Evaluation of groundnut shell as a reductant for microwave reduction of low grade banded iron ore

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Abstract. This study investigates the utilization of low-grade banded iron ore for its utilization as a blast furnace feedstock. The complex association of the quartz-hematite phase and a fine liberation size prohibits the direct use of these ores in the steel production cycle. Conventional reduction experiments using different reductants yielded limited iron enrichment. Microwave carbothermal reduction using economical and abundantly available groundnut shell was investigated using a Taguchi L9 statistical design. The design optimal condition of 900W power, 20 min time and 3% equivalent carbon yielded an enriched iron concentrate with Fe 58% at 85.6% recovery. Characterization studies reveal the formation of sequential hematite, magnetite and wustite formation with groundnut shell dosage. The concentrate obtained can be used as feedstock for blast furnace burden. Microwave reduction was found better in terms of product control than conventional reduction, as fayalite formation was not observed.

1. Introduction
India’s steel vision 2030 targets 300 million tons of steel production, which require approximately 550 million tons of quality iron ores (~60% Fe). India does not have enough high-grade hematite ores but possesses abundant resources of banded iron ores namely banded hematite quartzite/Jasper (BHQ, BHJ), banded magnetite quartzite (BMQ) and discarded slimes. During conventional mining of hematite ores, there is a significant generation of banded iron ores, which often ends up in unused stockpile at the mine sites [1, 2]. The iron bands in these ores are of hematite and magnetite along with quartz-rich bands of varying thickness ~0.5 to 1.5 cm. These ores possess different beneficiation characteristics primarily because of negligible alumina content, excessive quartz content and fine liberation size (<100 microns) which makes them hard compared to conventional hematite ores. The iron content in these ores varies from 30-45% and are located in the states of Odisha, Karnataka, Chattisgarh, and Rajasthan, India [1]. The investigations on the beneficiation of BHQ, BHJ, and BMQ are few and includes processing techniques such as the flotation, magnetic separation, jigging and conventional roasting [3, 4]. The carbothermal exposure involves ore reduction in a reducing environment at 500-700°C for partial reduction of hematite to magnetite followed by low-intensity magnetic separation (LIMS) to obtain iron-rich concentrate. The reduction process suffers because of an associated energy penalty but includes a simpler separation step of magnetic separation, and reduced grinding costs due to the increased friability of the roasted ore [5, 6]. The reduction of low-grade iron ores, on an average yields 10-15% increment with 50-70%, Fe recovery [7-9].
BHJ ore resembles taconite ore processed in North America in terms of the banded structure of the iron and quartz phase. However, the absence of the magnetite phase in BHJ makes the beneficiation difficult compared to conventional magnetic processing of taconite ore. The microwave treatment on taconite and magnetite ore causes selective thermal expansion leading to reduced comminution energy along with a cleaner liberation improving the concentrate grade and recovery [10, 11]. The various applications of microwave exposure include faster-controlled temperature ramp-up, enhanced kinetics, rock disintegration, better liberation, and enhanced magnetic properties along with enhanced separation [12-18]. It is reported that oxides-sulfides are good receivers of microwave radiations whereas silicates are poor receptors of microwaves [13]. Since BHJ ore comprises hematite and quartz, it is expected that selective heating of hematite can occur with microwave irradiation. The prime objective of microwave treatment is to selectively transform the hematite phase in the ore to magnetite followed separation in a low-intensity magnetic separator. Unlike conventional ores, BHJ ore consists of alternate bands of hematite and jasper phase in bonded form, therefore, it is expected that the reduction conditions will differ from the ideal thermodynamic conditions [5, 12, 14, 16, 17, 19-21].

It is known that iron oxide can be reduced to Fe, at 700 °C, whereas Al2O3 and SiO2 cannot be reduced below 1450 °C [19, 23]. The reduction is dominated by the direct reduction (with solid carbon) at the initial stage of reduction and is finally determined by indirect reduction (gaseous CO/CO2) together with the carbon solution loss reaction [22, 23]. Compared to the reduction of iron oxides in conventional heating, the solid-state reaction occurred at low temperatures for the microwave reduction along with a different sequence of chemical reactions [12, 14, 19]. The microwave electromagnetic field selectively induces the magnetite dissociation which is a strong microwave absorbing material, to produce oxygen gas that can react with solid carbon, to form CO and CO2 gases. The microwave absorbing power of magnetite diminishes at about 650 °C and reduction to wustite are accomplished below this temperature. It is reported that as the fraction of carbonaceous material increases, the attained temperature increases resulting in the higher reduction ores [12, 19, 24]. This is because the main heat source of microwave heating is carbonaceous material rather than iron oxides. It takes a longer time to initiate the heating reduction than magnetite because hematite is hardly heated from room temperature by microwaves [19]. Microwave reduction is a non-isothermal process and considering this, the effect of reductant dosage, temperature and microwave power on the reduction process is systematically pursued. Previous studies do not emphasize on the carbon requirement, underlying reduction mechanism, and hence lack a systematic approach for the evolution of iron oxides during reduction. There are research works for up-gradation of low-grade iron ores but to the best of author’s knowledge, no systematic investigation employing microwave carbothermal reduction is reported on BHJ ore. The purpose of the present study is to evaluate the conventional and microwave-assisted carbothermal reduction for processing of low grade banded iron ore. Further, an attempt is made to evaluate an alternative economical reductant ground nutshell for the enrichment of the low-grade Indian BHJ ore through the carbothermal reduction process. Different reductant parameters such as reductant dosage, time, power, and temperature were evaluated for both the routes. The obtained concentrate through different processes was further characterized to identify the iron enrichment along with underlying phase transformations.

2. Materials and methodology

BHJ ore sample used in this study was procured from a working mine situated in Karnataka, India, assaying 51.8% iron oxide and 46.1% quartz as a significant impurity. The photograph of the as-received sample and corresponding optical micrograph shown in Fig. 1a, b depicts the dispersed and interlocked structure of hematite within the jasper matrix. The XRD spectra are shown in Fig. 1c reflects the hematite and quartzite phase along with the traces of magnetite. The quantitative phase analysis determined by the area under the respective peaks yielded the phase fraction of hematite, quartzite, and magnetite as 47.7%, 51.7%, and 0.5% respectively. The sample was stage-wise crushed using jaw and roll crusher followed by grinding in a laboratory ball mill. The standard riffler sampling method is used for obtaining the representative sample and the effect of particle size on iron grade is shown in Fig. 1d. Particle size below 75 microns possesses higher iron grade suggesting better
liberation and is chosen as a representative sample with an overall 38.7 % iron. The overall experimental plan followed is shown in Fig. 2a. The thermo-gravimetric analysis (TGA) is conducted for feed, activated charcoal, and groundnut shell as shown in Fig. 2b reveals a similar behavior with all reductants (activated charcoal and groundnut shell) having a weight loss of approximately 80-85%. The oxidation of reductants around temperature 200°C - 550°C caused evaporation of volatile matter and a small weight loss (approximately 4-5%) between 350°C-800°C temperature due to ore dehydroxylation.

Figure 1. (a) Photograph of hand specimen (b) Optical microscope image (c) XRD spectra (d) Variation in iron grade with particle size (e) Chemical composition of BHJ ore.

The carbothermal reduction experiments were carried out in a refractory grade crucible with lid in a muffle furnace (Carbolite, CWF1200) and microwave unit (LG make, 900 Watts, 2.45 GHz) using charcoal and GNS. The CHNS analysis of the charcoal and GNS reveals the presence of 0.7% nitrogen, 79.6% carbon, 2.1% hydrogen, 0.4% sulfur and 1.2% nitrogen, 44.1% carbon, 5.5% hydrogen, 0.3% sulfur respectively. The GNS sample was procured from the local vendor contains carbon values almost half compared to activated charcoal. GNS was oven-dried for 6h at 70°C moisture prior to pulverization in attritor mill (IKA-A100). The stoichiometric amount of carbon required for the complete reduction of hematite to metallic iron is calculated as 6.03 % according to Eq. (1). The reduced product is water quenched to prevent the re-oxidation of the reduced phases. The quenched sample is subsequently pulverized and subjected to LIMS at 1800 Gauss to recover the
magnetic values. The quantitative iron analysis present in the magnetic concentrate is determined using a standard potassium dichromate titration procedure. The change in the magnetic characteristics is evaluated through vibratory sample magnetometer (VSM). The process yield and iron recovery are calculated as shown in Eq. (2-3).

\[ \text{Fe}_2\text{O}_3(s) + 3\text{C}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow 2\text{Fe}(s)+2\text{CO}(g)+\text{CO}_2(g) \]  

(1)

3. Results and discussion

3.1 Muffle furnace reduction

The preliminary experiments conducted below the temperature of 700ºC with charcoal dosage below 9% could not yield suitable iron enrichment as a concentrate, because the reductant and ore mixture was found partially unburnt. Therefore based on literature, the reduction experiments were conducted in a muffle furnace using charcoal and GNS at a fixed temperature of 700ºC, 30 min at varying
reductant dosage (4-12%) whereas stoichiometric value is ~6% as shown in Eq (1). As shown in Fig. 3a, the iron grade lies in between 39-46% and iron recovery of 94-99% with GNS as reductant, however, with charcoal, the iron grade of 39-56% and iron recovery of 94-99% was attained. The XRD spectrum shown in Fig. 3(b) depicts a significant reduction of hematite to magnetite up to 6% carbon, however, above 6%, the formation of wustite phase was observed. The formation of wustite phase leads to the fall in the iron grade being non-magnetic in nature. The VSM analysis of the feed and the magnetic fractions is shown in Fig. 3c reveals an increase in saturation magnetization value from 5 to ~40 emu/g with the addition of GNS, however, the formation of wustite phase appeared beyond 6%. The quantitative XRD analysis depicts the formation of wustite above 6% carbon, whereas the hematite phase reduces drastically from ~54 to 10% and stepwise iron oxide reduction (hematite-magnetite-wustite) was also observed. It should be noted that the saturation magnetization is almost constant beyond 3% carbon.

\[
\text{Fe}_{\text{Recovery}}\% = \frac{(\text{Fe}_{\text{Grade}} \times \text{Weight})_{\text{magnetic}}}{(\text{Fe}_{\text{Grade}} \times \text{Weight})_{\text{feed}}} \times 100
\]  

(2)

\[
\text{Yield}\% = \frac{\text{Weight}_{\text{magnetic}}}{\text{Weight}_{\text{Total}}} \times 100
\]  

(3)

**Figure 3** Effect of carbon dosage on (a) iron grade and recovery (b) XRD plot of magnetic concentrate (c) Quantitative phase analysis 700C 30 min in a muffle furnace

### 3.2 Microwave reduction

Due to limited iron enrichment in the conventional reduction, the microwave reduction was pursued. The experiments were conducted at 900W for 10 min using both charcoal and groundnut shell. The
effect of reductant dosage on the iron concentrate parameters is reflected in Fig. 4. The iron grade and recovery show a similar trend with both reductants, however, GNS was found comparable and was hence further pursued to identify the optimal conditions. In both reductants, the grade of concentrate is close to 50% with an iron recovery of more than 90%. The carbothermal reduction process was investigated using a statistical Taguchi-L₉ orthogonal array design using three factors. Power, time, and reductant dosage were the factors considered whereas iron grade and recovery were process responses. The prime objective is to determine an optimal condition, i.e., conditions to maximize iron grade and recovery and evaluating the significant factor. It is important to mention that a residence time of fewer than 10 min, does not lead to the flame formation resulting in unburnt GNS and ore mixture. Each experiment was conducted twice and mean values are reported in the response Table 1. As expected the temperature attained during the design experiments significantly varied from 200-700°C. Fig. 5 show the contour plots for the iron grade, recovery, and temperature with statistically significant experimental factors. It is evident that low reductant dosage is favorable for the higher iron grade at a power of 720-900W. The effect of reductant dosage and microwave power on the concentrate recovery is shown in Fig. 5(b). The iron recovery increases from 84% to 94% and it decreases at both ends i.e., lower and higher reductant dosage. The effect of reductant dosage and power on the attained temperature in the magnetic concentrate shown in Fig. 5(c) depicts that the temperature increases with increasing reductant dosage and at higher power levels. Based on analysis of variance, the sequential order of dominating/influential factors on iron grade, iron recovery, and the temperature is shown in Fig. 5(d).

As expected at higher reductant dosage, both iron recovery, and iron grade falls however higher iron grade is attained at a lower dosage (3-4%) and is in line with conventional reduction. It can be concluded that reductant dosage and time are the most influential factors for both grade and recovery response. It can be observed from Table 1 that increasing reductant dosage leads to an increase in temperature, decreasing grade, and higher iron recovery. The regression equation derived for iron grade and recovery based on experimental response with all the factors is shown in Table 2. The statistical fit “R²” for the equations indicate the adequateness of the derived model. The plot of means of individual factors of the design for an iron grade, recovery, and the temperature is shown in Fig. 6.

### Table 1. Experimental design conditions and their respective response.

| S. No. | Reductant (%) | Time (min) | Power (W) | Temperature (°C) | Fe grade (%) | Fe recovery (%) | Yield (%) |
|--------|---------------|------------|-----------|------------------|--------------|----------------|----------|
| 1      | 3             | 10         | 540       | 206              | 55.85        | 88.77          | 58.81    |
| 2      | 3             | 15         | 720       | 285              | 55.63        | 84.83          | 56.43    |
| 3      | 3             | 20         | 900       | 402              | 58.08        | 85.61          | 54.53    |
| 4      | 6             | 10         | 720       | 427              | 51.38        | 92.85          | 66.86    |
| 5      | 6             | 15         | 900       | 693              | 51.83        | 94.54          | 67.49    |
| 6      | 6             | 20         | 540       | 409              | 49.15        | 79.29          | 59.69    |
| 7      | 9             | 10         | 900       | 608              | 45.57        | 90.83          | 73.74    |
| 8      | 9             | 15         | 540       | 384              | 45.35        | 97.83          | 79.82    |
| 9      | 9             | 20         | 720       | 613              | 49.15        | 85.49          | 64.36    |
| 10     | 3             | 20         | 900       | 398              | 58.1         | 87.6           | 55       |

### Table 2. Regression equation for iron grade and recovery based on statistical design.

- **Iron grade**: \( \text{Grade (\%) = 56.164 \times \text{Reductant dosage (\%) + 0.119 \times \text{Time (min) + 0.00475 \times \text{Power (W)}} \text{ (R}^2=0.92) \)

- **Iron recovery**: \( \text{Recovery (\%) = 91.6 + 0.83 \times \text{Reductant dosage (\%) - 0.735 \times \text{Time (min) + 0.0047 \times \text{Power (W)}} \text{ (R}^2=0.47) \)


Temperature (°C) = 351 + 39.6 Reductant dosage (%) + 6.1 Time (min) + 0.652 Power (W) (R²=0.84)

**Figure 4.** Microwave reduction at 900W for 10 min.

**Figure 5.** Contour plots of significant factors power and reductant for (a) iron grade (b) iron recovery and (c) temperature.

### Table

| Response      | Impact sequence         |
|---------------|-------------------------|
| Grade (%)     | Reductant > Power > Time|
| Recovery (%)  | Time > Reductant > Power|
| Temperature (°C) | Reductant > Power > Time |
For the iron grade, increasing the residence time and power, SN ratio initially increases slightly and on boundary condition, it falls below mean value. However, reductant dosage shows the opposite trend. For iron recovery, increasing the time from low to middle level, the SN ratio increases and on further increasing to the maximum level the value decreases significantly and falls below the mean value. The factor power and reductant dosage show a similar trend as in iron grade, whereas the SN ratio shows an increasing trend. Higher carbon dosage leads to increased absorption of microwaves resulting in high temperature. But for temperature, it shows an increasing trend with all the factors such as reductant dosage, residence time and power.

Fig. 7a shows the XRD and VSM analysis of the feed and magnetic concentrate corresponding to run 1, 3 and 5. These experiments were selected as they represent higher iron enrichment in terms of grade and iron recovery. The VSM analysis of the feed and the magnetic concentrate shown in Fig. 7b depicts a distinct difference in the saturation magnetization and is in agreement with iron grade recovery results. The XRF analysis for non-magnetic fractions depicts that silica content is enhanced in the nonmagnetic fraction along with some iron values which are significantly lower compared to the original sample. In all these experiments, hematite and magnetite are the major bearing phases and the magnetic saturation values increased from 4-5 emu/g (feed) to 9 emu/g (concentrate). As shown in Fig. 8, the backscattered electron micrograph and EDS atomic percent analysis of such reduced sample reveals the presence of magnetite, hematite, and cristobalite phases and is in agreement with XRD results. The points marked as 1, 2, 3, 5 reveals the wustite formation with formula Fe$_3$O$_y$ (x: 1-1.3 and y:1) along with some silica and magnetite.
Figure 7. (a) XRD plot, (b) Hysteresis loop (c) XRF of feed and Nonmag fractions of different experiments.

Figure 8. Backscattered electron micrograph and EDS analysis of reduced particles at 900 W, 20 min, 6% GNS.

4. Conclusions
In this study, up-gradation of low grade, banded hematite jasper is investigated. The conventional reduction with charcoal and GNS yielded an iron grade of 39-46% with an iron recovery of 94-99%. The formation of wustite phase inhibits the iron enrichment in the product. The microwave reduction offers suitable iron enrichment and shows a similar trend irrespective of reductants. GNS being economical and abundantly available was evaluated by Taguchi L9 statistical design optimization. The
optimal condition includes 900W power, 20 min time, 3% carbon and yielded a concentrate Fe$_G$ 58.08%, Fe$_R$ 85.61% with a yield of 54.53%. It is concluded that microwave carbothermal reduction employing cheap and abundant reductant GNS offers controlled reduction and the resulting concentrate can be used for blast furnace feedstock.

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