Effect of Na$_2$SO$_4$ on the Embedding Direct Reduction of Beach Titanomagnetite and the Separation of Titanium and Iron by Magnetic Separation

Chao GENG, Tichang SUN,* Huifen YANG, Youwen MA, Enxia GAO and Chengyan XU

School of Civil and Environmental Engineering, University of Science and Technology Beijing, 396# letter box, Beijing, 100083 China.

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A novel process for separating iron and titanium from Indonesian beach titanomagnetite (TTM) concentrates is proposed. This process involves several steps, including mixing the TTM concentrate and additive, pressing the mixture into pellets, embedding direct reduction of the pellets, and magnetic separation. Given that coal and additives are the main factors influencing the coal-based direct reduction of beach TTM, this study employed embedding reduction, where pellets are embedded under the coal to be reduced, and Na$_2$SO$_4$ was used as an additive. The best result was obtained when the Na$_2$SO$_4$ dosage was 4%, and the direct reduction iron powder (DRI powder) with an iron grade of 94.45%, iron recovery of 85.18%, and TiO$_2$ content of 0.44% were obtained. Titanium concentrate assay yielded 40.43% TiO$_2$ containing main titanium minerals of ilmenite and ferrous pseudobrookite. The results showed that a suitable Na$_2$SO$_4$ addition (4–6%), DRI powder and titanium concentrate presented better iron recovery and TiO$_2$ grade as compared without addition, while this advantage disappeared as Na$_2$SO$_4$ addition increased (>6%). The characteristics of roasted pellets were analyzed through X-ray diffraction, scanning electron microscopy, and energy dispersive spectrometry. Results showed that FeS and nepheline are formed by addition of Na$_2$SO$_4$, thereby benefiting the migration and growth of metallic iron particles in the redox system and separation of titanium and iron. While a suitable dosage of Na$_2$SO$_4$ could promote porosity and induce a reducing atmosphere, but more liquid phase formed by an excessive Na$_2$SO$_4$ was unfavorable and caused expansion of the pellets.

KEY WORDS: beach titanomagnetite; embedding direct reduction; sodium sulfate; titanium and iron separation.

1. Introduction

Iron and titanium are important strategic resources. Titanium, because of its light weight, high specific strength, corrosion resistance, and biocompatibility, is a material of high demand in the aerospace and chemical processing industries and utilized in biomedical applications; in fact, its prospects are even better than those of iron.$^{1-3}$ With the continuous depletion of high-grade titanium ores and the increasing demand for titanium dioxide, low-grade beach titanomagnetite (TTM) ironsand has become an important resource. Unfortunately, since beach TTM ironsand is mainly separated by gravity concentration and magnetic separation to recover iron,$^{4-7}$ the titanium resource is often wasted. Therefore, an effective process that can separate titanium and iron from TTM ore must be developed.

Previous studies show that coal-based direct reduction followed by magnetic separation is the most effective method to achieve titanium and iron separation from TTM ore.$^{8-15}$ The process involves the following steps: First, TTM ore of the proper size, coal, and additives are mixed together. Second, the mixture is placed in a crucible and roasted at a high temperature. During this step, iron minerals can be reduced to metallic iron, and titanium remains as titanium minerals. Finally, the roasted ore is separated through grinding and magnetic separation, and the magnetic product obtained is called DRI powder. The titanium minerals are enriched in the non-magnetic product. This process has been subjected to several recent investigations. Gao et al.$^{15}$ investigated this process by using Indonesian beach TTM concentrate as a sample and bituminous coal as the reductant, and performed reduction at 1150°C for 90 min followed by wet magnetic separation. DRI powder with an iron grade of 91.06%, TiO$_2$ content of 1.6%, and iron recovery of 97.27% was obtained. Assay of the non-magnetic product yielded 26.69% TiO$_2$. Gao et al.$^{13}$ separated iron from Indonesian beach TTM ironsand using bituminous coal as the reductant and NCS as an additive; DRI powder with an iron grade of 93.74%, iron recovery of 95.91%, and TiO$_2$ content of 0.45% was obtained. Assay of the non-magnetic product also showed a TiO$_2$ grade of 22.33%. Yu et al.$^{14}$ separated iron and titanium from Indonesian beach TTM using coal slime as the reductant and YSE and YHG as additives; here, DRI powder with an iron grade of 92.72%, TiO$_2$ content of 0.72%, and iron recovery of 91.93% was obtained. The TiO$_2$
grade of the non-magnetic product was about 20%.

According to the aforementioned studies, coal-based direct reduction and magnetic separation can separate iron and titanium from TTM ore to a fairly high extent and high-quality DRI powder may be obtained. However, a high-grade non-magnetic product (TiO_2 > 40%) was not obtained in these studies. When the reductant and the additive were mixed together with TTM, and high reactivity bituminous coal and coal slime used as reductant were high ash, and high dosages of the reductant and additive (about 20 wt.% and 10 wt.%, respectively) were required. Coal ash and most additives could fall into the non-magnetic product after direct reduction and magnetic separation, thereby leading to poor TiO_2 grades, complex structures, and a variety of titanium minerals in the roasted ore. Therefore, mixing together the reductant and additive with TTM ore is disadvantageous to obtaining a high-grade titanium product.

To address these problems, this study employs embedding direct reduction and magnetic separation to separate iron and titanium. In this work, the beach TTM concentrate, binder, and additives are pressed into pellets and then completely embedded into the coal to avoid the impact of coal ash and ensure excellent reduction conditions. Several researchers\(^{16-18}\) have shown that Na_2SO_4 can be used as an additive in the direct reductions of laterite nickel ore, high-aluminum iron ore, and red mud to decrease the impurity content of the resultant DRI powder. Therefore, Na_2SO_4 was used as an additive in the present study.

2. Materials and Methods

2.1. Raw Material

The raw beach TTM was obtained from Indonesia, ground to 90 wt.% passing 0.074 mm. The TTM concentrate used in this study was obtained by using low-intensity magnetic separation at a magnetic field intensity of 80 kA/m from raw beach TTM. The chemical analysis results of the TTM concentrate are shown in Table 1; in contrast to the corresponding values in raw beach TTM iron sand, the treated TTM concentrate showed an iron grade of 57.29% (improvement of 3.55%) and TiO_2 grade of 11.42% (improvement of 1.00%). The SiO_2 and Al_2O_3 contents of the concentrate, which are the main components of gangue minerals, totaled only 3.01% and 2.90%, respectively.

Bituminous coal was used as a reductant. The industrial analysis results of the bituminous coal showed 54.83% fixed carbon, 13.97% ash, 31.21% volatile matter, and 13% moisture content. The Na_2SO_4 used was of chemical grade.

2.2. Pellet Formation, Reduction and Separation

The test flowsheet and crucible charging method are shown in Fig. 1. CMC, which shows good adhesion properties and excellent volatility at high-temperature was used as a low-dosage binder. The mixture of TTM concentrate and Na_2SO_4 was pressed to form pellet before subjecting to reduction roasting by the following procedures: first, 20 g TTM concentrate, a variable Na_2SO_4 addition (from 0 wt.% to 8 wt.%), CMC (0.5 wt.%) and water (5 wt.%) were mixed together, and then the mixture was pressed to form pellet using a die with a size of 30 mm diameter with the aid of hydraulic equipment. Three pellets were embedded in excessive bituminous coal placed in a crucible with a cover (Fig. 1(b)). The crucible was then placed into a muffle furnace at 1200°C and withdrawn after 300 min. After roasting, the roasted pellets were cooled to room temperature in the crucible, crushed to ~2 mm, and then separated by two-stage grinding and wet magnetic separation. Grinding was conducted in a rod mill (RK/BM-1.0 L). First-stage grinding was performed for 15 min, while second-stage grinding was performed for 20 min. An XCGS-73 magnetic tube with a magnetic field intensity of 151 kA/m was used to recover metallic iron. The magnetic and non-magnetic products were designated DRI powder and titanium concentrate.

| Table 1. Chemical analysis of the TTM concentrate %. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | TFe  | TiO_2 | SiO_2 | Al_2O_3 | MgO  | CaO  | MnO  | Na_2O | P_2O_5 | K_2O  |
| Content wt.%    | 57.29 | 11.42 | 3.01  | 2.90   | 2.73 | 0.02 | 0.37 | 0.30  | 0.07  | 0.12  |

Fig. 1. Test flowsheet and crucible charging method.
Iron grade, iron recovery, and TiO₂ content in the DRI powder and TiO₂ grade, as well as TiO₂ recovery in the titanium concentrate, were used to assess the effect of embedding direct reduction roasting followed by magnetic separation.

2.3. Analysis and Characterization

XRD patterns were recorded using a diffractometer (Rigaku D/Max 2500, Japan) under the following conditions: radiation Cu Kα of 150 mA tube current and voltage of 40 kV, scanning range of 10° to 100°, step size of 0.02°, and scanning speed of 5°/min. Polished sections were prepared to observe the morphological changes and analyze the element content of the roasted pellets using Scanning Electron Microscopy (Carl Zeiss EVO18, Germany) equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector (Bruke XFlash Detector 5010, Germany). ESEM images were recorded in backscatter electron modes operating in low vacuum mode at 20 kV.

3. Results and Discussion

3.1. Effect of Na₂SO₄ Dosage on the Separation of Titanium and Iron

The magnetic separation results of roasted pellets with the addition of Na₂SO₄ at dosages ranging from 0% to 8% are shown in Fig. 2.

Figure 2 shows that Na₂SO₄ greatly influences the results of roasting magnetic separation. Figure 2(a) shows that the iron grade of DRI powder increases initially from 88.12% to 94.45% as the Na₂SO₄ dosage increases from 0% to 4%. Afterward, the iron grade of DRI powder remains stable at about 94%. The TiO₂ content decreases from 1.26% to 0.44% as the Na₂SO₄ dosage ranges from 0% to 4% and then remains stable at about 0.4% when the Na₂SO₄ dosage exceeds 4%. The data above indicate that addition of Na₂SO₄ is beneficial to iron and titanium separation. Iron recovery of DRI powder increases from 74.27% to 85.18% as the Na₂SO₄ dosage increases from 0% to 4%. A sharp drop in iron recovery from 85.18% to 74.10% was further observed as the Na₂SO₄ dosage increases from 6% to 8%. These results indicate a suitable range of Na₂SO₄ contents is conducive to iron recovery; beyond this range, poor recovery is observed.

Figure 2(b) shows that the TiO₂ grade of the titanium concentrate without Na₂SO₄ is low. The TiO₂ grade of the titanium concentrate increases from 33.77% to 40.94% as the dosage of Na₂SO₄ varies from 0% to 6% but decreases from 40.94% to 29.96% with further increases in Na₂SO₄ dosage from 6% to 8%. As the Na₂SO₄ dosage varies from 0% to 8%, TiO₂ recovery in the titanium concentrate slowly improve and all are over 96%. These results prove that addition of some Na₂SO₄ is conducive to titanium and iron separation and enrichment. Within the optimal range of Na₂SO₄ contents, the TiO₂ grade of the titanium concentrate may exceed 40%. However, excessive Na₂SO₄ decreases the grade of the titanium concentrate. Good results are achieved when the Na₂SO₄ dosage is between 4% and 6%. And the sulfur content of DRI powder with Na₂SO₄ dosage of 4% and 6% are 0.07% and 0.12% respectively. The optimal Na₂SO₄ dosages obtained in this work are lower than those reported in a previous study, which required about 15% Na₂SO₄.13,16,18) Thus, higher Na₂SO₄ dosages lead to lower-grade TiO₂ in the non-magnetic product and introduction of more sulfur impurities to the products.

3.2. Phase Transformation of the Roasted Pellets with Different Na₂SO₄ Dosages

To analyze the phase transformation of the roasted ore, X-ray diffraction (XRD) was used. Prior to analysis, the roasted pellets were ground to less than 38 μm. The mineralogical phase transformations of iron and titanium minerals caused by different dosages of Na₂SO₄ are presented in Fig. 3.

The XRD patterns of the different roasted pellets show that the main phase of the raw pellets is TTM, as shown in Fig. 3(1). All of the XRD patterns obtained demonstrate no more than three titanium minerals in the roasted pellets, regardless of the added Na₂SO₄ content. Compared with previous results,12–15) the previous study showed not only iron–titanium minerals but also magnesium–titanium minerals in the roasted products. The results obtained in this paper illustrate that the proposed process could decrease the number of titanium mineral species in the resultant products.

The XRD pattern of the roasted pellet without Na₂SO₄ exhibits high contents of metallic iron (b) and ulvospinel (c) and small amounts of wustite (h), ilmenite (d), and ferrous pseudobrookite (a), as shown in Fig. 3(2).
result illustrates that the reducing atmosphere in the present system is insufficient. According to the experimental phenomenon, there was amounts of remaining bituminous in crucible, thus, pellets with inadequate porosity in the pellet are obtained. Low porosity decreases the efficiency of gas diffusion and reduces the reducing atmosphere, thereby resulting in the emergence of wustite (h) and large amounts of ulvospinel (c). Wustite (h) and ulvospinel (c) fall into the titanium concentrate during grinding and magnetic separation because they are non-magnetic materials. Ulvospinel (c), in particular, is a titanium mineral with high-grade iron and poor-grade TiO₂. These results explain the low iron recovery in DRI powder and the low-grade TiO₂ in titanium concentrate without Na₂SO₄ in Fig. 2.

The roasted pellet with a Na₂SO₄ dosage of less than 4% exhibits high contents of metallic iron (b), ilmenite (d), and ferrous pseudobrookite (a) and a small amount of ulvospinel (c), as shown in Figs. 3(3)–3(4). The main titanium minerals are ferrous pseudobrookite (a) and ilmenite (d), both of which feature high TiO₂ contents. As the Na₂SO₄ dosage increases from 0% to 4%, the diffraction peaks of ilmenite (d), ferrous pseudobrookite (a), and iron (b) become weaker, whereas that of ulvospinel (c) becomes stronger; peaks of nepheline (e) and troilite (f) also appear, as shown in Figs. 3(4)–3(6). In particular, when the Na₂SO₄ dosage is 8%, the diffraction peaks of ferrous pseudobrookite (a) and ilmenite (d) nearly completely disappear, the iron peak clearly decreases, and the peak intensity of ulvospinel (c) increases, as shown in Fig. 3(6). The increase in the ulvospinel (c) peak and the disappearance of ilmenite (d) indicate that the latter could react with wustite (h) to form ulvospinel (c) through reaction (V) in a weak reducing atmosphere.¹⁰ Because Na₂SO₄ reacts with silicate minerals to form low-melting point nepheline through reaction (II). The reducing atmosphere is weak in the molten ore because the diffusion rate of the reducing gas decreases through formation of low-melting point minerals.¹⁰ Reduction of FeO to Fe, which requires a strong reducing atmosphere, is more difficult to process than reaction (V) in a weak reducing atmosphere. The standard Gibbs free energy of reaction (II) and (V) are both negative (ΔGT < 0) at the temperature 1 200°C according the thermodynamic calculations.²⁹ So troilite (f) and ulvospinel (c) can be formed by reaction (II) and (V). Given that troilite (f) and ulvospinel (c) are non-magnetic, its formation are in accordance with the a decrease in iron recovery in DRI and TiO₂ grade of the titanium concentrate, as shown in Fig. 2.

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\begin{align*}
\text{Na}_2\text{SO}_4 + 4\text{CO}(g) &= \text{Na}_2\text{S} + 4\text{CO}_2(g) \\
\Delta G^\theta_T &= -146,879.92 + 60.96T \\
\text{Na}_2\text{S} + \text{FeO} + 2\text{SiO}_2 &= \text{Na}_2\text{Si}_3\text{O}_5 + \text{FeS} \\
\Delta G^\theta_T &= -81,990.96 - 27.71T \\
\text{Na}_2\text{SO}_4 + 3\text{CO}(g) &= \text{Na}_2\text{O} + \text{S} + 3\text{CO}_2(g) \\
\Delta G^\theta_T &= 114,368 + 14.68T \\
\text{Fe} + \text{S} &= \text{FeS} \\
\Delta G^\theta_T &= -100,537 - 4.59T \\
\text{FeO} + \text{FeTiO}_3 &= \text{Fe}_3\text{TiO}_4 \\
\Delta G^\theta_T &= 40,964 - 107.17T
\end{align*}
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In order to fully explain the experimental data and further explore the mechanism, roasted pellets obtained with different dosage of Na₂SO₄ were studied by SEM.

3.3. The Macrostructure of the Roasted Pellets

The roasted pellets with Na₂SO₄ contents ranging from 0% to 8% are cut and polished, and then all polished pellets are took a picture in Fig. 4.

As shown in Fig. 4, the light white phase covers the entire pellet as the Na₂SO₄ dosage increases from 0% to 4% (Fig. 4(a)). With increasing Na₂SO₄ dosage, the roasted pellet sections become more and more heterogeneous, and the outer edges of the distribution of light white phase are larger than those in the central regions. When the Na₂SO₄ dosage is 8%, a clear boundary around the central region are observed. Based on the different colors obtained, the roasted pellets explain the high iron recovery of DRI powder and the high-grade TiO₂ of the titanium concentrate in Fig. 2.

By increasing the Na₂SO₄ dosage from 4% to 8%, the diffraction peaks of ilmenite (d), ferrous pseudobrookite (a), and iron (b) become weaker, whereas that of ulvospinel (c) becomes stronger; peaks of nepheline (e) and troilite (f) also appear, as shown in Figs. 3(4)–3(6). In particular, when the Na₂SO₄ dosage is 8%, the diffraction peaks of ferrous pseudobrookite (a) and ilmenite (d) nearly completely disappear, the iron peak clearly decreases, and the peak intensity of ulvospinel (c) increases, as shown in Fig. 3(6). The increase in the ulvospinel (c) peak and the disappearance of ilmenite (d) indicate that the latter could react with wustite (h) to form ulvospinel (c) through reaction (V) in a weak reducing atmosphere.¹⁰ Because Na₂SO₄ reacts with silicate minerals to form low-melting point nepheline through reaction (II). The reducing atmosphere is weak in the molten ore because the diffusion rate of the reducing gas decreases through formation of low-melting point minerals.¹⁰ Reduction of FeO to Fe, which requires a strong reducing atmosphere, is more difficult to process than reaction (V) in a weak reducing atmosphere. The standard Gibbs free energy of reaction (II) and (V) are both negative (ΔGT < 0) at the temperature 1 200°C according the thermodynamic calculations.²⁹ So troilite (f) and ulvospinel (c) can be formed by reaction (II) and (V). Given that troilite (f) and ulvospinel (c) are non-magnetic, its formation are in accordance with the a decrease in iron recovery in DRI and TiO₂ grade of the titanium concentrate, as shown in Fig. 2.
could be divided into a central region and edges.

Figure 4 also shows that when the Na$_2$SO$_4$ dosage is at least 4% (Fig. 4(c)), the roasted pellets begin to expand; expansion continues with increasing dosage of Na$_2$SO$_4$. When the Na$_2$SO$_4$ dosage is 8%, a large crack develops in the middle of the roasted pellet (Fig. 4(e)), the volume increases and expands significantly.

3.4. The Microstructure of the Roasted Pellets

The microstructures of the roasted pellets and the occurrence of the main elements were analyzed by SEM coupled with energy dispersive spectrometry (EDS); areas in Fig. 4 were further magnified in Fig. 5. SEM images of roasted pellets with different dosages of Na$_2$SO$_4$ are illustrated in Figs. 5(1)–5(3). Figures 5(1-A)–5(3-A) and 5(1-B)–5(3-B) represent the magnified views of the areas marked in Figs. 5(1)–5(3).

Figure 5 shows that increasing the Na$_2$SO$_4$ dosage increase the size of metallic iron particles (white). Without Na$_2$SO$_4$, the size of metallic iron at the edges of the particles is identical to that at the center of the particles (Figs. 5(1-A) and 5(1-B)). The iron measures only a few microns, and some of the particles are closely associated with the titanium minerals. The boundary between iron particles and titanium minerals is not clear. Metallic iron and titanium mineral liberation is difficult to achieve because of these fine structures. As well, some of the fine iron particles are covered by titanium minerals, while some of the coarse iron particles are associated with ferrous pseudobrookite (a). Wustite (h) is observed in Fig. 5(1-B). The results explain that the iron recovery and grade both are poor when the dosage of Na$_2$SO$_4$ is 0% in Fig. 2(a), and TiO$_2$ grade of titanium concentrate is poor in Fig. 2(b). Thus, the finely disseminated minerals respond very poorly to physical separation methods. Ferrous pseudobrookite (a) is observed at the edges of the products by using EDS in Fig. 5(1-A), and ulvospinel (c) is observed around wustite (h) at the central region of the products in Fig. 5(1-B). These results illustrate that the reducing atmosphere is weaker at the central region of the roasted pellets than at their edges. Because of the pellets were embedded by bituminite, the reducing gas diffused from the edges to the central region. Figure 5(1-A) shows that the edges of the roasted pellet are not porous, which can reduce the diffusion rate of CO and result in the emergence of wustite (h) and ulvospinel (c).

Figure 5(2-A) shows that 4% Na$_2$SO$_4$ causes particles at the edges of the products to grow larger than those in Fig. 5(1-A). Significant growth and aggregation of the metallic iron particles existing at the edges of the roasted pellet is observed; and the shape of iron particles are round in Fig. 5(2-A), but irregular in Fig. 5(1-A). The changed shape illustrate that addition Na$_2$SO$_4$ is benefit to form melting phase and change the surface tension of iron particles. The metallic iron particles are enclosed by a small amount of troilite (f). Troilite (f) serves as an activating agent that facilitates melting phase formation and improves the transport rate to accelerate iron particle aggregation. Thus, troilite (f) could reduce surface tension and increase the metallic particle size. Ilmenite (d) is found among the metallic iron particles. Edges in Fig. 5(2-A) are looser than those in Fig. 5(1-A), which proves that reaction (I) promotes porosity. Figure 5(2-B) shows grown iron particles associated with titanium minerals, which aggregate together at the center of the pellets. Most of the titanium minerals are composed of ilmenite (d). The roasted ore surface is saponaceous, which illustrates that the pellets are molten during the reduction roasting process by addition of Na$_2$SO$_4$. Nepheline (e) is observed by using EDS. Nepheline (e) could decrease the melting point of the whole system; the molten structure of the roasted ore accelerates the migration rate of the metallic iron particles, which benefits particle growth. Therefore, the particle size of most iron particles exceeds 50 μm, and an obvious boundary between the iron particles and titanium minerals is observed. This boundary allows metallic iron
separation from non-magnetic titanium minerals through grinding-magnetic separation. The evidence obtained thus far supports the observation of increasing iron recovery and grade in Fig. 2(a) and increasing TiO\textsubscript{2} grade of the titanium concentrate in Fig. 2(b) with increasing addition of Na\textsubscript{2}SO\textsubscript{4} from 0\% to 4\%.

Figure 5(3-A) shows that when the Na\textsubscript{2}SO\textsubscript{4} dosage is 8\%, the metallic iron particles grow further and eventually aggregate extensively. In addition to several large holes, no porosity is observed in the products, and more FeS (f) enclose the iron particles. This phenomenon indicates excessive molten phase formation with increasing Na\textsubscript{2}SO\textsubscript{4} dosage, which inhibits the reducing gas from entering them. Figure 5(3-B) shows that titanium minerals are mainly concentrated in the central part of the products and that ulvospinel (c) is the main component. The TiO\textsubscript{2} content in these particles is much lower than those in ilmenite (d) and ferrous pseudobrookite (a), and nearly no iron particles are observed. Therefore, reduction of the titanium minerals could be suppressed by decreasing the diffusion rate of the reducing gas in the molten structure. Since ulvospinel (c) is non-magnetic, it falls into the titanium concentrate after grinding and magnetic separation, leading to poor iron recovery and low TiO\textsubscript{2} grades in the titanium concentrate.

These results demonstrate that excessive molten phase formation suppresses reduction, which explains the experimental data in Fig. 2. When the Na\textsubscript{2}SO\textsubscript{4} dosage exceeds 6\%, iron recovery of DRI powder and the TiO\textsubscript{2} grade of the titanium concentrate sharply decline. These results also explain the phenomenon of the pellets expansion in Fig. 4. Excessive molten phase formation stops gases, including CO\textsubscript{2} produced through iron oxide reduction and the gas produced by the Na\textsubscript{2}SO\textsubscript{4} reaction, from being releasing outside of the pellets. As gases accumulate inside the pellets, the inside pressure results in volume expansion.

Compared with the dosage of Na\textsubscript{2}SO\textsubscript{4} adding 8\%, metallic iron particles of Na\textsubscript{2}SO\textsubscript{4} 4\% addition are big enough and more than 50 um, iron oxide and titanium are further reduced in the products, and the main titanium minerals found in the titanium concentrate include ilmenite (d) and ferrous pseudobrookite (a). Complete recovery of iron and a rich titanium concentrate are finally obtained, and a dosage of 4\% Na\textsubscript{2}SO\textsubscript{4} is found to be optimal.

4. Conclusions

(1) High-grade DRI powder and titanium concentrate may simultaneously be achieved through embedding direct reduction and magnetic separation. The best result could be achieved when Na\textsubscript{2}SO\textsubscript{4} dosage of 4\% is used; under this condition, DRI powder with an iron grade of 94.45\%, iron recovery of 85.18\%, TiO\textsubscript{2} content of 0.44\%, and TiO\textsubscript{2} grade
of 40.43% in the titanium concentrate may be obtained.

(2) The XRD analysis of roasted pellet and the experimental data with Na$_2$SO$_4$ indicated that iron recovery of DRI powder and TiO$_2$ grade of titanium concentrate has an increase at first, because of a suitable Na$_2$SO$_4$ addition (2%–6%) promoted the porosity of the pellets and reduction of titanium mineral and iron oxide. With continue addition, the results were opposite. Because of excessive Na$_2$SO$_4$ addition (>6%) formed more molten phases, which inhibited the diffusion rate of the reducing gas and minerals reduction. Meanwhile, excess formation of the molten phase stopped the gases within the pellets from being released, thereby resulting in volume expansion of the pellets.

(3) The roasted pellets with the addition of Na$_2$SO$_4$ had a closed microstructure. Without Na$_2$SO$_4$, fine metallic iron particles associated with titanium minerals could not be separated by grinding and magnetic separation. With Na$_2$SO$_4$ addition, metallic particles grew up obviously. The mechanism of Na$_2$SO$_4$ in promoting size of metallic iron particles was that Na$_2$SO$_4$ could react with silicate and wustite to form troilite and nepheline in reducing atmosphere. Troilite can be enriched in the surface of metallic iron particle and decrease the surface tension of metallic iron particles to promote the growth of metallic particle size. Moreover, the low-melting point nepheline was formed, which could accelerate the migration rate of metallic iron particles and promote the growth of metallic iron particles.

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REFERENCES
1) S. Amarchand, T. Ramamohan and P. Ramakrishnan: Miner. Process. Extr. Metall. Rev., 22 (2001), 279.
2) C. V. Sundaram: Miner. Process. Extr. Metall. Rev., 10 (1992), 239.
3) V. T. Kalinnkov and A. I. Nikolaev: Miner. Process. Extr. Metall. Rev., 22 (2002), 453.
4) L. Z. Chen, S. M. Wen and G. D. Xu: Miner. Process. Extr. Metall. Rev., 34 (2013), 139.
5) R. J. Longbottom, O. Ostrovski and E. Park: ISIJ Int., 46 (2006), 641.
6) L. Lv, S. J. Wang and T. B. Yue: Metal Mine, 1 (2012), 73 (in Chinese).
7) M. S. Jena, H. K. Tripathy, I. K. Mohanty and J. N. Mohanty: Sep. Sci. Technol., 50 (2015), 1221.
8) L. Zhao, L. Wang and D. Chen: Trans. Nonferrous Met. Soc. China, 25 (2015), 1325.
9) E. Park and O. Ostrovski: ISIJ Int., 44 (2004), 74.
10) E. Park and O. Ostrovski: ISIJ Int., 43 (2003), 1316.
11) J. Liu, G. Cheng and Z. Liu: Steel Res. Int., 86 (2015), 808.
12) D. Chen, B. Song and L. Wang: Miner. Eng., 24 (2011), 864.
13) E. X. Gao, T. C. Sun, C. Y. Xu, Z. G. Liu and C. X. Yu: Metal Mine, 14 (2013), 46 (in Chinese).
14) C. X. Yu, T. C. Sun, C. Y. Xu and E. X. Gao: Min. Metal. Eng., 5 (2014), 93 (in Chinese).
15) B. H. Gao, H. J. Wang, Y. Qu and L. Li: Min. Metal. Eng., 5 (2012), 44 (in Chinese).
16) G. Li, T. Shi and M. Rao: Miner. Eng., 32 (2012), 19.
17) M. Jiang, T. C. Sun, Z. G. Liu, J. Kou, N. Liu and S. Y. Zhang: Int. J. Miner. Process., 123 (2013), 32.
18) M. D. Liu, T. Jiang, G. H. Li, Y. Liu and Z. Z. Liu: Chin. J. Nonferrous Met., 8 (2014), 2129 (in Chinese).
19) R. Inoue and H. Suito: ISIJ Int., 46 (2006), 174.
20) D. L. Ye and J. H. Hu: Practical Inorganic Thermodynamic Data Sheet, Metallurgical Industry Press, Beijing, (2002), 175 (in Chinese).