

Feasibility of co-reduction roasting of a saprolitic laterite ore and waste red mud

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Abstract: Large scale utilization is still an urgent problem for waste red mud with a high content of alkaline metal component in the future. Laterite ores especially the saprolitic laterite ore are one refractory nickel resource, the nickel and iron of which can be effectively recovered by direct reduction and magnetic separation. Alkaline metal salts were usually added to enhance reduction of laterite ores. The feasibility of co-reduction roasting of a saprolitic laterite ore and red mud was investigated. Results show that the red mud addition promoted the reduction of the saprolitic laterite ore and the iron ores in the red mud were co-reduced and recovered. By adding 35wt% red mud, the nickel grade and recovery were 4.90wt% and 95.25wt%, and the corresponding iron grade and total recovery were 71.00wt% and 93.77wt%, respectively. The X-ray diffraction (XRD), scanning electron microscopy, and energy dispersive spectroscopy (SEM-EDS) analysis results revealed that red mud addition was helpful to increase the liquid phase and ferronickel grain growth. The chemical compositions “CaO and Na₂O” in the red mud replaced FeO to react with SiO₂ and MgSiO₃ to form augite.

Keywords: laterite ore; red mud; reduction roasting; phase transformation

1. Introduction

Nickel laterite deposits are divided into two primary parts: limonite and saprolite [1]. The reduction of saprolitic laterite ores is much more difficult than that of limonitic laterite [2]. Since serpentine undergoes dehydroxylation during roasting, the resulting phases, such as olivine and pyroxene, are not conducive to reduction [3]. So, the key issues in the reduction roasting–magnetic separation of saprolitic laterite ores are: (1) the liberation of nickel and iron from their host minerals, (2) adequate reduction of iron and nickel oxides, and (3) the growth of ferronickel particles. Previous research showed that the addition of alkali compounds, such as sodium and calcium salts, was usually used for the efficient recovery of nickel from laterite ores. Some researchers [4–7] studied the effect of calcium salts on the reduction of a saprolitic laterite ore. And several studies completed a simulation study on the mechanism of sodium salts on promoting the reduction of laterite ores [3,8–12]. The effects of additives such as sodium and calcium salts on the reduction of

laterite ores are significant, but their prices are high. Therefore, it is necessary to study the use of low cost alternatives to replace them in the reduction of laterites.

Red mud is an alkaline waste byproduct generated by the extraction of alumina from bauxite [13]. Appropriate management of red mud is becoming a global concern following increased awareness of the need for environmental protection. The red mud is mainly composed of a mixture of oxides and hydroxides such as Fe₂O₃, TiO₂, SiO₂, Al₂O₃, CaO, Na₂O, Al(OH)₃, and very small amounts of other metal oxides [14]. Therefore, a comprehensive use for red mud is also crucial for economic reasons [15].

Therefore, in this study, waste red mud containing large amounts of CaO and Na₂O was added to a saprolitic ore. This mix was then subjected to reduction roasting followed by magnetic separation. This was then tested to determine the effect of red mud on the reduction of as-received saprolitic laterite and test the feasibility of co-reduction. In addition, the effects of red mud on phase transformations and ferronickel grain growth were investigated.

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2. Experimental

2.1. Materials

The laterite ore was dried at 80°C for 6 h and then crushed using a laboratory double-roll crusher to pass through 1 mm screen (100wt%). The chemical composition

of the saprolitic laterite ore was determined by chemical analysis, as shown in Table 1. The SiO₂ and MgO contents of the ore were high, whereas the iron grade was low. Therefore, the ore was considered to be saprolitic. Fig. 1 shows the X-ray diffraction (XRD) analysis of the saprolitic laterite ore.

Table 1. Chemical analysis of as-received saprolitic laterite ore and red mud

Materials	Ni	TFe	CaO	Na ₂ O	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃
Laterite ore	1.62	14.70	0.84	—	45.58	4.32	22.46	—	—	—	—
Red mud	—	26.18	19.66	7.07	12.76	14.39	0.27	0.13	7.03	0.37	0.41

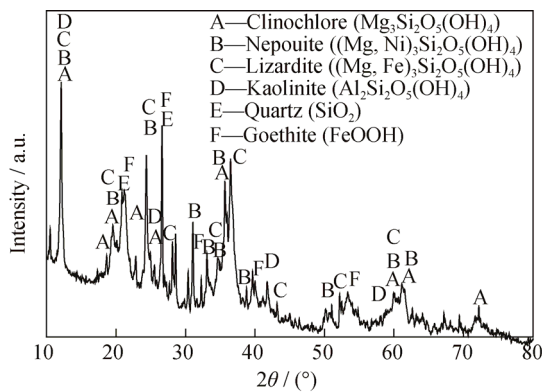


Fig. 1. XRD pattern of the saprolitic laterite ore.

The composition of the red mud is given in Table 1. The main minerals in the red mud were hematite (Fe₂O₃), corundum (Al₂O₃), andradite (Ca₃(Fe_{0.87}Al_{0.13})₂(SiO₄)_{1.65}(OH)_{5.4}), calcite (CaCO₃), and cancrinite (Na₆Ca₂Al₆Si₆O₂₄(CO₃)₂). Iron occurred in the form of hematite and andradite, sodium existed mainly in the form of cancrinite, and calcium existed mainly as calcite, andradite, and cancrinite.

Anthracite coal was used as the reductant and its composition is given in Table 2. The anthracite was crushed and screened to 100wt% passing 0.5 mm.

Table 2. Composition of the anthracite coal sample used as a carbon source for reduction

Fixed carbon	Volatiles	Ash	Moisture	Sulfur
82.38	3.48	11.66	2.48	0.37

2.2. Methods

The saprolitic ore, anthracite coal, and waste red mud were mechanically mixed. The addition of anthracite coal was 10wt% of the saprolitic ore. The red mud additions varied from 0 to 35wt% of the saprolitic ore. The reduction roasting experiments were carried out in a muffle furnace. The reduction temperature was varied in the range of

1200–1300°C for 60 min. The roasted ores obtained were then ground, but because different roasting conditions resulted in different grindabilities, it was difficult to obtain the same grinding fineness in each sample. Thus, here a grinding time of 15 min was used instead of grinding fineness. To obtain the ferronickel products, magnetic separation tests were performed in a CXG-99 magnetic tube using a magnetic field intensity of 144 kA/m.

Nickel grade, nickel recovery rate, iron grade, and total iron recovery were adopted as evaluation indices of the process of co-reduction followed by magnetic separation. The total iron recovery of ferronickel products was calculated based on the following formula:

$$\varepsilon_{\text{Fe}} = \frac{M_{\text{FN}} \cdot \beta_{\text{FN}}}{M_{\text{S}} \cdot \alpha_{\text{S}} + M_{\text{R}} \cdot \alpha_{\text{R}}}$$

where ε_{Fe} is the total iron recovery of ferronickel products, M_{FN} is the mass of ferronickel products, β_{FN} is the iron grade of ferronickel products, M_{S} is the mass of the saprolitic ore, α_{S} is the iron grade of the saprolitic ore, M_{R} is the mass of the added red mud which is based on its dosage, and α_{R} is the iron grade of the red mud.

2.3. XRD and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis

The XRD experiments were performed on a Japan Science Ultima IV diffractometer using Cu K_α radiation ($k = 0.15406$ nm) at an operation voltage of 40 kV and a current of 40 mA. The microstructure and particle size were determined using a scanning electron microscope (Zeiss EVO 18) equipped with energy dispersive spectroscopy (Quantax, Bruker, Germany).

3. Results and discussion

Using a reduction time of 60 min, the saprolitic laterite ores were reduced at 1200 and 1300°C to determine the ef-

fect of temperature on the nickel grade, iron grade, nickel recovery, and iron recovery of the ferronickel products.

Table 3 reveals that a high roasting temperature is conducive to increased nickel and iron grades and recoveries. However, nickel recovery only increases from 51.75wt% to 54.29wt%, which is still low. The results show that increasing the reducing temperature can promote the reduction of the saprolitic laterite ore. However, such effects are limited.

Table 3. Effect of roasting temperature on the grade and recovery of nickel and iron wt%

Temperature / °C	Iron grade	Nickel grade	Iron recovery	Nickel recovery
1200	36.02	3.30	60.76	51.75
1300	52.23	3.73	81.78	54.29

3.1. Effect of red mud dosage

Under a roasting temperature of 1300°C and a duration of 60 min, the effect of red mud dosage on nickel and iron mineral reduction was investigated. The results are shown in Fig. 2.

As the amount of red mud increases from 0 to 35wt%, nickel grade increases from 3.73wt% to 4.90wt%. This is accompanied by a significant increase in nickel recovery

from 54.29wt% to 95.25wt%, which means that nickel recovery is sensitive to red mud dosage. Iron grade and the total iron recovery basically show an increasing trend with an increasing dosage of red mud. In the presence of 35wt% red mud, the iron grade of the ferronickel product obtained is as high as 71.00wt%. Meanwhile, the total iron recovery is 93.77wt%.

It suggests that the added red mud intensifies the reduction of iron and nickel oxides in the saprolitic laterite ore and contributes to the nickel concentration. In other words, the red mud plays the role of an additive. Meanwhile, iron oxides in the red mud can be co-reduced and co-recycled. This provides a new way to use waste red mud.

3.2. Effect of red mud on the appearance of roasted ores

The appearance of the roasted ores with different dosages of red mud is presented in Fig. 3. As shown in Fig. 3(a), without any red mud, the roasted ore remains loose and does not melt. At a red mud dosage of 10wt%, the roasted ore shows slight melting, as shown in Fig. 3(b). Increasing the red mud dosage to 20wt%, the degree of melting obviously increases (Fig. 3(c)). Figs. 3(d)–3(f) show that when the red mud dosage is in the range of 25wt%–35wt%, the roasted ores show significant sintering densification. This indicates that the red mud addition increases the quantity of the liquid phase in the roasted ores.

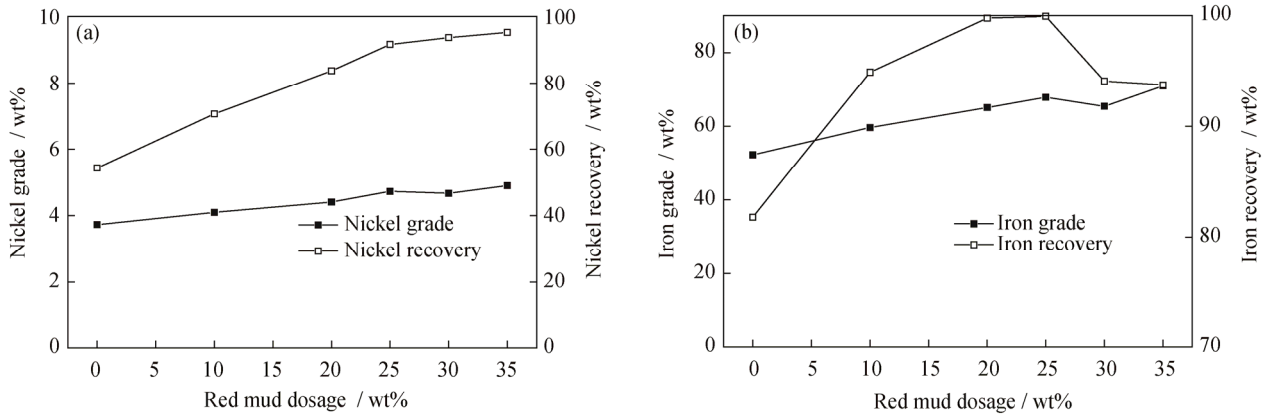


Fig. 2. Nickel grade and recovery (a) and iron grade and recovery (b) of the ferronickel products as a function of red mud dosage.

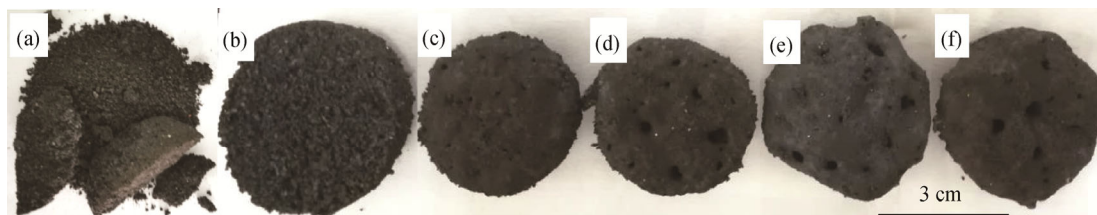


Fig. 3. Appearance of the roasted ores as the function of red mud dosage: (a) 0; (b) 10wt%; (c) 20wt%; (d) 25wt%; (e) 30wt%; (f) 35wt%.

3.3. Phase transformation relationship to red mud dosage

To reveal the mechanism of liquid phase formation in the roasted ores as a result of red mud addition, the phase transformations of roasted ores with different red mud dosages were investigated. The saprolitic laterite ores were reduced at 1300°C using different dosages of red mud from 0 to 35wt%. The XRD patterns of the roasted ores under different conditions are shown in Fig. 4.

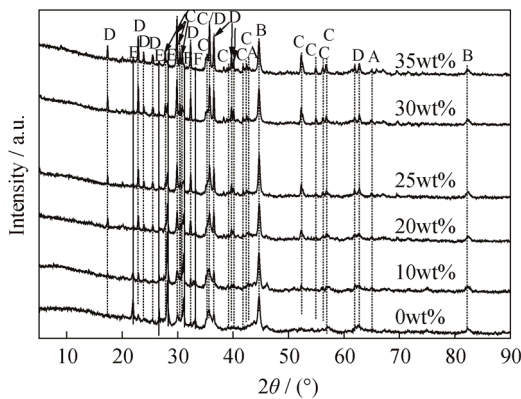


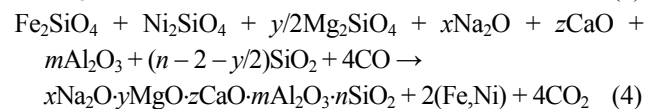
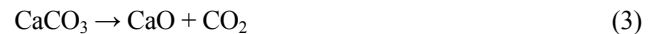
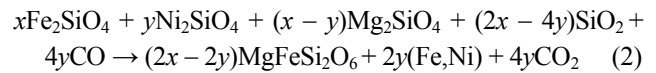
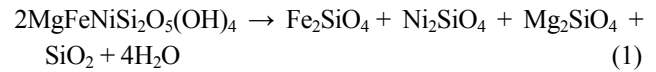
Fig. 4. XRD patterns of the roasted ores obtained at various red mud dosages. A—taenite (Ni,Fe); B—kamacite (Fe,Ni); C—augite ((Mg,Al)(Ca,Na)(Si,Al)₂O₆); D—forsterite (Mg₂SiO₄); E—quartz (SiO₂); F—enstatite ferroan (MgFeSi₂O₆).

By increasing the red mud dosage from 0 to 35wt%, the diffraction peaks of taenite (A) and kamacite (B) show a little increase; the peak intensities of augite (C) and forsterite (D) increase; however, the peak intensities of quartz (E) and enstatite ferroan (F) decrease.

Without the waste red mud a lot of dissociative quartz occurs. Research has shown that NiO and FeO react with free quartz to form olivine in the reducing stage, making further reduction difficult [16]. So, in the absence of the red mud, the nickel and iron recoveries were only 54.29wt% and 81.78wt%, respectively. The main reactions in the absence of red mud can be represented by Eqs. (1) and (2).

The red mud contained alkaline compounds including CaO and Na₂O. Yu [17] found that additives containing CaO and Na₂O reacted with SiO₂ prior to FeO, or that CaO and Na₂O replaced FeO from ferric silicate, improving the reduction of iron minerals. Similarly, CaO and Na₂O would improve the reduction of nickel minerals. Here, the alkaline compositions CaO and Na₂O in the red mud reacted with SiO₂ to replace NiO and FeO, resulting in the formation of augite and forsterite. Augite and forsterite are low fusion point minerals, the formation of which increased the liquid phase in the roasted ores and resulted in significant sintering

densification. So, at a red mud dosage of 35wt%, a ferro-nickel product with a high nickel recovery of 95.25wt% and a relatively high total iron recovery of 93.77wt% was obtained. The reactions in the presence of the red mud can be represented by Eqs. (1), (3), and (4).



3.4. Effect of red mud on ferronickel grain growth in the roasted ores

The liquid phase promotes mass transfer and ferronickel particle growth [6]. In this case, examining the distribution relationship among various minerals may shed light on the function of the liquid phase. Microstructures of the reduced ores without and with 35wt% red mud are shown in Figs. 5 and 6.

Fig. 5(a) shows that, in the absence of the red mud, the roasted ore includes particles of different sizes, with lots of crevices among them. However, with 35wt% red mud, no crevices occur and the roasted ores sinter-bond together as a whole (Fig. 6(a)), but there are holes in the roasted ore, that may be due to the formed liquid phase. The liquid phase prevents diffusion of reducing gases after coal gasification. This is one of the significant differences between the microstructures of roasted ores without and with 35wt% red mud.

The bright white particles are ferronickel grains. In the roasted ore without red mud there are a lot of fine ferronickel grains, as shown in Fig. 5(b). However, by adding 35wt% red mud, this phenomenon weakens and the ferronickel grains grow and gather (Fig. 6(b)). This is another significant difference between the microstructures of the roasted ores without and with 35wt% red mud. This phenomenon can be explained as follows: Fig. 3(a) shows that the roasted ore without red mud remains loose and does not melt. There may be only a small amount of liquid phase generated and this is disadvantageous to ferronickel particle aggregation. Therefore, fine ferronickel particles remain in their original positions. As shown in Fig. 3(f), with 35wt% red mud, the roasted ore shows significant sintering densification, indicating that a large amount of liquid phase is generated during the reduction stage. The generated liquid phase promoted the growth of ferronickel particles.

Fig. 5(g) reveals that without the red mud, the nickel and iron in the laterite ore occur partly in the gangue mineral enstatite ferroan, except for that reduced to form ferronickel particles. This is extremely detrimental to the recovery of nickel and iron. The calcium and sodium in the roasted ore obtained with 35wt% red mud (Figs. 6(h) and 6(i)) originated from the red mud. This is the third significant differ-

ence between the microstructures of the roasted ores without and with 35wt% red mud. Calcium and sodium occur in the form of augite, magnesium in the form of forsterite, and these two constitute the main gangue minerals. This further verified that the amount of nickel and iron in the gangue was decreased, contributing to an increase in the recovery of nickel and iron.

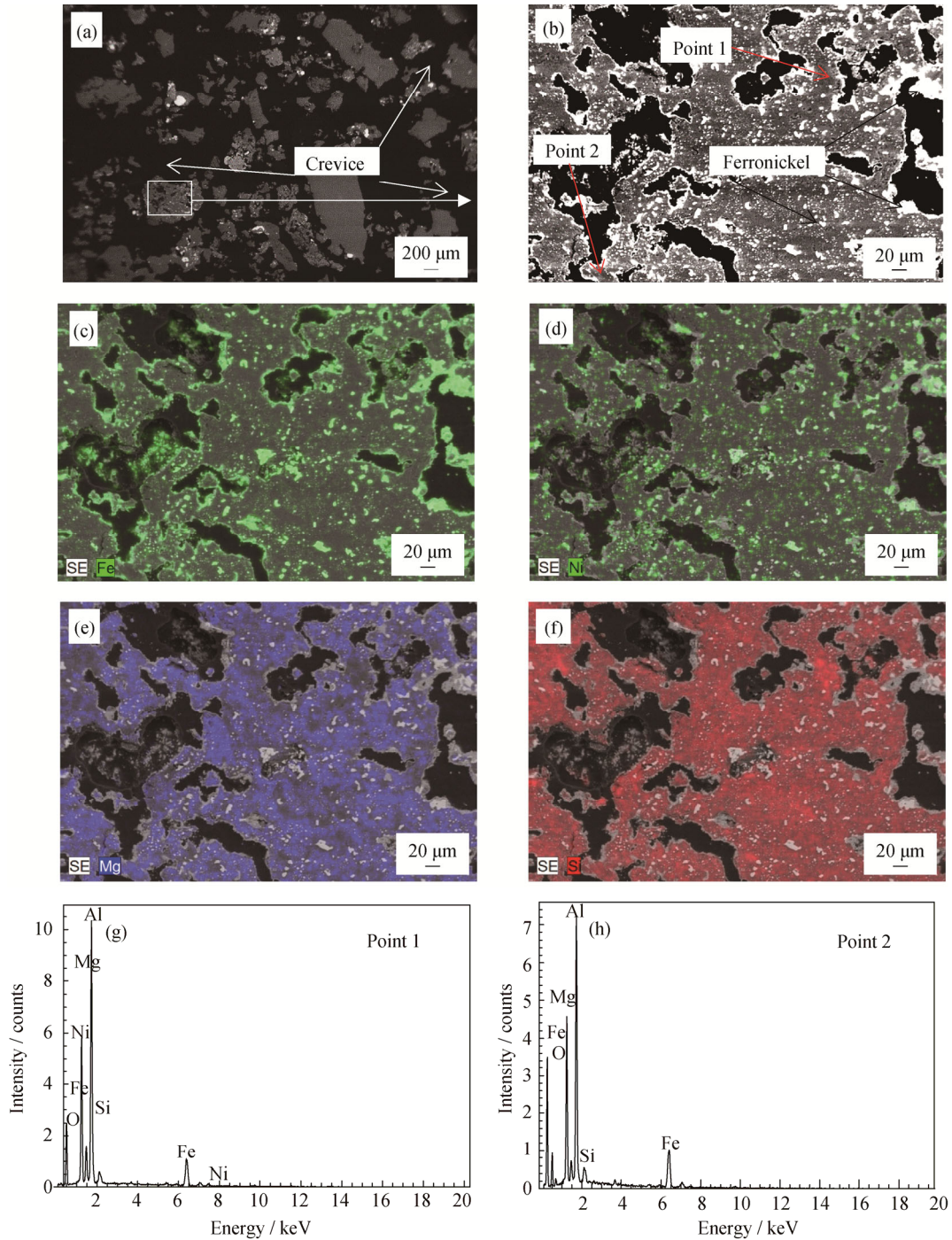


Fig. 5. SEM-EDS and element mapping of the roasted ores without red mud: (a) SEM image; (b) an enlargement of (a); (c,d,e,f) element mapping of (b); and EDS of points 1 (g) and 2 (h).

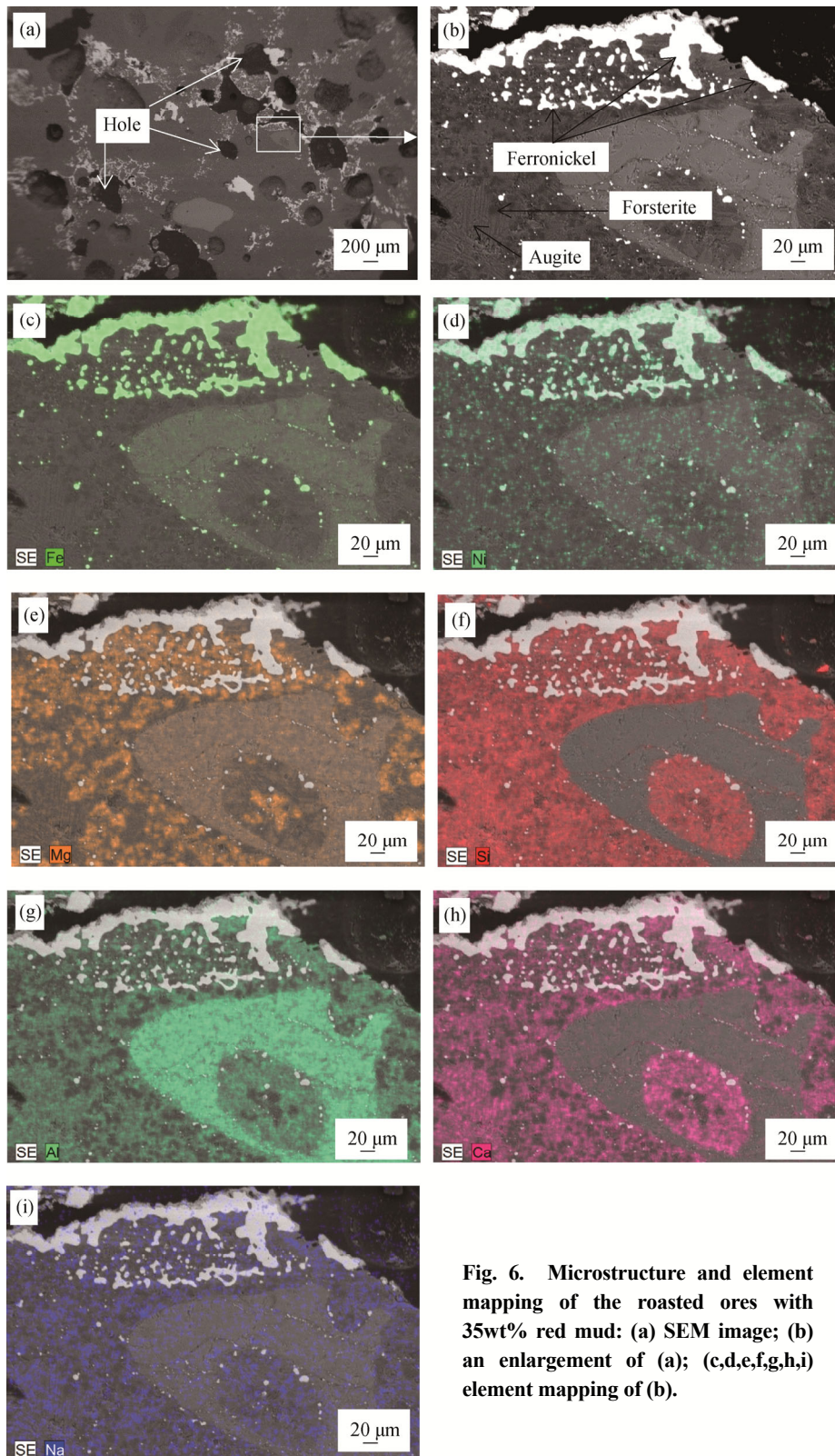


Fig. 6. Microstructure and element mapping of the roasted ores with 35wt% red mud: (a) SEM image; (b) an enlargement of (a); (c,d,e,f,g,h,i) element mapping of (b).

4. Conclusions

(1) Red mud with high contents of CaO and Na₂O benefits the reduction of nickel and iron ores in saprolitic laterite.

The co-reduction of red mud and saprolitic laterite ore is feasible and provides a new way to use waste red mud.

(2) The addition of red mud leads to an increase in nickel and iron grades and recoveries under the same roasting

temperature. A ferronickel product with 4.90wt% nickel and 71.00wt% iron was prepared by reduction at 1300°C for 60 min and adding 35wt% red mud. The corresponding nickel and total iron recoveries were 95.25wt% and 93.77wt%, respectively.

(3) The contents of CaO and Na₂O are high in the red mud and replace FeO and NiO to react with SiO₂, leading to the generation of augite and the formation of a liquid phase.

(4) The ferronickel particle size increases significantly with the addition of 35wt% red mud. This is due to the liquid phase, which provides access for the transfer and growth of ferronickel particles.

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