RESEARCH ARTICLE

Mechanistic and Kinetic Analysis of Na$_2$SO$_4$-Modified Laterite Decomposition by Thermogravimetry Coupled with Mass Spectrometry

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Abstract

Nickel laterites cannot be effectively used in physical methods because of their poor crystallinity and fine grain size. Na$_2$SO$_4$ is the most efficient additive for grade enrichment and Ni recovery. However, how Na$_2$SO$_4$ affects the selective reduction of laterite ores has not been clearly investigated. This study investigated the decomposition of laterite with and without the addition of Na$_2$SO$_4$ in an argon atmosphere using thermogravimetry coupled with mass spectrometry (TG-MS). Approximately 25 mg of samples with 20 wt% Na$_2$SO$_4$ was pyrolyzed under a 100 ml/min Ar flow at a heating rate of 10°C/min from room temperature to 1300°C. The kinetic study was based on derivative thermogravimetric (DTG) curves. The evolution of the pyrolysis gas composition was detected by mass spectrometry, and the decomposition products were analyzed by X-ray diffraction (XRD). The decomposition behavior of laterite with the addition of Na$_2$SO$_4$ was similar to that of pure laterite below 800°C during the first three stages. However, in the fourth stage, the dolomite decomposed at 897°C, which is approximately 200°C lower than the decomposition of pure laterite. In the last stage, the laterite decomposed and emitted SO$_2$ in the presence of Na$_2$SO$_4$ with an activation energy of 91.37 kJ/mol. The decomposition of laterite with and without the addition of Na$_2$SO$_4$ can be described by one first-order reaction. Moreover, the use of Na$_2$SO$_4$ as the modification agent can reduce the activation energy of laterite decomposition; thus, the reaction rate can be accelerated, and the reaction temperature can be markedly reduced.

Introduction

Nickel has good plasticity, corrosion resistance and magnetic properties and is widely used in the iron and steel, nickel-based alloy electroplating, and the battery industries. These uses have led to a dramatic increase in the production of nickel in recent years [1]. Nickel can be obtained
from nickel sulfide ores and nickel laterite ores. Although nickel sulfide ores can be treated to make them easier to process to obtain high grade nickel and improve recovery, they are becoming increasingly rare. Therefore, nickel laterite, which composes more than 70% of nickel resources and is easy to mine and transport, has attracted large amounts of attention in recent years and will be the main source of nickel in the future [2].

Nickel laterite ores can be divided into two different types based on their chemical and physical characteristics: saprolitic and limonitic ores [3]. Saprolitic ores contain a heterogeneous distribution of quartz, talc, serpentine, olivine, garnierite and high-grade nickel. Limonitic ores are buried near the ground surface and contain goethite, gibbsite, and chromite [4,5]. However, these nickel laterites cannot be effectively used in physical methods because of their poor crystallinity and fine grain size. Moreover, nickel cannot be identified in laterites by normal X-ray diffraction (XRD) detectors because of their low Ni concentrations and variable distributions. Goethite and silicate minerals (lizardite and olivine) are the Ni host phases [6]. Therefore, effectively upgrading these ores by physical treatment processes can be challenging. To solve this problem, pyrometallurgical production methods have been applied to extract nickel from laterite ores, which can obtain high nickel recoveries [7]. However, because of their high energy consumption and the low accumulation rate of Ni, the use of these methods is limited by low-grade laterite ores and extremely high operating temperatures [8]. Therefore, pre-reduction followed by magnetic separation has been proposed as an easy, low-energy-consumption and environmentally friendly process [9,10]. Laterite contains large amounts of water, which includes water that is adsorbed on the crystals and water in the mineral structure [1,7]. Water makes up 35% of the total quantity of the laterite; thus, laterite must be dried before the pre-reduction process. Moreover, the complex mineral composition of laterite will strongly affect the reduction roasting process. Therefore, studying the decomposition of laterite is important for the pre-reduction of laterite.

Recently, several researchers have focused on the reductive roasting of laterite ore with different reductants, such as carbon, CO or H2, followed by magnetic separation [9,10]. Reductive roasting of laterite can provide high nickel recovery, but the grade of the nickel remains low. Because nickel is hosted in goethite and silicate minerals, something must be added to break the bonds of the silicate and nickel; the nickel can then be easily reduced by a reductant. Therefore, additives such as Na2CO3, S, NaCl and Na2SO4 are used to enhance the enrichment ratio of Ni and reduce the reaction temperature [11,12]. Na2SO4 is the most efficient additive in terms of both grade enrichment and the recovery of Ni. The addition of 10–20 wt% Na2SO4 and 2% wt% coal, which was reduced at 1100–1200°C, resulted in a Ni content of 9.87% and a nickel recovery of 90.90% [11,12]. The Na2SO4 has two main effects: forming low-melting-point FeS to aggregate the ferronickel particles and suppressing the reduction of the ferrous minerals [13]. However, exactly how Na2SO4 reacts with laterite and when the reaction occurs has not been clearly investigated. Considering the potential application of Na2SO4 as a modification agent, the optimal operational conditions of the system should be determined. Based on the discussion presented above, this study investigated the decomposition characteristics of laterite with and without the addition of Na2SO4 using thermogravimetry coupled with mass spectrometry (TG-MS) to explore the effect of Na2SO4 on laterite decomposition. To further explore the reduction-promoting mechanisms of Na2SO4 on laterite ores, we also performed reduction roasting experiments of laterite ores with and without Na2SO4 at different roasting temperature points. The results of this study may provide a reference for the application of additives in related industries.
Materials and Methods

Materials

The feedstock material that was used in this study was a low-grade laterite ore from Indonesia. The as-received sample was ground to a particle size of less than 0.83 mm. Reagent-grade sodium sulfate was selected as the modification reagent. An inductively coupled plasma atomic emission spectrometer (ICP-AES-9000(N+M)), which was a commercial product of Thermo Jarrell-Ash Corp., USA, was used to determine the chemical composition of the materials. A chemical phase analysis was performed to identify the distribution of nickel in the laterite; the results are listed in Table 1.

Table 1 shows the main chemicals and the nickel distribution of the studied laterite, which contained 1.41 wt% Ni, 24.14 wt% Fe, 14.58 wt% MgO, 29.36 wt% SiO2 and 3.15 wt% Al2O3 and thus was a typical saprolite laterite [14]. The nickel was mainly hosted in silicate minerals (84.40%).

Methods

Samples

The laterite ore was mixed with sodium sulfate by mechanical stirring. The content of the sodium sulfate was 20 wt%, and the corresponding samples were denoted by Na2SO4/laterite blend ores. Laterite ore without Na2SO4 was used as the control.

Laterite decomposition

The decomposition of the laterite was carried out using a Setaram SETSYS TGA coupled with a Hiden HPR20 QIC R&D mass spectrometer. Approximately 25 mg of the sample was pyrolyzed under a 100 ml/min Ar flow at a heating rate of 10°C/min from room temperature to 1300°C. The mass loss (TG) and the derivative thermogravimetric (DTG) curves with the temperature were obtained from the results of the experiment [15]. The kinetic study was based on the derivative DTG curves. The evolved gaseous compounds that were generated during the decomposition of the laterite were detected by MS. The different crystalline phases of the ores were determined by XRD using Cu-Kα radiation with a scanning rate of 3°/min from 5°–85° [15].

To ensure the uniformity of the sample and considering the small amount needed for the TG test, three sets of duplicate experiments were performed.

Decomposition of the Na2SO4/laterite blends

The samples of the Na2SO4/laterite blends were subjected to pyrolysis following a process similar to that described in the preceding subsection. MS and XRD were performed. Three sets of duplicate experiments were performed for the TG test.

Table 1. The main chemicals and nickel distribution of the studied laterite (wt%).

| Ni_{total} | Adsorption | Sulfides | Oxides | Silicates |
|-----------|------------|----------|--------|----------|
| 1.41      | 0.03       | 0.07     | 0.12   | 1.19     |
| Fe_{total}| Cr_{2}O_{3} | Al_{2}O_{3} | CaO | MgO | SiO_{2} | P_{2}O_{5} | MnO_{2} | Co | LOI^a |
| 24.14     | 1.08       | 3.15     | 1.46   | 14.58   | 29.36   | 0.018   | 1.46   | 0.065 | 12.95 |

^aLOI: Loss on ignition.
Kinetic analysis

The kinetic parameters were determined by the integral method, which assumed that the decomposition of laterite with and without the addition of Na$_2$SO$_4$ occurred in multiple stages and is a first-order reaction for each stage [16–18]. The following results indicate that this assumption is reasonable. The rate reactions of the solid-state can be then expressed using differential kinetic equations [19–20]. The decomposition reaction of laterite with and without the addition of Na$_2$SO$_4$ was obtained from the literature [18] and is expressed by the following formula:

\[
\frac{d\alpha}{dt} = k(t) \cdot f(\alpha)
\]

(1)

where \(\alpha\) is the decomposition conversion, \(t\) is time, \(k(t)\) is the temperature-dependent rate constant, and \(f(\alpha)\) is a function that represents the reaction model.

The decomposition conversion, \(\alpha\), can be expressed by [18]

\[
\alpha = \frac{W_0 - W_i}{W_0 - W_f}
\]

(2)

where \(W_0\) is the original weight of the test sample, \(W_i\) is the weight at time \(t\), and \(W_f\) is the final weight at the end of the decomposition.

Generally, \(k(t)\) is written as an Arrhenius relation [21]:

\[
k(t) = A \exp\left(-\frac{E}{R T}\right) f(\alpha)
\]

(3)

where \(E\) is the activation energy, \(A\) is the pre-exponential factor, and \(T\) is the temperature.

Because \(\Theta = \frac{dT}{dt}\), which is a constant heating rate, we can rearrange and integrate Eq (3); the integration can then be expressed as follows [22]:

\[
\ln\left[-\ln\left(\frac{1 - \alpha}{T^2}\right)\right] = \ln\left[\frac{AR}{\Theta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}
\]

(4)

Because \(\Theta\) is a constant (10°C/min) during decomposition and the temperature range of laterite decomposition is much larger than \(2RT\) for most values of \(E\), the expression \(2RT/E\) is nearly equal to 0 [16]. Therefore, Eq (4) can be rearranged as follows [19]:

\[
\ln\left[-\ln\left(\frac{1 - \alpha}{T^2}\right)\right] = \ln\left(\frac{AR}{10E}\right) - \frac{E}{RT}
\]

(5)

The straight line that can be obtained from the left side of Eq (5) is plotted versus \(1/T\) because the process can be assumed to be a first-order reaction.

The evolutions of the weight and weight loss rate with increasing temperature were obtained for the decomposition. The weight loss rate was calculated by the following expression [23]:

\[
\frac{dW}{dt} = -\frac{1}{W_0} \frac{dW_0}{dt}
\]

(6)

where \(W_0\) is the original weight of the test sample, and \(W_t\) is the weight at time \(t\).

Reduction experiments

Laterite with 20% Na$_2$SO$_4$ with a combined mass of 100 g was prepared for the reduction process, which was performed in a stirred fixed-bed reactor [9]. After the samples were heated to
the determined temperature (700, 800, or 900°C) under a nitrogen flow rate of 0.7 L/min, a
reaction was achieved by mixing gas (70% H₂ and 30% N₂) at 2.7 L/min for 120 min. The N₂
was used as a protective gas as the reduction process completed until the samples cooled to
room temperature.

The reduced samples were ground to 90 wt% passing 0.043 mm using a rod mill. Then,
approximately 5 g of each ground sample was separated in an XCGS-73 Davies magnetic tube
with a magnetic field intensity of 0.1 T [7]. The final magnetic product consisted of FeNi con-
centrates. The content of Fe and Ni in each sample was determined by chemical analysis. The
recovery rate of Fe and Ni was calculated as described in the literature [9].

The reduced products were analyzed using scanning electron microscopy (SEM; Carl Zeiss
EVO18, Germany) according to the literature [11].

Results and Discussion
Decomposition of laterite with and without the addition of Na₂SO₄

Figs 1 and 2 show the TG and DTG curves of the decomposition of the laterite nickel ore and
the Na₂SO₄/laterite blends, respectively. The weights of both samples decreased with increasing
temperature.

In Fig 1, four obvious stages of mass loss were identified. The first stage reaction occurred
between 34°C and 100°C and included the evaporation of the free water in the laterite. The
second stage was between 238°C and 278°C and was caused by the transformation of goethite ores to iron oxide. The third stage involved the dehydroxylation of kaolinite and serpentine and occurred between 554°C and 602°C. The last stage occurred between 1100°C and 1145°C and involved only 3% of the total mass loss.

In Fig 2, five stages of mass loss were identified. Before reaching 863°C, the weight loss curves of the Na2SO4/laterite blends displayed almost the same trend as those of the laterite, which indicates that they had the same decomposition behavior. At temperatures of 987–1300°C, the TG curves of the Na2SO4/laterite blends decreased sharply compared to those of laterite, which is attributed to the decomposition of Na2SO4; Na2SO4 thus reacted with laterite in this temperature range.

Tables 2 and 3 show the parameters that were obtained from the decomposition experiments, including the initial decomposition temperature ($T_I$), the final decomposition temperature ($T_F$), the corresponding peak temperatures ($T_P$), and the maximum weight loss rates.

Table 2. Characteristic parameters of laterite decomposition (wt%).

| Stage | Decomposition range (°C) | $(dW/dt)_{\text{max}}$ (min$^{-1}$) | Peak temperature (°C) |
|-------|--------------------------|----------------------------------|----------------------|
|       | $T_I$ | $T_F$ |                                  |                      |
| a     | 238  | 278  | -0.1684                           | 268                  |
| b     | 554  | 602  | -0.08106                          | 587                  |
| c     | 1100 | 1145 | -0.01893                          | 1126                 |

Fig 2. Differential thermal analysis–TGA curves for the Na2SO4/laterite blends.

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(dW/dt)\text{max}. From room temperature to 100\(^\circ\)C, free water evaporated from the samples, which made the determination of \(T_1\) difficult \cite{24,25}. Regular decomposition data cannot be obtained until 238\(^\circ\)C; therefore, the initial temperature of decomposition \(T_1\) is defined as 238\(^\circ\)C.

At 600\(^\circ\)C, the weight loss without Na\(_2\)SO\(_4\) is 11.18 wt\%, but with Na\(_2\)SO\(_4\), it is 8.86 wt\%. As Na\(_2\)SO\(_4\) cannot be decomposed at 600\(^\circ\)C and as the initial the initial Na\(_2\)SO\(_4\) content of the Na\(_2\)SO\(_4\)/laterite blend was 20 wt\% Na\(_2\)SO\(_4\), the weight loss of the Na\(_2\)SO\(_4\)/laterite blends was due to the decomposition of laterite alone. Then, based on the weight of the 20 wt\% Na\(_2\)SO\(_4\), we can deduce that the weight loss is 11.08 wt\%, which is similar to the weight loss without Na\(_2\)SO\(_4\).

When the decomposition of the laterite nickel ore is complete at 1300\(^\circ\)C, the volatile content is approximately 14.63 wt\%. The decomposition of the Na\(_2\)SO\(_4\)/laterite blends produces approximately 23.12 wt\% of volatiles under the same experimental conditions.

From room temperature to 890\(^\circ\)C, the laterite and the Na\(_2\)SO\(_4\)/laterite blends have similar corresponding peak temperatures in their DTG curves. At temperatures higher than 897\(^\circ\)C, the decomposition of laterite has only one peak temperature in its DTG curve at 1126\(^\circ\)C, but the Na\(_2\)SO\(_4\)/laterite blends have two peak temperatures at 897\(^\circ\)C and 1252\(^\circ\)C.

### Kinetic characteristics

The values of \(E\) and \(A\) (pre-exponential factor) can be determined by Eq (3) and are shown in Tables 4 and 5, respectively.

Figs 3 and 4 show plots of \(\ln(-\ln(1-\alpha)/T^2)\) versus \(1/T\), respectively. The plots for laterite are similar to those for the Na\(_2\)SO\(_4\)/laterite blends at temperatures between room temperature and 890\(^\circ\)C. However, above 897\(^\circ\)C, laterite behaves differently from the Na\(_2\)SO\(_4\)/laterite blends.

The kinetic parameters are calculated from the characteristic peaks, which were selected from Figs 1 and 2. Thus, these plots can be represented by the main decomposition region. From Figs 3 and 4, the plots of \(\ln(-\ln(1-\alpha)/T^2)\) versus \(1/T\), 7 straight lines can be obtained, which indicated that the laterite decomposition and Na\(_2\)SO\(_4\)/laterite blend decomposition can be classified as a first order reaction. Therefore, the entire decomposition process can be described by one first-order reaction, which is consistent with the results from the literature \cite{16–18}.

The relative activation energies of the decomposition of laterite closely resemble those of the Na\(_2\)SO\(_4\)/laterite blends, which indicates that Na\(_2\)SO\(_4\) did not change the decomposition of

### Table 3. Characteristic parameters of Na\(_2\)SO\(_4\)/laterite blend decomposition (wt\%).

| Stage | Decomposition range (\(^\circ\)C) | (dW/dt)\text{max} (min\(^{-1}\)) | Peak temperature (\(^\circ\)C) |
|-------|---------------------------------|----------------------------------|-------------------------------|
|       | \(T_1\) | \(T_F\) |                              |                                |
| a     | 238    | 278    | -0.1177                       | 268                            |
| b     | 554    | 602    | -0.0562                       | 573                            |
| c     | 892    | 914    | -0.0556                       | 897                            |
| d     | 1241   | 1286   | -0.1368                       | 1252                           |

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### Table 4. Kinetic parameters for laterite decomposition.

| Stage | Temp (\(^\circ\)C) | Conversion range (%) | E (kJ/mol) | A (min\(^{-1}\)) | \(R^2\) |
|-------|--------------------|----------------------|------------|-----------------|---------|
| a     | 238–278            | 25.88–42.43          | 87.13      | 2.83×10\(^5\)  | 0.9947  |
| b     | 554–602            | 70.44–81.18          | 123.63     | 9.75×10\(^4\)  | 0.9927  |
| c     | 1100–1145          | 94.77–97.21          | 145.66     | 2.82×10\(^5\)  | 0.9999  |

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laterite between room temperature and 897°C. The melting point of Na$_2$SO$_4$ is 884°C [26], which is very close to 897°C. As the solid-state reaction requires more energy than the solid-liquid heterogeneous reactions [27], when the Na$_2$SO$_4$ begins to melt, it can accelerate the reaction of Na$_2$SO$_4$ with laterite. Therefore, the temperature of 897°C, which yields one of the fastest reaction rates, is very close to the melting point of Na$_2$SO$_4$.

However, above 897°C, the Na$_2$SO$_4$/laterite blends are different from laterite, which undergoes only one reaction with a relative activation energy of 145.66 kJ/mol. In the presence of Na$_2$SO$_4$, there are two reaction processes with relative activation energies of 108.50 and 91.37 kJ/mol.

Li et al. reported a lower melting point in the presence of Na$_2$SO$_4$, which could lead to the precipitation of larger particles [12]. Therefore, Na$_2$SO$_4$ significantly influences laterite decomposition through direct involvement and by changing the mechanism. Although adding Na$_2$SO$_4$ cannot change the reaction order, it can reduce the activation energy of laterite decomposition; thus, the reaction rate could be accelerated, and the reaction temperature could be markedly reduced.

Decomposition mechanism

**Laterite decomposition mechanism.** To identify the mechanism of laterite decomposition, the laterite ores were roasted under a 100 ml/min Ar flow for 4 h at temperatures of 87°C, 268°C, 587°C, and 1126°C.

The phase of the roasted ores can be elucidated from the XRD patterns (Fig 5), and the volatile component was analyzed by TG-MS. The variations in the H$_2$O content during the thermal decomposition of laterite with and without the addition of Na$_2$SO$_4$ are shown in Figs 6 and 7, respectively.

Figs 1, 5 and 6 show that the decomposition process of laterite can be divided into four stages. The first stage (34°C<T<100°C) included the evaporation of the free water in the laterite. In the second stage (238°C<T<278°C), the goethite phase disappears after being roasted.

### Table 5. Kinetic parameters for the decomposition of Na$_2$SO$_4$/laterite blends.

| Stage | Temp (°C) | Conversion range (%) | $E$ (kJ/mol) | $A$ (min$^{-1}$) | $R^2$ |
|-------|-----------|----------------------|--------------|-----------------|-------|
| a     | 238–278   | 9.88–17.50           | 66.35        | 2.77×10$^5$     | 0.9968|
| b     | 554–602   | 29.57–34.19          | 109.58       | 1.43×10$^5$     | 0.9939|
| c     | 892–914   | 41.50–43.68          | 108.50       | 2.58×10$^5$     | 0.9930|
| d     | 1241–1286 | 89.09–99.24          | 91.37        | 4.14×10$^6$     | 0.9832|

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![Fig 3. Plots of ln(−ln(1−α)/T²) vs. 1/T for laterite decomposition recalculated by the multi-step integral method. (a), 238–278°C; (b), 554–602°C; (c), 1100–1145°C.](https://doi.org/10.1371/journal.pone.0157369.g003)
Fig 4. Plots of $\ln(-\ln(1-\alpha)/T^2)$ vs. $1/T$ for Na$_2$SO$_4$/laterite blend decomposition recalculated by the multi-step integral method. (a), 238–278°C; (b), 554–602°C; (c), 892–914°C; (d), 1241–1286°C.

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Fig 5. XRD patterns of laterite ores roasted under Ar at different temperatures. (a) raw ore, (b) 87°C, (c) 268°C, (d) 587°C, (e) 1126°C.

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under Ar flow for 4 h (Fig 5B). Jang et al. investigated the transformation process of goethite ores to pure iron and found that water was released from the ores at low temperatures [28]. Our results show that water was the main volatile component in the second stage (Fig 6), which is consistent with results from the literature [28]. This process can be expressed by Eq (7):

$$2\alpha-\text{FeOOH}(s) = \alpha-\text{Fe}_2\text{O}_3(s) + \text{H}_2\text{O}(g)$$ (7)

As a result, new crystalline phases ((Fe,Ni)$_2$SiO$_4$, (Mg,Ni)SiO$_3$, (Fe,Ni)$_2$SiO$_4$, (Fe,Ni)SiO$_3$, SiO$_2$, Al$_2$Si$_2$O$_7$) formed (Fig 5C) during laterite decomposition at 587°C for 4 h, and the main volatile component was H$_2$O (Fig 6). The water was produced by the dehydroxylation of kaolinite and serpentine at temperatures between 554°C and 602°C [29]. The process can be expressed by the following formulas:

$$2(\text{Mg}, \text{Fe}, \text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4 = (\text{Mg}, \text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4 + (\text{Fe}, \text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4$$ (8)

$$2(\text{Mg}, \text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4 = (\text{Mg}, \text{Ni})_2\text{SiO}_4 + (\text{Mg}, \text{Ni})\text{SiO}_3 + 2\text{SiO}_2 + \text{H}_2\text{O}$$ (9)

$$2(\text{Fe}, \text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4 = (\text{Fe}, \text{Ni})_2\text{SiO}_4 + (\text{Fe}, \text{Ni})\text{SiO}_3 + 2\text{SiO}_2 + \text{H}_2\text{O}$$ (10)

$$\text{Al}_2\text{Si}_3\text{O}_7(\text{OH})_4 = \text{Al}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}$$ (11)
The mechanism of laterite decomposition in the fourth stage (1100°C < T < 1145°C) has not been determined in the literature. MS was used to identify the main volatile component in this temperature range, and the roasted sample, which was roasted under Ar flow for 4 h at 1126°C, was analyzed with XRD to identify the main component of the decomposition of the laterite. Fig 5D shows that CaO and MgO were identified as the new phases. CO₂ was determined to be the main volatile component by MS at temperatures between 1100 and 1145°C (Fig 8). Dolomite is a component of laterite [4]. Yoshida et al. investigated the decomposition of dolomite ores to CaO and MgO and found that CO₂ was released from the ores [30], which is consistent with our observations. However, our results partially contradict those reported by Conesa et al., who found that the primary decomposition temperature of dolomite was 780–800°C during the gasification and pyrolysis of Posidonia oceanica in the presence of dolomite [31]. Presumably, this difference was caused by the dispersion of dolomite in the laterite and the interaction with the laterite complex. The reaction [31] in the fourth stage of our study can be expressed by

\[
\text{Ca, Mg(CO}_3\text{)}_{2}^{1126\degree\text{C}} \rightarrow \text{CaCO}_3 + \text{MgCO}_3
\]  

(12)

\[
\text{Ca, Mg(CO}_3\text{)}_{2}^{1126\degree\text{C}} \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2
\]  

(13)
At temperatures between room temperature and 890°C, water was the product of laterite decomposition, which caused approximately 92% of the total mass loss. At temperatures above 890°C, the main volatile component was CO₂, which caused only 3% of the total mass loss.

Decomposition mechanism of the Na₂SO₄/laterite blends

To identify the mechanism of decomposition of the Na₂SO₄/laterite blends, the samples of the Na₂SO₄/laterite blend ores were roasted under a 100 ml/min Ar flow for 4 h at temperatures of 87°C, 268°C, 573°C, 897°C, and 1252°C.

Fig 9 shows the phase of the roasted ores, which were roasted under a 100 ml/min Ar flow for 4 h at temperatures of 84°C, 268°C, 573°C, and 897°C, as elucidated from the XRD patterns. The volatile component was analyzed by TG-MS. Fig 7 shows the variation in the H₂O content during the thermal decomposition of the Na₂SO₄/laterite blends.

Figs 2, 7 and 9 show that the decomposition of the Na₂SO₄/laterite blends can be divided into five stages. The decomposition ranges of the Na₂SO₄/laterite blends are similar to those of the laterite in the first three stages, and H₂O is the volatile component. Therefore, the first three stages are similar to the decomposition process of the laterite ores, which suggests that Na₂SO₄ does not affect laterite decomposition below 700°C. Increasing the roasting temperature to 892°C results in a sharp decrease in the amounts of the Na₂SO₄/laterite blends; a weight loss of approximately 14 wt% occurred between 897°C and 1300°C, where the laterite had experienced a weight loss of approximately 1 wt%. It can be inferred that Na₂SO₄ has a significant impact on the decomposition of laterite at temperatures above 897°C.
To determine whether the weight loss was caused by the Na$_2$SO$_4$ decomposition itself, pure Na$_2$SO$_4$ was heated under a 100 ml/min Ar flow from room temperature to 1300°C by TG-MS. Reagent-grade Na$_2$SO$_4$ was pyrogenated via thermogravimetric analysis, and no significant decomposition of Na$_2$SO$_4$ was observed. The result indicates that the mass loss of the Na$_2$SO$_4$/laterite blends cannot be due to Na$_2$SO$_4$ decomposition alone. Freyer et al. investigated the phase diagram of the Na$_2$SO$_4$—CaSO$_4$ system and found that Na$_2$SO$_4$ cannot be decomposed until 1404°C [32], which indicates that the mass loss of Na$_2$SO$_4$/laterite blends cannot be caused by only Na$_2$SO$_4$ decomposition. In addition, SO$_2$ was detected by MS (Fig 10) along with the emitted CO$_2$ beginning at 892°C. Based on the MS fragmentation intensities of CO$_2$ during the thermal decomposition of the Na$_2$SO$_4$/laterite blends (Fig 11), the initial temperature of CO$_2$ emission is 897°C, which is 200°C lower than the decomposition temperature of the laterite.

The roasted products of the Na$_2$SO$_4$/laterite blends, which were roasted at 897°C for 4 h, were detected by XRD. CaO and MgO were found in the roasted residue (Fig 9). Gunasekaran et al. investigated the thermal decomposition of natural dolomite and found that the decomposition temperature of dolomite is 600–850°C [33], which indicates that in the presence of Na$_2$SO$_4$, the decomposition temperature of dolomite can be reduced to nearly the decomposition temperature of natural dolomite. Lu et al. investigated the reduction of prepared nickel laterite ore by H$_2$. The experiments were conducted at 800°C with the addition of 20 wt% Na$_2$SO$_4$ and obtained a maximum nickel content of 5.63% and a nickel recovery of 83.59% [9], which indicates that the pyrometallurgical operating temperature can be reduced to a range of 892–1080°C in the presence of Na$_2$SO$_4$, which is approximately 200°C lower than in the conventional process [7]. Therefore, in the fourth stage (897°C<T<914°C), it can be inferred that dolomite can be decomposed in the presence of the Na$_2$SO$_4$ in this temperature range. The process is described in the literature [9,32] and can be expressed as Eq (12) and Eq (13).

Nevertheless, it is worth investigating whether the CaO, which decomposed from the dolomite, can affect the emission of SO$_2$, as the CaO can react with SO$_2$ to form CaSO$_3$. Cubicciotti et al. investigated the thermal decomposition of CaSO$_4$ and its enthalpy of formation and found that CaSO$_3$ decomposed in the temperature range of 500–550°C [34]. Therefore, CaSO$_3$ could not stably exist between 897°C and 914°C. In addition, the content of dolomite in the
laterite ores was low and the amount of CaO released would be low. Therefore, the presence of CaO would have little influence on the emission of CO₂ and SO₂.

In the last stage (1241°C < T < 1286°C), CO₂ and SO₂ were the main volatiles of the decomposition of the Na₂SO₄/laterite blends (Fig 10). Based on the products of the fourth stage of the decomposition of the Na₂SO₄/laterite blends, CO₂ may be generated by the decomposition of the dolomite. Lu et al. investigated the standard Gibbs free energy and temperature diagram and found that SO₂ was released from the ores at temperatures above 727°C [9]. Our results show that Na₂SO₄ reacted with laterite and emitted SO₂, which was consistent with results that have been reported in the literature [9].

To determine what occurs when Na₂SO₄ reacts with laterite, the decomposition products, which were roasted at 1252°C for 4 h, were analyzed by XRD (Fig 12). (Mg,Ni)₂SiO₄, (Mg, Ni)₂SiO₄, (Fe,Ni)₂SiO₄ and (Fe,Ni)₂SiO₄ disappeared (Fig 9D), and several new phases formed, such as (Mg,Na)₂SiO₄, Na₂SiO₃, (Mg,Na)₂SiO₄ and Na₂SiO₃. Li et al. investigated the purification of nickeliferous laterite by reduction roasting in the presence of sodium sulfate and found that sodium sulfate can liberate Fe and Ni from lizardite and leave behind an Mg-rich olivine phase [12]. The results of this study show that the main residue of the Na₂SO₄/laterite blends under 1252°C in the last stage were consistent with those that have been reported in the literature [12]. Therefore, Na₂SO₄ reacted with (Mg,Ni)₂SiO₄ and (Mg,Ni)₂SiO₄, and a considerable amount of Na⁺ then replaced Ni²⁺ in (Mg,Ni)₂SiO₄ and (Mg,Ni)₂SiO₄. Meanwhile, the free Ni²⁺ formed NiO, which is beneficial for the ensuing nickel enrichment.

Mobin et al. found that transition-metal carbides interact with Na₂SO₄ to form a soluble sodium metal oxide or a metal sulfide depending upon the local conditions during the high
temperature reaction [35]. Our research shows that the Na₂SO₄/laterite blends reach the molten state after roasting at 1252°C for 4 h, which is consistent with results from the literature [12].

Alkali ions preferentially take up next-nearest neighbor positions with respect to tetrahedral Fe³⁺ ions [36]. In our study, the Na⁺ replaced Fe³⁺ and Mg²⁺ in (Mg,Ni)₂SiO₄ and (Mg, Ni)₂SiO₄ to form Na₂SiO₃. Composite materials with mixed spinel nickel ferrite–barium titanate as co-existing phases can be synthesized [37]. Therefore, the Fe₂O₃, NiO and MgO that are released from (Mg,Ni)₂SiO₄ and (Mg,Ni)₂SiO₄ then react and form MgFe₂O₄ and NiFe₂O₄ (Eqs 14, 19 and 20). At the same time, Na⁺ replaces some of the Al³⁺ in the Al₂Si₂O₇ and forms NaAlSiO₄ (Eq 17). O’Neill et al. experimentally investigated the effect of the melt composition on trace element partitioning based on the activity coefficients of FeO, NiO, CoO, MoO₂ and MoO₃ in silicate melts and found that the activity coefficients of FeO, NiO and CoO vary by a factor of two over the same range of melt compositions [38]. In this study, we found that all of the materials combine to form a hard low-melting-point amorphous substance at high temperature with some alkaline metals. In the last stage of the laterite with and without the addition of Na₂SO₄, this mechanism is supported by the phase composition of the decomposition products (Fig 12) and the MS fragmentation intensities of SO₂ during the decomposition at temperatures between 1241 and 1286°C (Fig 10). Therefore, the mechanism of laterite decomposition by Na₂SO₄ involved reacting some of the Na₂SO₄ with the calcined laterite ores, which resulted in laterite decomposition and the release of Ni²⁺ from the laterite and is beneficial for nickel

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**Fig 11.** MS fragmentation intensities of CO₂ during thermal decomposition of the Na₂SO₄/laterite blends. doi:10.1371/journal.pone.0157369.g011
enrichment. This process can be expressed as follows:

\[
(Mg, Ni)_2SiO_3 + Na_2SO_4 = (Mg, Na)_2SiO_4 + 2NiO + SO_2(g)
\] (14)

\[
(Mg, Ni)_2SiO_3 + Na_2SO_4 = Na_2SiO_3 + 2MgO + 2NiO + SO_2(g)
\] (15)

\[
(Fe, Ni)_2SiO_3 + Na_2SO_4 = (Fe, Na)_2SiO_4 + 2NiO + SO_2(g)
\] (16)

\[
(Fe, Ni)_2SiO_3 + Na_2SO_4 = Na_2SiO_3 + 2FeO + 2NiO + SO_2(g)
\] (17)

\[
Al_2SiO_3 + Na_2SO_4 = 2NaAlSiO_4 + SO_2(g)
\] (18)

\[
Fe_2O_3 + MgO = MgFe_2O_4
\] (19)

\[
Fe_2O_3 + NiO = NiFe_2O_4
\] (20)

Reduction results

Reduction roasting-magnetic separation of the laterite with/without Na_2SO_4. In the absence of Na_2SO_4, hydrogen reduction roasting-magnetic separation was conducted at 700, 800 and 900°C. The other experimental conditions were fixed, including the reducing time of 120 min, the gas rate of 2.7 L/min (H_2:70%, N_2:30%), grinding fineness of 90 wt% passing 0.043 mm and magnetic field intensity of 0.1 T. Fig 13 shows that the grade and recovery of Ni
increases with increasing roasting temperature from 700 to 900°C. However, only a maximum of 1.61% Ni grade with recovery of 45.09% Ni is achieved at 900°C.

When the nickel laterite ore with the addition of 20 wt% Na₂SO₄ was reduced at 700, 800 and 900°C for 120 min, the Ni grade increased from 2.06% to 6.01% and the recovery of Ni increased from 58.29% to 100% from 700°C to 900°C, as shown in Fig 14. The roasting reduction temperature of the commercially existing pyrometallurgical process for nickel from nickel
laterite is 1250–1400°C [12]. Therefore, in terms of operating temperature, the reduction in operating temperature to 900°C in the current work is an advantage.

**SEM analysis.** To reveal the effects of the Na$_2$SO$_4$ on the beneficiation of laterite ore, the reduced products were analyzed by SEM. The microstructure of the roasted ore (with/without Na$_2$SO$_4$) at different temperatures are shown in Fig 15.

Fig 15(A)–15(C) show the general microstructure of the roasted ores of laterite. The structure of the roasted ore is loose with a dispersed metallic mineral distribution. Furthermore, the roasted ore of Na$_2$SO$_4$/laterite blends exhibits a saponaceous surface and a compact structure as shown in Fig 15D–15F, which indicates that the roasted ore is molten with Na$_2$SO$_4$ during the reduction process [13]. The molten phase is beneficiated to achieve rapid grain coarsening and a higher concentration of Ni [9–12].

**Conclusions**

The results of this study can be summarized as follows:

1. The decomposition of laterite can be divided into four stages: water evaporation, goethite decomposition, kaolinite and serpentine dehydroxylation, and dolomite decomposition with CO$_2$ as the main volatile component. The activation energies for the different stages were 45.64 kJ/mol, 87.13 kJ/mol, 123.63 kJ/mol and 145.66 kJ/mol, respectively.

2. The decomposition of Na$_2$SO$_4$/laterite blends can be divided into five stages. The decomposition process is similar to that of laterite blends at 700°C. However, dolomite decomposed at 200°C lower than the temperature at which laterite decomposed in the fourth stage, and the activation energy was 108.50 kJ/mol. In the final stage, laterite decomposed in the presence of Na$_2$SO$_4$ and emitted SO$_2$ with an activation energy of 91.37 kJ/mol.
3. Kinetic analyses revealed that the decomposition of laterite with and without the addition of Na$_2$SO$_4$ in an argon atmosphere can be described by one first-order reaction. However, Na$_2$SO$_4$ significantly influences laterite decomposition through direct involvement and can reduce the activation energy of laterite decomposition; thus, the reaction rate can be accelerated, and the reaction temperature can be markedly reduced.

4. The mechanism of the decomposition of Na$_2$SO$_4$/laterite blends may involve the reaction of Na$_2$SO$_4$ with laterite and the consequent decrease in the laterite decomposition temperature. Na$^+$ was then replaced with Ni$^{2+}$, which is an isomorphic host in the lattice of (Ni, Mg)$_2$SiO$_4$. Ni$^{2+}$ was released and reacted with O$^2-$ to form NiO, which facilitated nickel enrichment through the ensuing reduction. At the same time, Na$_2$SO$_4$ reacted with Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$ to form low-melting-point compounds.

5. The roasted ore with the addition of Na$_2$SO$_4$ exhibits a compact structure and can be formed in the molten phase with Na$_2$SO$_4$ during the reduction process. The molten phase is beneficiated to achieve rapid grain coarsening and a higher concentration of Ni. Moreover, the pyrometallurgical operating temperature can be reduced to a range of 892–1080°C in the presence of Na$_2$SO$_4$, which is approximately 200°C lower than in the conventional process.

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Author Contributions
Conceived and designed the experiments: SY WGD. Performed the experiments: PZS. Analyzed the data: SJL CHZ. Contributed reagents/materials/analysis tools: PC QZ HLF. Wrote the paper: SY JSG.

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