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The Conversion of Calcium-Containing Phases and Their Separation with NaCl in Molten Salt Chlorinated Slags at High Temperature

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Abstract: The titanium resources in Panxi reign, China, have a high-impurities content of Ca and Mg, which is usually processed by the molten salt chlorination process. This process allows higher Ca and Mg content in its furnace burdens. However, there is a huge amount of molten salt chlorinated slag produced by this process, consisting of complex compounds and waste NaCl/KCl salts. These slags are always stockpiled without efficient utilization, causing serious environmental pollutions. To recycle the NaCl in the slag back to the molten salt chlorination process, a novel process to deal with those molten salt chlorinated slags with phase conversion at high temperature is presented in this paper. The calcium-containing solid phase was generated when Na_2SiO_3 was added to the molten salt chlorinated slags at high temperature, while NaCl was kept as a liquid. Thus, liquid NaCl was easily separated from the calcium-containing solid phase, and it could be reused in the molten salt chlorination process. The conversion of calcium-containing phases and their separation of NaCl are the key parts of this work, and they have been systematically studied in this paper; thermodynamic analysis, phase transformation behavior, and calcium removal behavior have all been investigated. The calcium removal rate is 78.69% when the molar ratio of $CaCl_2$:Na_2SiO_3 is 1:1.5 at 1173 K and N_2 atmosphere.

Keywords: molten salt chlorinated slag; phases conversion at high temperature; calcium removal rate

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1. Introduction

Titanium is known as a strategic metal and also as the “third metal” [1,2]. Titanium sponge and titanium dioxide chloride are key strategic materials that support the development of modern society [3–5]. $TiCl_4$ is an important intermediate product used for the production of titanium sponge and titanium dioxide chloride from titanium resource. There are two main processes for the production of $TiCl_4$: the boiling chlorination process and the molten salt chlorination process. There are strict demands regarding the impurities Ca and Mg of furnace burden in the boiling chlorination process.

There is a large amount of titanium resources in Panxi reign, China. However, they contain a high-impurities contents of Ca and Mg [6,7], which is usually processed by the molten salt chlorination process in many titanium production enterprises in China [8–10]. This process allows higher Ca and Mg content in its furnace burdens.

However, the largest problem of the current molten salt chlorination technology is the generation of a large amount of waste molten salt [11,12]. Approximately 300–500 kg of molten salt chlorinated slag can be generated as 1 t of $TiCl_4$ is produced. This slag is always stockpiled without efficient utilization, causing serious environmental pollution.

The treatment of molten salt chlorination waste slag has become a serious problems in the molten salt chlorination process.

Currently, there is little research on the treatment and utilization of molten salt chlorinated slag, both domestic and overseas. The main treatment used had been the water-soluble method. In [13–17], scholars first dissolved molten salt chlorinated slag in water and then processed the dissolved solution and filtered slags to recover useful substances Other researchers dissolved molten salt chlorinated slag after some high-temperature roasting [18–23]. The water-soluble method is the main method of treatment for molten salt chloride slag, but currently, research cannot radically solve the problem of molten salt chlorination slag, resulting in lower recycling efficiency, complex processes, and massive secondary waste generation [13].

The composition of molten salt chlorination slag is complex [19,24] because the slag contains a large amount of soluble chloride salts. $CaCl_2$ is a critical impurity that affects the properties of NaCl molten salt [25–27], including density, viscosity, and surface tension. Thus, the removal of $CaCl_2$ from NaCl molten salt is a key problem of the treatment of molten salt chlorination slag.

To recycle the NaCl in the slag back to the molten salt chlorination process, a novel process to deal with those molten salt chlorinated slags with phase conversion at high temperature is presented in this paper. The calcium-containing solid phase was generated when Na_2SiO_3 was added to the molten salt chlorinated slags at high temperature, while NaCl was kept as a liquid. Thus, liquid NaCl is easily separated from the calcium-containing solid phase, and it can be reused in the molten salt chlorination process.

The conversion of calcium-containing phases and their separation of NaCl are the key parts of this work, and they are systematically studied in this paper; thermodynamic analysis, phase transformation behavior, and calcium removal behavior are all investigated.

2. Experimental Materials and Methods

2.1. Experimental Materials

In the study of using pure reagent simulating molten salt chlorination slag to achieve phase conversion and impurity removal, the main chemical reagents used in the experiment were sodium chloride, anhydrous calcium chloride, and anhydrous sodium silicate, which are all chemical analysis reagents. The specifications are as follows.

Sodium Chloride (NaCl): analysis reagent;

Anhydrous calcium chloride ($CaCl_2$): analysis reagent;

Sodium silicate (Na_2SiO_3): SiO_2 44–47%;

The molar ratio of NaCl to $CaCl_2$ content in the raw material is 9:1. The molar ratio of $CaCl_2$ to Na_2SiO_3 is 1:0.5, 1:1 or 1:1.5.

2.2. Experimental Equipment and Methods

2.2.1. Experimental Equipment

The thermodynamic calculation software used in the experiment was Factsage7.0 software, which was purchased by the laboratory. The "Phase Diagram" and "Reaction" modules were used to perform thermodynamic reaction calculations and phase diagram drawing operations. Microsoft Visio was used to perform picture modification.

A high-temperature roasting muffle furnace (Hefei Kejing Material Technology Co., Ltd., Hefei, China, KSL-1400X-A3) was used for the high-temperature phase conversion operation. The experimental temperature range was 973–1273 K. The filter equipment was a self-purchased zirconia honeycomb filter with a pore size of 30 ppi (approximately 0.8 mm).

2.2.2. Experimental Methods

(1) Thermodynamic analysis

In the experiment, Factsage7.0 software was used to calculate the thermodynamics of each substance in the molten salt chlorination slag. The aim of the experiment was to calculate the chemical reaction between the components and the state of the product under the conditions of different temperatures, atmospheres, and component ratios in order to clarify the phase composition of the product and determine whether the conditions were suitable for solid–liquid separation. Through comprehensive analysis, the conditions under which the phase conversion experiment could be carried out were determined.

(2) High temperature phase conversion experiment

The reagents used in the experiment had to be dry and anhydrous because the experimental reagents could easily absorb water. The raw materials were dried in an oven at 383 ± 5 K to a constant weight before the experiment. The experiment was carried out in a high-temperature muffle furnace. The pure reagent used in the experiment simulated the $CaCl_2$ impurity in the molten salt chlorinated slag. In the experiment, a quantitatively mixed sample was placed in a 100 mL corundum crucible and reacted for 1 h at a set temperature.

The specific steps are as follows:

a. The prepared sample is mixed evenly and placed in a 100 mL crucible, Crucible A, for later use.
b. The muffle furnace is heated to the set temperature. The prepared sample is placed in the muffle furnace and reacts at high temperature for 1 h.

(3) High temperature filtration experiment

After the substances are completely reacted, the substances of different phases are separated by a filtration operation, and the schematic diagram of filtration is shown in Figure 1.

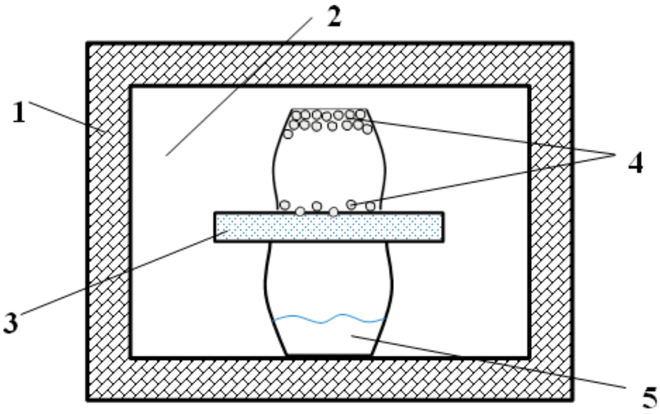

Figure 1. Schematic diagram of high-temperature filtration operation; 1. Muffle furnace; 2. Furnace; 3. Honeycomb filter; 4. Filter slags; 5. Filtrate.

After the experiment, the quality of the filtrate and filter slag are recorded separately. The specific steps are as follows:

a. The honeycomb filter is placed on another crucible, Crucible B, and the crucible is placed in a muffle furnace for preheating for 10 min.
b. In the muffle furnace, Crucible A is placed upside down on Crucible B and allowed to stand for 20 min at a high temperature to ensure it is completely separated.
c. The quality of filtrate and filter slag are weighed and calculated separately.
d. The filtrate and filter slag are sampled after cooling. The phase composition and the content of each element in the sample are tested.

The zirconia honeycomb filter is shown in Figure 2.

2.3. Analytical Method

(1) Phase analysis

All the products involved in this study were tested using an X-ray diffraction analyzer, provided by the Analysis and Testing Centre of the Zhongnan Institute of Mining and Metallurgy. The physical phases were retrieved and analyzed using MDI jade 6.5 software. The resulting data was plotted using Origin 2021 software.

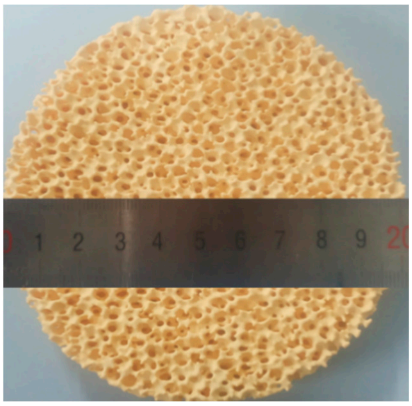

Figure 2. Schematic diagram of ZrO_2 honeycomb filter.

(2) Ca removal rate

The purpose of using Na_2SiO_3 as an additive to perform high-temperature solid-phase conversion of $CaCl_2$ is to separate calcium from NaCl, so as to obtain high-purity NaCl molten salt. Therefore, the research focus was the solution obtained after the solid–liquid separation of the reaction product. Calcium impurity element content was analyzed. The removal rate of calcium before and after the high temperature reaction was calculated. The higher the removal rate, the better the quality of the new molten salt obtained after filtration will be. The calculation formula for the removal rate of calcium is as follows:

$$\eta_{Ca} = \left(1 - \frac{m_1 \times w_{Ca}}{m \times w_{Ca}}\right) \times 100\% \tag{1}$$

In formula 1, w_{Ca} refers to the mass content of calcium in the filtrate after solid–liquid separation, total w_{Ca} refers to the total mass content of calcium in the reactant, and m and m_1 are the masses of raw materials and filtrate, respectively. According to formula 1, the higher the calcium removal rate, the higher the purity of the NaCl molten salt phase obtained in the filtrate will be, which is more conducive to recycling into the molten salt chlorination furnace.

3. Thermodynamic Analysis

The thermodynamic analysis begins with a calculation of the Gibbs free energy for the reaction of calcium chloride with the additive to determine whether Na_2SiO_3 is a suitable additive. The phase diagram of the $NaCl\text{-}CaCl_2\text{-}Na_2SiO_3$ system at different temperatures was then analyzed to clarify the conditions under which the reaction occurs.

3.1. Thermodynamic Reactions of Phase Transformation of Calcium Chloride at High Temperatures

Na_2SiO_3 was used as an additive, and the chemical reaction that could occur between the calcium chloride and the additive in the molten salt chlorination waste was analyzed—(2)–(8). At the same time, the Gibbs free energy of the reaction at different temperatures was calculated to clarify the possibility of the reaction. The result is shown in Figure 3.

$$CaCl_2 + Na_2SiO_3 = CaSiO_3 + 2NaCl \tag{2}$$

$$2CaCl_2 + 2Na_2SiO_3 = Ca_2SiO_4 + 4NaCl + SiO_2 \tag{3}$$

$$4CaCl_2 + 2Na_2SiO_3 + O_2 = 2Ca_2SiO_4 + 4NaCl + 2Cl_2 \tag{4}$$

$$3CaCl_2 + 3Na_2SiO_3 = Ca_3SiO_5 + 6NaCl + 2SiO_2 \tag{5}$$

$$6CaCl_2 + 6Na_2SiO_3 = Ca_6Si_4O_{14} + 12NaCl + 2SiO_2 \tag{6}$$

$$CaCl_2 + 2Na_2SiO_3 + 2SiO_2 = Na_2CaSi_3O_8 + 2NaCl \tag{7}$$

$$6CaCl_2 + 8Na_2SiO_3 = Na_4Ca_4Si_6O_{18} + 2CaSiO_3 + 12NaCl \tag{8}$$

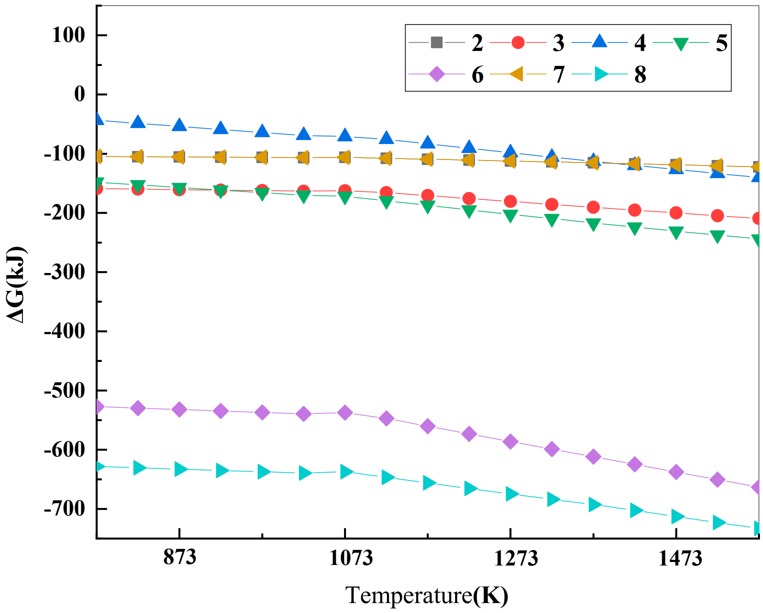

Figure 3. Reaction (2)–(8) Gibbs free energy change with temperature graph.

In the temperature range of 773–1573 K, the ΔG^{θ} of the reaction between Na_2SiO_3 and $CaCl_2$ is less than 0, as shown in Figure 3. This shows that the high temperature phase transformation of Ca in the molten salt system can be realized thermodynamically. In the temperature range of 773–1573 K, all of the reactions (2)–(8) can take place. After the reaction, Ca exists in the form of silicate. At the same time, molten NaCl is generated. $CaCl_2$ reacts preferentially with Na_2SiO_3 at high temperatures, and $Na_4Ca_4Si_6O_{18}$ and $CaSiO_3$ are formed.

3.2. Reaction Equilibrium Phase Diagram Analysis

The thermodynamic ternary phase diagrams of pure substances in the system NaCl-$CaCl_2$-Na_2SiO_3 at a temperature of 1073 K and 1173 K are shown in Figures 4 and 5.

There is 5–10 wt% calcium chloride in typical molten salt chlorinated slags. Thus, the main phases in phase equilibrium at 1073 K of the typical molten salt chlorinated slags are Ca_2SiO_3(s), NaCl(l), and SiO_2(s2), shown in the green area of Figure 5 (the second Figure of phase equilibrium). The NaCl is completely converted to liquid phase in this area and could be completely separated with impurity Ca. When the temperature continues to rise to 1173 K, the main phases in phase equilibrium (the third Figure of phase equilibrium) are similar to those when the temperature is at 1073 K, and complete separation with impurity Ca can be achieved.

Above all, this indicates that the increase in temperature favors the increase in the rate of phase conversion reaction. Starting from 1073 K, NaCl is completely transformed into the liquid phase, which can achieve complete separation from impurity Ca. When the temperature is 1173 K, the reaction efficiency is further promoted to facilitate the separation.

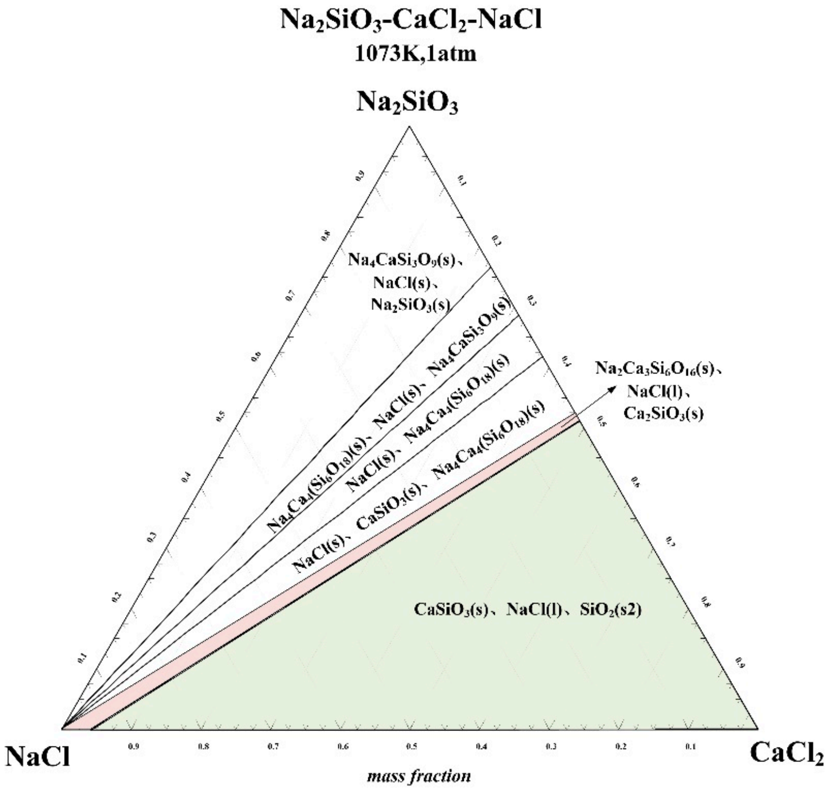

Figure 4. Ternary phase diagram of NaCl-$CaCl_2$-Na_2SiO_3 system at 1073 K. (l—liquid; s—solid; s_X—solid with different crystalline form).

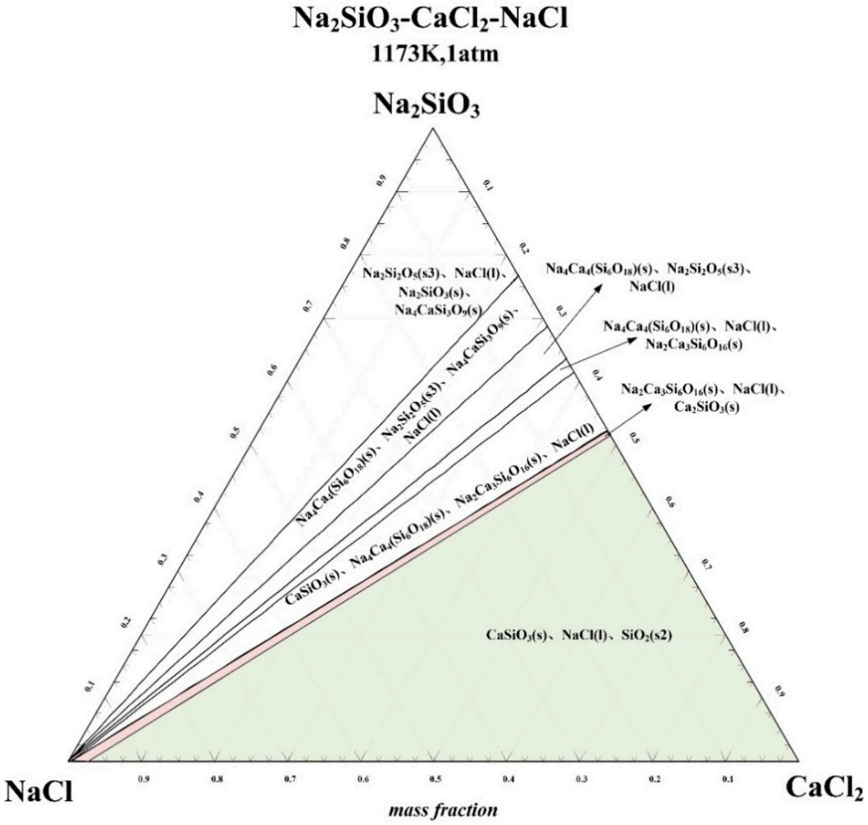

Figure 5. Ternary phase diagram of NaCl-$CaCl_2$-Na_2SiO_3 system at 1173 K. (l—liquid; s—solid; s_X—solid with different crystalline form).

4. Phase Conversion and Removal Behavior of Calcium at High Temperature

The influence of additive dosage, phase conversion temperature, and atmosphere on the high temperature phase conversion of $CaCl_2$ was studied. The influence of different conditions on the phase transformation of the product and the removal of Ca in the actual reaction process is determined. Experiments have determined the most suitable conditions for removing impurities.

4.1. Additive Dosage

By changing the amount of additives used, the phases of the substances in the filtrate after filtration were tested at 1073 K. The influence of the amount of additives on the phase transition of the reaction product was analyzed. When the mass content of $CaCl_2$ in the raw material was 10%, the phases of the filtrate obtained after the high-temperature filtration of samples with different additive usage levels were tested. The results are shown in Figure 6.

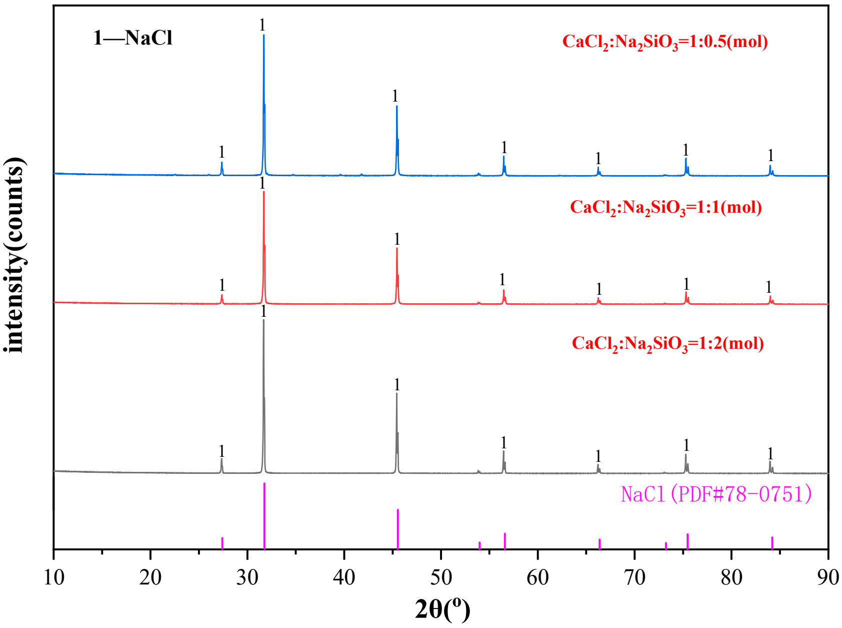

Figure 6. The influence of the amount of additives on the phase of the filtrate.

From the X-ray diffraction analysis pattern of the filtrate, it can be seen that changing the amount of the external additive under different additives has no obvious effect on the phase of the filtrate. The main phase in the filtrate is NaCl, and there is no diffraction peak of other obvious Ca-containing substances. This is because the X-ray diffraction analysis is a semi-quantitative analysis. From the analysis of the content of Ca in the filtrate, it can be seen that there are Ca elements in the filtrate. However, the content is below the detectable limit, which makes it impossible to detect by XRD.

Figure 7 shows the content of Ca in the filtrate at different additive dosages. The content of Ca in the filtrate decreases with the increase in the amount of additives. This is because the increase in the amount of Na_2SiO_3 leads to an increase in the amount of Ca ions consumed during the reaction and an immediate decrease in the amount of Ca ions remaining in the molten salt. When the amount of $CaCl_2$:Na_2SiO_3 molar ratio was 1:1.5, the resulting filtrate contained the least amount of Ca and the new molten salt was of good quality.

The change in the removal rate of Ca of the filtered sample under different additive dosages is shown in Figure 7. When the amount of additives increases, the removal rate of Ca of the sample shows an upward trend. The higher the removal rate of Ca, the higher the quality of the recoverable molten salt will be. However, more additives will introduce Si impurities into the molten salt. In order to ensure the quality of molten salt, the experiment determined that the appropriate amount of Na_2SiO_3 should be selected. The molar ratio of $CaCl_2$:Na_2SiO_3 should be kept between 1:1 and 1:1.5. When achieving a higher Ca removal rate, the quality of the collected molten salt should also be higher.

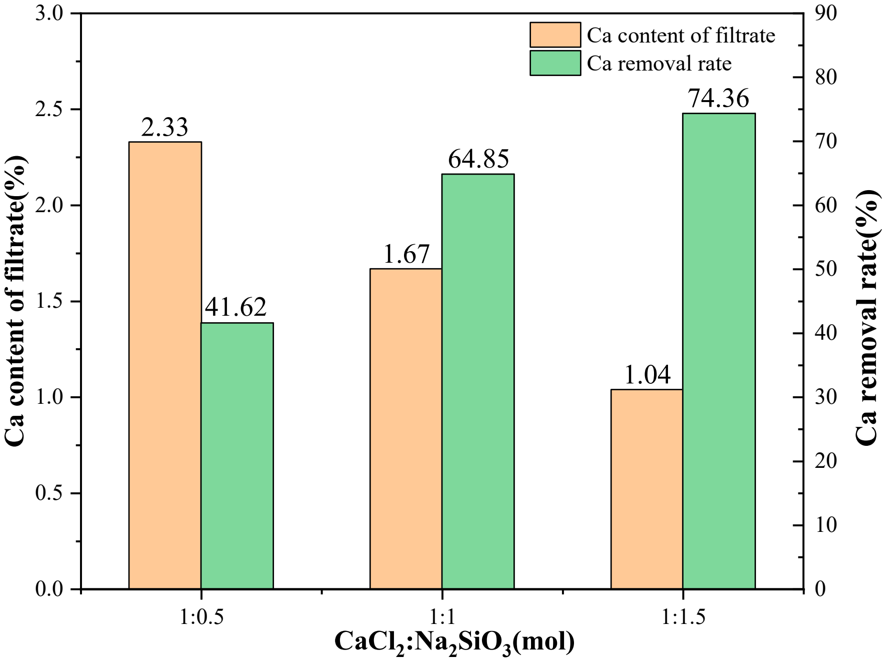

Figure 7. The effect of additive usage on the content of Ca in the filtrate and the effect of additive usage on the removal rate of Ca.

4.2. Phase Conversion Temperature

The influence of temperature on the high-temperature phase conversion rule of $CaCl_2$ in molten salt chlorinated slag was determined. The experiment was carried out under the condition that the content of $CaCl_2$ in the raw material was 10%. The amount of additive $CaCl_2$:Na_2SiO_3 molar ratio was 1:1. The reaction temperature was 1073 K, 1173 K, and 1273 K. The phase detection results of the filtrate are shown in Figure 8.

While changing the reaction temperature, the phase of the filtrate obtained after the phase conversion is basically unchanged, and the chemical substances contained are all NaCl. Due to the properties of molten NaCl, such as high viscosity, surface tension, and wettability, this leads to incomplete solid–liquid separation during filtration.

The Ca content in the filtrate at different temperatures is shown in Figure 9. The Ca content in the filtrate increased from 1.58% to 1.77% and finally changed to 1.30% when the reaction temperature was increased from 1073 K to 1273 K. In the temperature range of 1073–1273 K, the Ca content in the filtrate first increased and then decreased with the increase of additive dosage. When the $CaCl_2$:Na_2SiO_3 molar ratio reached 1:1, the lowest content of Ca in the filtrate was achieved at the reaction temperature of 1273 K.

The Ca removal rate of the process was calculated by measuring the content of Ca in the filtrate after filtration. The experimental results are shown in Figure 9. When the molar ratio of $CaCl_2$:Na_2SiO_3 added was 1:1, the removal rate of Ca showed a trend of first decreasing and then increasing with the increase of the reaction temperature. When the phase conversion temperature was 1173 K, the removal rate of Ca by this process was the smallest. When the phase conversion temperature was 1273 K, the removal rate of Ca reached the maximum.

4.3. Phase Conversion Atmosphere

The effect of phase conversion atmosphere on the high-temperature phase conversion of $CaCl_2$ was investigated. The experiments were carried out at 1173 K. The content of raw material $CaCl_2$ was 10%. Additive amount of Na_2SiO_3 $CaCl_2$: Na_2SiO_3 (mol) is 1:1. The reaction atmospheres were air and nitrogen, respectively.

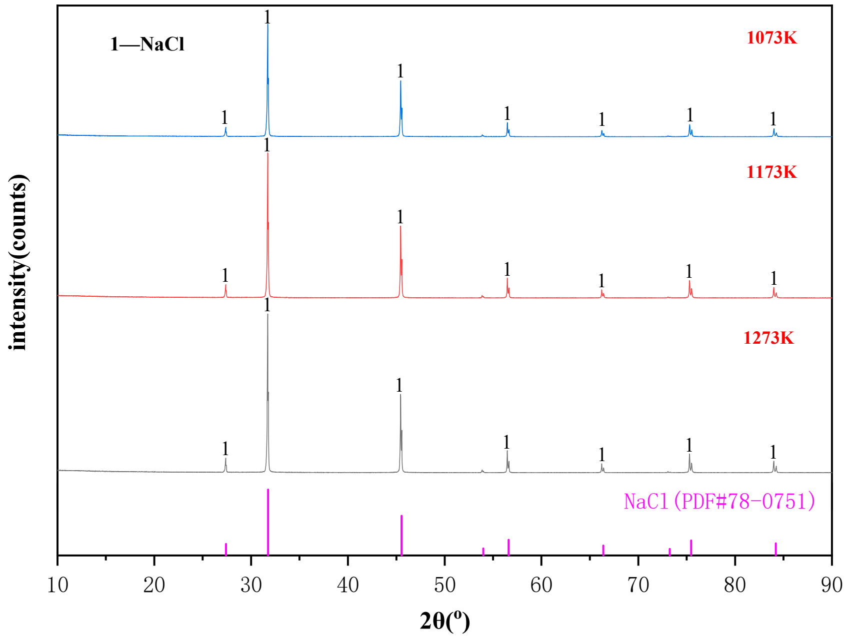

Figure 8. The influence of temperature on the phase transition law of filtrate.

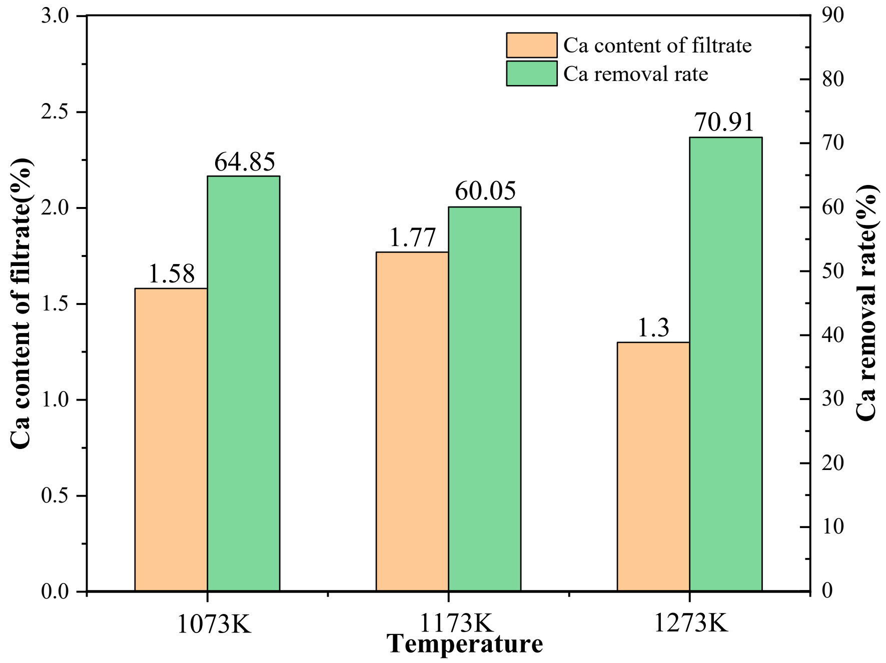

Figure 9. The influence of temperature on the content of Ca in the filtrate and the influence of temperature on the content of Ca in the filtrate.

The filtrates obtained by the filtration operation were examined under different reaction atmospheres to investigate the effect of reaction atmosphere on the phase conversion of the products after phase conversion. The results of the physical phase analysis of the filtrate under different atmospheric conditions are shown in Figure 10. It can be seen that the results of the physical phase detection of the resulting filtrate under different atmospheres were all sodium chloride, which basically did not contain diffraction peaks of other substances, indicating that the phase conversion experiments under N_2 conditions do not affect the quality of the recovered new molten salt.

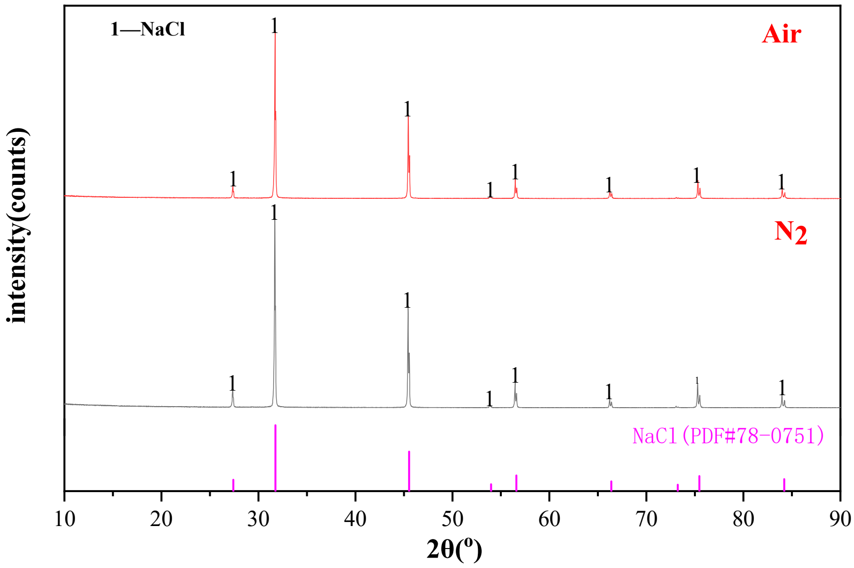

Figure 10. The effect of phase conversion atmosphere on the phase of filtrate.

The calcium content in the filtrate during the phase conversion process was investigated under different atmospheric conditions. The experimental results are shown in Figure 11. When the experimental atmosphere conditions were changed, the Ca content in the filtrate obtained by using N_2 as the reaction atmosphere was significantly reduced compared with that obtained in air atmosphere under the same conditions. At this point, the N_2 was chosen as the experimental condition to obtain the new molten salt with better quality.

The detection of Ca content in the filtrate under different atmospheric conditions showed that the N_2 phase conversion conditions could effectively reduce the content of Ca elements in the filtrate and improve the quality of the recovered new molten salt. The rate of Ca removal under different atmospheric conditions was investigated, and the results are shown in Figure 11. It can be seen that, when the phase conversion removal is performed under air or N_2 conditions, the Ca removal rate under nitrogen atmosphere is higher than that under air atmosphere when the additive content is certain. When the phase change atmosphere was N_2 and the additive $CaCl_2$:Na_2SiO_3 (mol) value was changed from 1:0.5 to 1:1.5, the conversion rate of Ca removal rate reached 78.69%. When the amount of additives used is certain, the Ca removal rate after the filtration operation under N_2 conditions is greater than that under air atmosphere conditions, when the N_2 conditions are selected for the phase transformation atmosphere to maximize the Ca removal rate.

In summary, too much or too little Na_2SiO_3 content will adversely affect the quality of the molten salt obtained. When ensuring the maximum removal rate of Ca, the influence of the addition of Na_2SiO_3 on the experiment should be reduced. In the case of using the same additives, temperature has little effect on the removal rate of Ca. The results of phase conversion filtration experiments under N_2 atmosphere are better than those under air conditions.

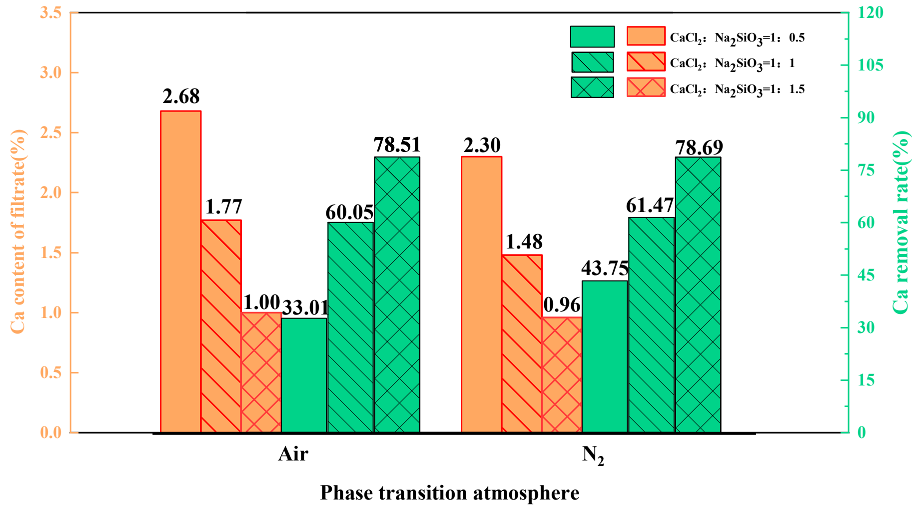

Figure 11. The effect of phase conversion atmosphere on the change of Ca content in the filtrate and the effect of the phase conversion atmosphere on the removal rate of Ca.

5. Conclusions

High temperature phase conversion recycling of molten salt chlorination slag is a clean and efficient method of treating molten salt chlorination slag. The conversion of calcium-containing phases and their separation with NaCl were systematically studied in this paper, including thermodynamic analysis, phase transformation behavior, and calcium removal behavior. $CaCl_2$ can transform to $CaSiO_3$, which is a solid phase, and NaCl is kept as a liquid phase when Na_2SiO_3 was used as an additive at temperatures beyond 1073 K.It was proved in the XRD analysis that $CaSiO_3$ sediment was generated because the phases in the filtrate were almost NaCl. This is the result of adding Na_2SiO_3 to react with $CaCl_2$. The calcium removal rate is 78.69% when the molar ratio of $CaCl_2$:Na_2SiO_3 is 1:1.5 at 1173 K and in N_2 atmosphere. The NaCl obtained in this method could be reused in the molten salt chlorination process.

Author Contributions: Data curation, F.Z.; formal analysis, L.Y.; methodology, F.C.; project administration, F.C.; software, S.W.; supervision, C.L. and Y.G.; validation, Y.W. and H.Y.; writing—original draft, Y.W. and H.Y.; writing—review and editing, Y.G. All authors have read and agreed to the published version of the manuscript.

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