Study on Reductive Smelting of High-Iron Red Mud for Iron Recovery

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Abstract: In this paper, the characteristics and current problems associated with red mud and the progress of research on iron extraction from high-iron red mud are briefly described. By adding conditioning materials to red mud and quenching and tempering, the iron tailings extracted from red mud were reconstructed by heating to form molten tailings in the laboratory. A thermodynamic analysis of the iron reduction reaction during tailings reconstruction was performed, and the best conditions for iron extraction by calcified slag reduction were verified. The contents of CaO, Al₂O₃ and Na₂O in the reduced tailings were 37.07, 37.67 and 0.48%, respectively. According to X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses, the main crystalline phases in the calcified extracted iron tailings were C₂AS and CT, which aggregated and met the expected composition standard for calcified extracted iron tailings.

Keywords: high-iron red mud; iron extraction; melting; reduction

1. Introduction

High-iron red mud refers to red mud with a total Fe (TFe) content above 25%. With the increasing scarcity of high-grade bauxite resources, China began to import Guinea bauxite in large quantities in 2016. Due to the high content of iron in Guinea bauxite, most of the iron in bauxite is enriched in the form of haematite (Fe₂O₃) in red mud. As a result, the annual discharge of high-iron red mud in China is over 75 million tons [1–3], which pollutes the environment and wastes metal resources.

In view of this situation, scholars at home and abroad have performed much research [4–9]. RAI [10] conducted a comparative study on two-stage magnetic separation by traditional reduction roasting and two-stage wet magnetic separation after red mud separation by hydrocyclone. Using pulverized coal for reduction roasting, the percentage of iron and the recovery rate of iron were both less than 60% after two-stage magnetic separation and more than 70% and 75%, respectively, after hydrocyclone separation and a two-stage magnetic separation process. Mukherjee et al. [11] proposed a method of reducing red mud by ironmaking with hydrogen. The mass fraction of iron in the reduced metal can reach 97.03%, but the disadvantages are the high cost of hydrogen storage and transportation, and the whole process is complicated and costly. GU et al. [12] studied the preparation of iron and magnetite by a red mud disproportionation reaction and the preparation of ferrate from red mud. Because silicon in red mud participates in the reaction between iron oxide and sodium peroxide, sodium ferrate is not generated at 600 °C. This study showed a disadvantage in the subsequent process of preparing ferrate by direct reaction between sodium peroxide and red mud, i.e., sodium peroxide cannot be stored for a long time because of the risk of explosion.
Although some progress has been made in the research of iron extraction from high-iron red mud, most of the achievements have not been industrialized on a large scale at present. Nonblast furnace ironmaking technology has been maturing in recent years, and pyrometallurgy has a strong processing capacity, which makes it easy to realize large-scale industrial production [13–16]. However, some problems need to be solved to extract iron by red mud reduction smelting. First, red mud has strong alkalinity, which causes heavy corrosion of the furnace lining in the smelting process, shortens the service life of the furnace lining and even worsens the furnace condition. Second, high-iron red mud is rich in iron, but its grade is still much lower than that of iron ore used in blast furnace ironmaking, which means that a large amount of iron extraction tailings would be produced in the smelting process [17–19]. It is considered that using tailings for iron extraction from red mud to prepare cement is an effective way to deal with red mud, which is in line with the policy of sustainable development and has good economic, environmental, and social benefits. In order to realize efficient utilization of red mud, it is necessary to carry out scientific research and innovation in the preparation of cement from iron extraction tailings.

In view of the current situation that the massive discharge of high-iron red mud in China needs to be dealt with urgently, this paper proposes a method for iron extraction by the direct reduction of high-speed rail red mud. Thermodynamic analysis of the reduction process was conducted, and the experiments investigated the effects of temperature, alkalinity, carbon ratio and holding time on the reduction of calcified slag of high-iron red mud.

2. Materials and Methods

2.1. Materials

The raw materials used in this experiment were bauxite imported from Guinea and high-iron red mud produced by the Bayer process in the Wei Qiao Alumina Plant, Shandong Province. Table 1 shows the chemical composition analysis of the red mud. The mass fractions of TFe and Na₂O in red mud were 39.19% and 3.10%, respectively. The principle of the calcification treatment of red mud from the Bayer process is that calcium and sodium are replaced in situ, sodium is liberated from the solid phase to the liquid phase, and then sodium in the original red mud is removed by washing [20–22]. The mass fraction of Na₂O in calcified high iron red mud decreased from 3.10% to 0.54%. The content of CaO in calcified slag increased to 15.91%, and the content of TFe decreased to 29.89%. As seen from Figure 1, the sodium-silicon slag in the original red mud was successfully transformed into hydrated garnet.

![X-ray diffraction pattern](image)

**Figure 1.** X-ray diffraction pattern of (a) high-iron red mud and (b) the calcified slag of high-iron red mud.
Table 1. Comparative analysis of the chemical composition of high-iron red mud (mass fraction, %).

| Composition             | NaO₂  | Al₂O₃ | SiO₂  | CaO   | TiO₂  | TFe   | Loss on Ignition |
|------------------------|-------|-------|-------|-------|-------|-------|-----------------|
| Red mud content/%      | 3.10  | 17.01 | 6.11  | 0.67  | 6.49  | 39.19 | 6.67            |
| Calcified slag content/%| 0.54  | 13.39 | 5.52  | 15.91 | 5.19  | 29.89 | 15.32           |

2.2. Experimental Procedures

For the experimental procedure, high iron red mud calcified slag was put into an oven at 150 °C to dry to constant weight, and free water was removed. The dried high-iron red mud calcified slag was ground and screened with 60 mesh for later use. One hundred grams of high-iron red mud calcified slag and coking coal were weighed according to the corresponding ratio and mixed with CaO and CaF₂ evenly in the mixing barrel. In the medium frequency induction furnace, magnesia was laid as a refractory lining, a graphite crucible was placed as a heat conduction source, and a corundum crucible was built inside. The uniformly mixed burden was placed to occupy two-thirds of the corundum crucible, the cooling water tank, cooling tower and medium frequency induction furnace were opened, and heating was started for the reduction test. When the furnace charge temperature in the induction furnace rose to 1000 °C, the experimental data were recorded, and the furnace charge temperature was measured every 3 min. The change in the burden in the crucible was observed. When the colour of the burden in the crucible changed from black to bright white balls, the burden began to melt, and the temperature of the burden and the experimental phenomenon were recorded at this time. Heating continued, and the burden turned bright white, which proved that it had completely melted.

3. Results and Discussion

3.1. Thermodynamic Analysis

Following the method of minimization of the total Gibbs free energy, FactSage 7.3 (developed by Thermfact/CRCT and GTT-Technologies, Quebec, Canada) was used to calculate the thermodynamics. The Reaction Module was used to calculate the Gibbs free energy of the reduction process to study the behaviour of the iron extraction reaction by calcification reduction in high-iron red mud, and the Equilib Module was used to calculate the equilibrium phase composition of iron extraction reaction products from high-iron red mud by calcification reduction [23,24].

In the process of reaction with coking coal as a reducing agent, a carbon combustion reaction occurs to form carbon monoxide in the process of heating due to the presence of bound water. Carbon and carbon monoxide are involved in the reduction of metal oxides as reducing agents for the reduction of calcified slag of high iron red mud. The calcified slag of high-iron red mud contains iron, manganese, silicon, titanium, aluminium and sodium oxides. The reactions for the direct reduction of metal oxides by carbon and carbon monoxide are shown in Table 2. Figure 2 shows that the Gibbs free energy of Reaction No. 1, 2, 3, 4, 11 and 13 are negative, indicates that iron can be reduced spontaneously in the presence of carbon and carbon monoxide.

The basicity of slag is an index of slag characteristics. It is the symbol of the free oxygen ion concentration in slag and the main index of the chemical properties of slag. It is also one of the important bases for determining the slag formation system of a blast furnace. Usually, it is expressed by the ratio of the mass percentage concentration of alkaline oxides to acidic oxides.

Figure 3 shows the simulated composition of the products of high-iron red mud calcified slag at different alkalinitities in the Equilib Module of FactSage. With increasing temperature, the phase equilibrium of the reactants showed no obvious change. With the increase in basicity (the amount of CaO added), the relative content of SiO₂ will decrease, the amount of C₂AS phase in the slag will gradually decrease, and the content of tricalcium aluminate (3CaO·Al₂O₃, C₃A) will gradually increase. In the simulated phase equilibrium results, the iron obtained by reduction does not change with the change in temperature or alkalinity.
Table 2. List of reactions for the direct reduction of metal oxides by carbon and carbon monoxide.

| Number | Reaction Equation                  | Number | Reaction Equation                  |
|--------|-----------------------------------|--------|-----------------------------------|
| Reaction (1) | Fe$_3$O$_4$ + C = 3FeO + CO       | Reaction (11) | Fe$_3$O$_4$ + CO = 3FeO + CO$_2$ |
| Reaction (2) | Fe$_3$O$_4$ + 4C = 3Fe + 4CO      | Reaction (12) | Fe$_3$O$_4$ + 4CO = 3Fe + 4CO$_2$ |
| Reaction (3) | Fe$_2$O$_3$ + 3C = 2Fe + 3CO     | Reaction (13) | Fe$_2$O$_3$ + 3CO = 2Fe + 3CO$_2$ |
| Reaction (4) | FeO + C = Fe + CO                | Reaction (14) | FeO + CO = Fe + CO$_2$           |
| Reaction (5) | MnO + C = Mn + CO                | Reaction (15) | MnO + CO = Mn + CO$_2$           |
| Reaction (6) | SiO$_2$ + 2C = Si + 2CO          | Reaction (16) | TiO$_2$ + 2CO = Ti + 2CO$_2$    |
| Reaction (7) | TiO$_2$ + 2C = Ti + 2CO          | Reaction (17) | SiO$_2$ + 2CO = Si + 2CO$_2$    |
| Reaction (8) | MgO + C = Mg + CO                | Reaction (18) | MgO + CO = Mg + CO$_2$           |
| Reaction (9) | Al$_2$O$_3$ + C = 2Al + 3CO     | Reaction (19) | Al$_2$O$_3$ + 3CO = 2Al + 3CO$_2$ |
| Reaction (10) | Na$_2$O + C = 2Na + CO          | Reaction (20) | Na$_2$O + CO = 2Na + CO$_2$     |

Figure 2. Calculation of the Gibbs free energy $\Delta G^\theta$ of (a) carbon reduction and (b) carbon monoxide reduction of calcified slag.

Figure 4 shows the simulated composition of the products of Factsage’s Equilib plate simulation of high-iron red mud calcified slag at different carbon ratios. With an increase in the carbon ratio, the reduction reaction proceeded in a favourable direction, and with further increases in the carbon ratio, the quality of the reduced iron increased continuously, so the carbon ratio was the limiting factor in the reaction process.

3.2. Effect of Experimental Parameters on the Reduction of Calcified Slag of High-Iron Red Mud

3.2.1. Effect of Temperature on the Reduction of Calcified Slag of High-Iron Red Mud

Temperature is an important reaction factor in the reduction process. A single-factor temperature experiment was conducted to investigate the influence of temperature on the reduction process of calcified slag, and the conditions were basicity 1.0, carbon ratio 1.0 and 3% CaF$_2$ addition to high-iron red mud calcified slag, and the temperature range was 1450 °C to 1650 °C.
As shown in Figure 5a, an increase in temperature is beneficial to the reduction reaction. Above 1600 °C, the mass fraction of TFe in calcified iron extraction tailings tended to be flat, and the continuous increase in temperature at this time could not greatly improve the degree of the reduction reaction. The direct reduction of iron oxide by carbon is an endothermic reaction, and with the gradual increase in reduction temperature, the reaction was more favorable in the forward direction. At the same time, the increase in reduction temperature leads to an increase in the CO concentration in the gas phase, which makes the reduction reaction favorable. However, with the increase in reduction temperature, a liquid phase will form on the surface of the material, which will hinder the infiltration of CO gas and inhibit the reduction reaction. Moreover, if the reduction temperature is too high, the self-stirring of the molten pool will be too strong, the solution will surge violently, and some reduced iron will be oxidized again, which will lead to the splashing of the melt and cause the loss of materials, thus affecting the recovery rate of iron. The mass fraction of TFe in calcified iron extraction tailings reflects the reduction degree of calcified slag of high-iron red mud to a certain extent. Figure 5b shows the effects of different reduction temperatures on the recovery rate of iron and the mass fraction of MFe in the metals. The recovery rate of iron first increased and then decreased, reaching the highest at 1550 °C, and the mass fraction of MFe in metals was relatively stable, reaching 93–94%. When the reduction temperature was 1550 °C, the recovery rate of iron was 83.61%, and the mass fraction of MFe in the metal was 93.54%. The experimental results were good. Therefore, 1550 °C was selected as the optimum temperature for the reduction of high-iron red mud calcified slag.
Figure 4. Calculation of the phase equilibrium of reduction reaction products for different carbon ratios.

Figure 5. Effect of reduction temperature on (a) TFe mass fraction in calcified iron extraction tailings and (b) iron recovery and mass fraction of MFe in metal.
3.2.2. Effect of Alkalinity on the Reduction of Calcified Slag of High-Iron Red Mud

Basicity has an important influence on the metallurgical reaction rate and iron recovery in the reduction smelting process and even determines whether the whole reaction can be conducted smoothly. Alkaline oxides have little attraction to \((O^2^-)\), which can provide free \((O^2^-)\) for slag, while acidic oxides have great attraction to \((O^2^-)\), which needs to be combined with \((O^2^-)\) in slag. The basicity adjustment in this section depends on the addition amount of CaO. As shown in Equation (1), adding basic oxides such as CaO to the slag promotes the disintegration of the silicon-oxygen complex, thus reducing the viscosity of the slag and making the reaction in the reduction process proceed in a more favourable direction. However, because CaO is a high melting point oxide, excessive addition leads to the presence of some CaO in the form of solid particles, which increases the viscosity and decreases the fluidity of slag and then affects the reaction rate and even blocks the progress of the reaction [25].

\[
\text{Polymerization} \xrightarrow{\text{disintegration}} (\text{SiO}_4^{4-}) + (\text{Si}_2\text{O}_7^{6-}) \rightarrow (\text{Si}_3\text{O}_9^{6-}) + 2(O^2^-)
\]

(1)

According to the single-factor experiment discussed in the previous section, the best reduction temperature of calcified slag was 1500 °C, and then the alkalinity single factor was determined. When all the raw materials in the crucible melted, the timing was started, the holding time was 30 min, and the CaO addition was selected according to the basicity calculation formula at five points: 0.9, 1.0, 1.1, 1.2 and 1.3. As seen from Figure 6a, with the increase in alkalinity, the TFe mass fraction in calcified iron extraction tailings did not change greatly, but when the alkalinity reached 1.3, the viscosity of the molten pool increased due to the increase in CaO addition, which affected the smooth progress of the reduction reaction. As shown in Figure 6b, the recovery rate of iron was above 80% under different alkalinities, and the mass fraction of MFe in the metal was between 93% and 95%. With increasing alkalinity, the recovery rate and metallization of iron first increased and then decreased. When the basicity was 1.1, the fluidity of the slag was the best, the recovery rate of iron was 85.67%, and the mass fraction of MFe in the metal was 94.21%.

![Figure 6](image_url)

**Figure 6.** Effect of alkalinity on (a) TFe mass fraction in calcified iron extraction tailings and (b) iron recovery and mass fraction of MFe in metal.

3.2.3. Effect of Carbon Ratio on the Reduction of Calcified Slag of High-Iron Red Mud

The carbon ratio affects the degree of direct reduction and the partial pressure of CO during reduction, which determines the process of iron extraction by calcification of high-iron red mud. Theoretically, before carbon saturation is reached, the recovery rate
of iron obtained by reduction increases with increasing carbon ratio. Studies have shown that with the increase in coking coal addition, a large amount of ash leads to an increase in volatilization loss of raw materials. At the same time, with the increase in the carbon ratio, the reduction reaction is more intense, and the raw materials splash molten iron during the reduction reaction, resulting in a decrease in the iron recovery rate and metallization rate [26–29].

When the optimum reduction temperature was 1550 °C and the basicity was 1.1, a single-factor experiment of the carbon ratio was conducted. As shown in Figure 7a, with the increase in the carbon ratio, the reduction reaction proceeded in a favourable direction. When the carbon ratio was 1.1, the TFe content in the calcified iron-extracting tailings reached 1.99%, and the TFe content in the calcified iron-extracting tailings did not change greatly when the carbon ratio increased to 1.3. Figure 7b shows the influence of different carbon ratios on the recovery rate of iron and the mass fraction of MFe in metals. Under the condition of a low carbon ratio, increasing the carbon ratio was beneficial to the carbothermal reduction reaction and CO reduction reaction. Continuing to increase the carbon ratio led to metal loss due to the volatilization of coking coal and splashing of molten iron in the reduction reaction, so the recovery rate of iron increased first and then decreased with increasing carbon ratio. When the proportion of carbon was 1.1, the recovery rate of iron was 90.6%, and the mass fraction of MFe in the metal was 93.76%.

![Figure 7. Effect of the carbon ratio on (a) TFe mass fraction in calcified iron extraction tailings and (b) iron recovery and mass fraction of MFe in metal.](image)

3.2.4. Effect of Holding Time on Reduction of Calcified Slag of High-Iron Red Mud

Holding time refers to the stable and continuous reaction time after the raw material is completely melted and reaches the specified reduction temperature. Under the conditions of temperature 1550 °C, alkalinity 1.1, carbon ratio 1.1 and addition of 3% CaF₂ to high-iron red mud calcified slag, the influence of holding time on the reduction process was investigated. Figure 8a,b show that the mass fraction of TFe in calcified iron extraction tailings decreased at 30 min, there was no obvious change at 40 min, and the reduction reaction ended at 30 min. The holding time was too short, and then part of the iron was still present in the form of oxide and had not been reduced. With time, the recovery and metallization rate of iron gradually increased, and the reduction reaction reached equilibrium after a certain time. Continuing to increase the time, oxygen in the air entered the slag due to the continuous surging of the molten pool, which oxidized some reduced metals again, resulting in a decrease in iron recovery. At 30 min, the recovery rate of iron was 90.6%, and the mass fraction of MFe in the metal was 93.76%. Therefore, 30 min is the best holding time for iron reduction and extraction from red mud calcified slag with high iron content.
3.3. Analysis and Characterization of Reduction Products

The experimental product with the highest iron recovery rate was characterized, and the experimental conditions were as follows: no stirring, no slow cooling, reduction temperature 1500 °C, heat preservation for 30 min, alkalinity and carbon ratio of 1.1, and addition of 3% CaF$_2$ to calcified slag. Figure 9 shows photographs of metal and tailings after reduction in the optimal group, and Figure 9a shows the cross section of slag-gold separation during reduction. The metal and calcified iron extraction tailings completely separated at the bottom of the crucible. Figure 9b is a photograph of the metal obtained by reduction. There was no porosity on the metal surface, and a slag layer covered the metal surface. Figure 9c is a photograph of the calcified iron extraction tailings. There were some vitreous bodies in the tailings. After the reduction experiment, the crucible was removed and cooled quickly in air. Because the cooling rate of iron extraction tailings was too fast, some phases crystallized too fast to form some glass phases.

Figure 9. Photographs of metal and tailings after reduction of the optimal group. (a)—slag-gold interface section (b)—metal (c)—calcified iron extraction tailings.

3.3.1. Chemical Composition Analysis and Characterization of Metals

The chemical composition analysis of the metals obtained under the optimal experimental conditions is shown in Table 3. The main components of the metals were Fe and C and a small amount of reduced Si. Among them, the mass fraction of Fe was 93.76%, and the mass fraction of C was 3.84%. Compared with the standard GB/T 717-1998, the Mn content was in accordance with the first-class standard of steel-making pig iron; the P content was in accordance with the third grade steel-making pig iron standard.

| Element | Fe | C | Si | Mn | P |
|---------|----|---|----|----|---|
| Mass Fraction (%) | 93.76 | 3.84 | 0.39 | <0.010 | 0.227 |

Figure 8. Influence of the holding time on (a) TFe mass fraction in calcified iron extraction tailings and (b) iron recovery and mass fraction of MFe in metal.
Table 3. Chemical composition analysis of the optimal group of metals (mass fraction, %).

| Element | Fe   | C    | Si   | Mn  | P     |
|---------|------|------|------|-----|-------|
| Content/% | 93.76 | 3.84 | 0.39 | <0.010 | 0.227 |

Figure 10 shows the SEM morphology and the distribution map of metal elements of the metal obtained by the reduction of the best group of calcified iron extracted from high-iron red mud. From the element distribution of surface scanning, Fe and C in the metal were uniformly distributed in the whole plane, C was aggregated and distributed in Fe in the form of needles, and small amounts of Al, Si, Ti and Na were reduced and dispersed in the whole plane. The main elements at point A were Fe and C. In addition, a small amount of Ti, in addition, to Fe and C, and small amounts of reduced Si and Na were enriched at point B. The concentration distribution of C at point C indicates that the white area in the whole metal was a large area of Fe dispersed and uniformly distributed, and Na, Si and Ti were reduced by side reactions during the reduction process. C mainly aggregated and distributed in acicular bodies.

Figure 10. SEM morphology and the distribution map of metal elements.

3.3.2. Chemical Composition Analysis and Characterization of Calcified Iron Extraction Tailings

The chemical composition analysis of calcified iron extraction tailings from high-iron red mud obtained under the optimal experimental conditions is shown in Table 4. After reduction, the mass fraction of Fe$_2$O$_3$ was reduced to 1.51%. In the reduction process, some of the Na$_2$O was discharged with flue gas, a small part was reduced, and the rest was enriched in iron extraction tailings, accounting for 0.48% of the total mass fraction.
Table 4. Chemical composition analysis of calcified iron extraction tailings (mass fraction, %).

| Composition | CaO  | Al₂O₃ | SiO₂  | TiO₂ | Na₂O  | Fe₂O₃ | LOI  |
|-------------|------|-------|-------|------|-------|-------|------|
| Content/%   | 37.07| 37.67 | 7.49  | 7.43 | 0.4848| 1.51  | 7.41 |

Figure 11 shows the XRD analysis of the optimal calcified iron extraction tailings. The main mineral phases in the tailings were anorthite (2CaO·Al₂O₃·SiO₂), calcium silicate (8CaO·5SiO₂) and titanopyroxene (CaO·TiO₂).

![XRD Pattern](image)

Figure 12 shows the SEM morphology and the distribution map of metal elements of the calcified iron extraction tailings obtained by the reduction of the best group of calcified iron extracted from high-iron red mud. Ca and O elements are densely dispersed in the whole plane, and the area where Al and Si are highly coincident contains a large number of irregular crystallized C₂AS particles. The distribution of Ti and Al is cross-complementary, and the area of Ti aggregation distribution is the area of CT massive crystallization. The content of Na is low, and it is uniformly distributed throughout the tailings. The crystalline phases of point a are C₂AS and CT, point B is C₂AS and point C is CT. In SEM, the dark part is C₂AS, and the bright part is CT.
4. Conclusions

In this study, a recycling method for high-iron red mud was investigated through high-temperature experiments and thermodynamic analysis. The results are shown as follows.

(1) Through the calculation of the Gibbs free energy and equilibrium phase, it was inferred that the direct reduction of carbon was dominant in the reduction of high-iron red mud calcified slag, and Fe, Si, Ti, Na and other elements were reduced in this process. The results of the equilibrium phase calculation showed that with increasing alkalinity, 2CaO·Al₂O₃·SiO₂ gradually decreased, 3CaO·Al₂O₃ gradually increased, and the increase in the carbon ratio was beneficial to the reduction reaction.

(2) The optimum reduction conditions for iron extraction by calcified slag reduction were obtained by single-factor investigations. The optimum reduction conditions were 1550 °C, alkalinity 1.1, carbon ratio 1.1, holding time 30 min, and CaF₂ content 3% of the calcified slag mass fraction. The recovery of iron was 90.06%, and the mass fraction of MFe in the metal was 93.76%.

(3) The levels of CaO, Al₂O₃ and Na₂O were 37.07, 37.67 and 0.48%, respectively, according to the analysis of the chemical composition and mineralogy of calcified iron tailings extracted from red mud with high iron content, which met the expected composition standard of calcified extracted iron tailings for preparing aluminate cement directly from tailings. Through XRD and SEM analyses, the main crystalline phases in calcified extracted iron tailings were identified as 2CaO·Al₂O₃·SiO₂ and CaO·TiO₂, which were distributed in aggregates.

Figure 12. SEM morphology and the distribution map of metal elements of the calcified iron extraction tailings.
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