenon was explained at the end of the text. Then, this value decreased with increasing molar ratio in the ratio range of 2.0–3.0 and reached a plateau in the ratio range of 3.0–6.0 (Figure 3A). Thus, the molar ratio of NaCl to Ni was fixed at 2.0 to achieve a high chlorination for the rest of the experiments.

The total chlorinated Ni values for the NaCl-free Ni powder were 73 ± 0.8, 75 ± 0.8, and 77 ± 0.8% at particle sizes of 50–74, 38–50, and 28–38 μm, respectively (Figure 3B). However, the total chlorinated Ni for the NaCl-added Ni powder were 95 ± 0.8, 96 ± 0.8, and 97 ± 0.8% at particle sizes of 50–74, 38–50, and 28–38 μm, respectively (Figure 3B).

The total chlorinated Ni values for the NaCl-added Ni powder were 95 ± 0.8, 96 ± 0.8, and 97 ± 0.8% at particle sizes of 50–74, 38–50, and 28–38 μm, respectively (Figure 3B). Thus, the chlorination of Ni powder was increased significantly by about 21% due to the NaCl addition. The evaporated chlorinated Ni decreased with increasing molar ratio of NaCl to Ni in the ratio range of 0–1.0 and then reached a plateau in the ratio range of 1.0–7.0 (Figure 3A). It seems that the addition of NaCl suppressed the evaporation of chlorinated products.

The total chlorinated Ni values were 1.4 ± 0.8, 3.3 ± 0.8, 6.5 ± 0.8, 11.8 ± 0.8, 64.0 ± 0.8, 65.5 ± 0.8, 81.0 ± 0.8, 92.1 ± 0.8, 97.1 ± 0.8, 97.4 ± 0.8, and 94.8 ± 0.8% at 300, 350, 400, 450, 500, 600, 650, 680, 700, 750, and 800 °C, respectively, at 2 h for the NaCl-added Ni powder specimens (Figure 3C). Thus, the starting temperature for the chlorination of metallic Ni in the presence of NaCl was 300 °C. The Ni chlorination was low and not more than 12% below 450 °C in the presence of NaCl (Figure 3C). It indicated that metallic Ni can effectively resist the chlorine corrosion below 450 °C even in the presence of NaCl. However, the Ni chlorination showed a sharp increase at 500 °C. There was a critical temperature of 450 °C for relative safe use of Ni-based alloy in the presence of Cl₂ and NaCl. The Ni chlorination increased significantly with decreasing temperature in the temperature range of 500–700 °C and reached a maximum at 700–750 °C (Figure 3C). A high temperature favored the high chlorination according to the reaction kinetics. The chlorination product of metallic Ni in the presence of NaCl started to evaporate at 680 °C (Figure 3C). The amounts of evaporated chlorinated product were 0.00, 1.52 ± 0.8, 15.15 ± 0.8, 34.21 ± 0.8, and 38.30 ± 0.8% at 600, 650, 700, 750, and 800 °C, respectively (Figure 3C).

The total chlorinated Ni increased with increasing chlorine flow rate for the NaCl-added Ni powder specimens and reached a maximum at the flow rate of 200 mL/min (Figure 3D). Thus, the flow rate of Cl₂ was fixed at 200 mL/min to achieve a high chlorination for the rest of the experiments.

After the chlorination at 700 °C for 2 h for the NaCl-added Ni powder specimen, the chloride in quartz tube (Figure 1) was removed by flushing the tube with argon. Meanwhile, the furnace temperature was decreased gradually to room temperature. At room temperature, the not evaporated product in the quartz boat was yellow solid (Figure 4A). When the not evaporated product was heated under an argon atmosphere, the product color changed from yellow to orange with increasing temperature (Figure 4A–D). The color of the not evaporated product was orange at 570 °C (Figure 4C). But at 585 °C, the color of the not evaporated product changed dramatically to deep black (Figure 4E). Meanwhile, it was observed that the not evaporated solid product melted and expanded in volume to form a liquid with a smooth surface at 585 °C (Figure 4E), which was the melting point of the eutectic complex of NiCl₂–NaCl according to the DTA result (Figure 5). The not evaporated product was still black at 600 °C (Figure 4F). The DTA of the not evaporated products were presented in Figure 5. It was found that the melting points of
all of the not evaporated products (not completely presented) were around 585 °C based on the DTA experiment (Figure 5), irrespective of the molar ratio of NaCl to Ni, which was exactly the same as the melting point revealed by visual observation (Figure 4E). Thus, it was inferred that a eutectic complex was formed by the reaction between anhydrous NiCl₂ and NaCl at a high temperature, since the melting point of anhydrous nickel chloride (mp 1001 °C) was much higher than 585 °C. It also indicated that the color of liquid eutectic complex was black, which was quite different from that of the corresponding orange solid. Moreover, the density of black complex liquid was smaller than that of the corresponding orange solid. A control experiment was also performed, in which the nickel powder was chlorinated at 700 °C without the addition of NaCl. An orange chlorinated product was obtained in this case (Figure 4G). However, this product did not melt or change color between 21 and 650 °C (Figure 4G–J). It indicated that only an orange anhydrous nickel chloride NiCl₂ was formed in the absence of NaCl.

The XRD patterns of the not evaporated chlorination product, the evaporated chlorination product, and the standard substance of anhydrous NiCl₂ (JCPDF no. 71-2032) are presented in Figure 6A–C, respectively. Three unknown XRD peaks at 2θ of 15.501, 64.406, and 83.559° from the evaporated product (Figure 6B) were found. These three unknown peaks cannot be found in the XRD patterns of the standard anhydrous NiCl₂ (JCPDF no. 71-2032) (Figure 6C) or standard NaCl. A later investigation indicated that these three peaks were attributed to the anhydrous NiCl₂. Three XRD peaks at 2θ of 15.501, 64.406, and 83.559° from the not evaporated product (Figure 6A) were almost the same as that of the anhydrous NiCl₂ standard (Figure 6C). It indicated that these two peaks were attributed to the anhydrous NiCl₂. Three XRD peaks at 2θ of 31.836, 45.622, and 75.467° were attributed to the NaCl (Figure 6A). Three XRD peaks of the complex NiNa₀.₃₃Cl₂.₃₃ at 2θ of 15.501, 64.406, and 83.559° were also found in the not evaporated product (Figure 6A). The XRD peak of the complex NiNa₀.₃₃Cl₂.₃₃ at 2θ of 15.501° was close to that of the anhydrous NaCl, at 2θ of 15.199° (Figure 6A). The height of the main NiNa₀.₃₃Cl₂.₃₃ peak at 2θ of 15.501° was much larger than the corresponding value of anhydrous NiCl₂ at 2θ of 36.230°. It implied that the content of the complex NiNa₀.₃₃Cl₂.₃₃ from the not evaporated product was much higher than that of anhydrous NiCl₂. In addition, the height of the main NiNa₀.₃₃Cl₂.₃₃ peak at 2θ of 15.501° was close to the corresponding value of NaCl at 2θ of 31.836°. The amount of one phase substance was proportional to the corresponding XRD peak height. Thus, both the complex NiNa₀.₃₃Cl₂.₃₃ and the NaCl were present in the not evaporated product. It indicated that the not evaporated chlorinated product was mainly composed of both the complex NiNa₀.₃₃Cl₂.₃₃ and the NaCl. It implied that the initially formed NiCl₂ has almost completely transformed to complex NiNa₀.₃₃Cl₂.₃₃ by reacting with NaCl.

The evaporated product was further observed with the SEM and analyzed with EDS, XRF, and the classic chemical analysis. The results are presented in Figure 7. The evaporated product consisted of some irregular flaky solids (Figure 7A). The EDS
analysis indicated the existence and the distribution of the elements of Ni, Na, and Cl in the evaporated product (Figure 7B,C). The weight percentages of Cl, Ni, and Na from the evaporated product analyzed by the classic chemical analysis with ICP-AES were 54.26, 38.42, and 4.91 wt %, respectively (Figure 7C). Thus, the molar ratio of Cl, Ni, and Na from the evaporated product was 2.33:1:0.33. Therefore, the simplified molecular formula of the evaporated complex can be written as NiNa$_{0.33}$Cl$_{2.33}$. The molar percentage of NaCl was approximately 25% in this eutectic complex. Thus, the schematic diagram of binary eutectic phases consisting of NiCl$_2$ and NaCl is shown in Figure 7D. The eutectic reactions between NiCl$_2$ and NaCl at 700 °C might be depicted by the following reaction equation:

$$3\text{NiCl}_2(s) + \text{NaCl}(s) = 3\text{NiNa}_{0.33}\text{Cl}_{2.33}(l)$$ (3)

### 3.2. Chlorination Kinetics of Nickel Powder

The weight fraction of total chlorinated Ni, which was denoted as $X$, could be approximately regarded as the weight loss fraction of nickel powder due to the chlorination. If the product layer of nickel chlorides covering the unreacted Ni core did not disappear during the reaction, such a process can be regarded in kinetics as a gas–solid reaction model with an unconstrained core. For such a gas–solid reaction, three kinds of models corresponding to the rate-controlling steps of the external diffusion through stagnant gas, the surface chemistry reaction of the chlorine with the metallic Ni, and the internal diffusion of the chlorine inside the product layer are expressed by eqs 4–6, respectively.

$$X = kt$$ (4)

$$1 - (1 - X)^{1/3} = kt$$ (5)

$$1 + 2(1 - X) - 3(1 - X)^{2/3} = kt$$ (6)

The plots of eqs 4–6 are presented in Figure 8A–C, respectively. The test of Figure 3D was to verify if in reality through Cl$_2$ flux control, the diffusion resistance associated with the stagnant gas film can in this case be neglected. The total chlorinated Ni increased with increasing Cl$_2$ flow rate in the range of 100–200 mL/min and then reached a plateau in the range of 200–250 mL/min (Figure 3D). Thus, the diffusion resistance associated with the stagnant film can be ignored when the Cl$_2$ flow rate was over 200 mL/min. Thus, the Cl$_2$ flow rate was fixed at 200 mL/min for the rest of kinetic experiments. Only the extending lines of the internal diffusion model passed through the zero point with an intercept of zero (Figure 8C) among the three models. Moreover, the plot curves of internal diffusion model were the closest to straight lines based on the linear regression coefficient (Figure 8C) among the three models. Therefore, the internal diffusion was the rate-
controlling step of the gas–solid reaction. It was found that the reaction rate constant (curve slope ($k$)) changed with time and the overall chlorination process underwent two stages (Figure 8C). The first stage (stage 1) and the second stage (stage 2) occurred in the first 60 min and the following 60–120 min, respectively (Figure 8C), and the corresponding internal diffusion rate constants (curve slope) for each temperature were denoted $k_1$ and $k_2$, respectively, and the corresponding reaction activation energies were denoted $E_{a1}$ and $E_{a2}$. The $k_1$ values were 0.0028, 0.0054, and 0.0086 at the temperatures of 600, 650, and 700 °C, respectively (Figure 8C). The $k_2$ values were 0.008, 0.0011, and 0.0033 at the temperatures of 600, 650, and 700 °C, respectively (Figure 8C). Obviously, the $k_1$ value was larger than the $k_2$ value at a certain temperature. In addition, the value of $k_1$ or $k_2$ increased with increasing temperature. The chlorination kinetics of Ni from 1.58 wt % Ni-containing reduced limonite laterite ore by HCl + O$_2$ at 420–460 °C was investigated by Fan et al.$^{23}$ They found that the gas–solid reaction rate was also limited by the internal diffusion process. Moreover, the rate constant of internal diffusion for that work also changed with time and the overall chlorination process also underwent two stages, which were very similar to the phenomena occurred in the present work. However, the first stage of that work ended at about 40 min, which was earlier than the corresponding time of the present work. In addition, the values of $E_{a1}$ and $E_{a2}$ of the present work were 79.4 and 99.0 kJ/mol, respectively (Figure 8D). It indicated that the internal diffusion of the second stage was more difficult than that of the first stage.

The possible reasons for explaining this curve slope change were as follows. The possible mechanisms for the chlorination of metallic Ni by chlorine in the presence of NaCl are presented in Figure 9A. In the first 60 min of the chlorination process (stage 1), only a small amount of chlorinated product of NiCl$_2$ was first formed and then reacted quickly with NaCl to form a final liquid product of NiNa$_{0.33}$Cl$_{2.33}$ (mp 585 °C) at 600–700 °C. However, most of the external surfaces of Ni particles were not covered by the liquid product layer in stage 1 and the internal diffusion of gaseous chlorine inside the liquid product layer proceeded quickly with a high $k_1$ value. After 60 min (stage 1), the external surface of one Ni particle was completely covered by the liquid product layer. The chlorine had to pass through the liquid product layer before contacting the unreacted Ni core in stage 2. In stage 2, the chlorine actually was first dissolved in the liquid product layer and then reacted with the unreacted Ni core. It is well known that chlorine has good solubility in the liquid eutectic of FeCl$_3$–NaCl.$^{24,25}$ Similarly, the gaseous chlorine probably also had good solubility in the liquid eutectic NiNa$_{0.33}$Cl$_{2.33}$. In stage 1, the chlorine passed through the sparse uncovered product layer and directly contacted the unreacted Ni core. In stage 2, the chlorine had to pass through the completely covered product layer of nickel chlorides (NiNa$_{0.33}$Cl$_{2.33}$) before contacting the unreacted Ni core. Thus, the internal diffusion rate constant in stage 2 ($k_2$) was slower than that in stage 1 ($k_1$) (Figure 8D).

In the absence of NaCl, the chlorinated product at 700 °C was solid NiCl$_2$ (mp 1001 °C). More Ni was chlorinated in the presence of NaCl compared to the situation in the absence of NaCl (Figure 3A,B). It indicated that the Ni chlorination rate was faster in the presence of NaCl than that without NaCl addition. Thus, the internal diffusion rate in the presence of NaCl was larger in the presence of NaCl than that without NaCl addition, since the internal diffusion was the rate-controlling step in kinetics. As long as the Ni core was not completely covered by the product layer of nickel chlorides (NiNa$_{0.33}$Cl$_{2.33}$ or NaCl$_2$), Cl$_2$ can directly contact Ni core. Thus, the diffusion rate constant $k_1$ should be close for both the Ni chlorination situations with and without NaCl addition. Therefore, the diffusion rate constant $k_1$ in the case with NaCl addition should be larger than that without NaCl addition, since total diffusion rate constant ($k_1$ plus $k_2$) in the case with NaCl addition was larger than that without NaCl addition. It implied that Cl$_2$ passed through the liquid product NiNa$_{0.33}$Cl$_{2.33}$ layer faster than the solid product NiCl$_2$ layer (Figure 9). It also implied that the substitution of liquid product NiNa$_{0.33}$Cl$_{2.33}$ layer for solid product NiCl$_2$ layer accelerated the transfer of the gaseous Cl$_2$ to contact the unreacted metallic Ni, which in turn accelerated the chlorination of metallic nickel. Thus, NaCl actually acted as a Cl$_2$-transferring catalyst of the Ni chlorination at high temperatures. The catalytic process might be described as follows.

Step 1: Formation of initial chlorinated solid product NiCl$_2$ at a high temperature

$$\text{Ni}(s) + \text{Cl}_2(g) \rightarrow \text{NiCl}_2(s)$$  \hspace{1cm} (7)

Step 2: The initial product NaCl$_2$ reacted immediately with NaCl to form the final liquid product NiNa$_{0.33}$Cl$_{2.33}$ on the surface of one unreacted Ni core

$$3\text{NiCl}_2(s) + \text{NaCl}(s) \rightarrow 3\text{NiNa}_{0.33}\text{Cl}_{2.33}(l)$$  \hspace{1cm} (8)

Step 3: External Cl$_2$(g) was dissolved in the liquid product layer surrounding the unreacted Ni core

$$\text{NiNa}_{0.33}\text{Cl}_{2.33}(l) + \text{Cl}_2(g) \rightarrow \text{Cl}_2(g)/\text{NiNa}_{0.33}\text{Cl}_{2.33}(l)$$  \hspace{1cm} (9)

Step 4: The dissolved Cl$_2$(g) in the liquid product layer reacted with the unreacted Ni core

$$\text{Cl}_2(g)/\text{NiNa}_{0.33}\text{Cl}_{2.33}(l) + \text{Ni}(s) + 0.33\text{NaCl}(s)$$

$$= 2\text{NiNa}_{0.33}\text{Cl}_{2.33}(l)$$  \hspace{1cm} (10)

With the increasing production of NiCl$_2$ during the Ni chlorination process, increasingly more NaCl were consumed to react with NiCl$_2$ to form the eutectic NiNa$_{0.33}$Cl$_{2.33}$. When
most of Ni was chlorinated at 700 °C, a chemical equilibrium was reached. If NaCl was still excess at this time, the product layer of one typical Ni particle will be covered by the remaining solid NaCl (mp 801 °C). This solid barrier will prevent the external Cl₂(g) to contact the unreacted Ni core. This explained why there existed an optimal molar ratio of NaCl to Ni (Figure 3A).

4. CONCLUSIONS
Chlorination of one commercial raw nickel powder by dry chlorine in the presence of NaCl was performed. The chlorinated products were characterized by XRD, SEM, and DTA. The following conclusions can be drawn from the experiments.

(1) The Ni chlorination by chlorine at 700 °C was increased by about 21% due to the NaCl addition.

(2) The starting temperature for the chlorination of metallic Ni by chlorine in the presence of NaCl was 300 °C, and metallic Ni can effectively resist the chlorine corrosion below 450 °C even in the presence of NaCl.

(3) The total chlorinated Ni was increased due to the addition of NaCl. The optimal molar ratio of NaCl/Ni, chlorination temperature, chlorination time, and chlorine flow rate for the nickel chlorination were 2.0, 700 °C, 2 h, and 200 mL/min, respectively, and the total chlorinated Ni was 97% under the optimal conditions.

(4) The internal diffusion of chlorine was the rate-controlling step of the chlorination process. The overall chlorination process underwent two consecutive steps. The first step was approximately in the first 60 min, and the second step was between about 60 and 150 min. The internal diffusion rate constant in the first step (k₁) was larger than that in the second step (k₂).

(5) The produced anhydrous nickel chloride reacted with sodium chloride to form a novel eutectic complex with larger than that in the second step (k₂).

(6) When heated at a temperature over 650 °C, the chlorinated product evaporated mainly in the form of complex NiNa₀.₃₃Cl₂.₃₃ instead of the individual NiCl₂ or NaCl.

(7) The amounts of evaporated chlorinated product were 0, 1.52, 15.15, 34.21, and 38.30% at 600, 650, 700, 750, and 800 °C, respectively.

(8) The NaCl catalyzed the Ni chlorination by accelerating the transfer of gaseous chlorine through the chlorinated product layer to contact the unreacted Ni core.

(9) The XRD peaks attributed to the novel complex NiNa₀.₃₃Cl₂.₃₃ were at 2θ of 15.501, 64.406, and 83.559°.

■ AUTHOR INFORMATION

Corresponding Author
Shaobo Shen — School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China; orcid.org/0000-0002-4775-629X; Phone: +86-10-62332525; Email: shaoboshen@metall.ustb.edu.cn; Fax: +86-10-62332525

Authors
Yuanyuan Chen — School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
Jinlang Gu — School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
Zhen Zhang — School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
Na Li — School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03486

Notes
The authors declare no competing financial interest.

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