Comparative analysis of the effect of microwave pretreatment on the milling and liberation characteristics of mineral matters of different morphologies

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Abstract
This study was carried out to understand the impact of variation in material morphology on the efficacy of microwave pretreatment. Three different types of mineral matter – coal, iron ore and manganese ore – were treated with microwaves at different energy levels, from 180 to 900 W, for different time durations of one to five minutes. The treated samples were subjected to microscopic, milling and liberation studies. Coal is a porous and amorphous material with low dielectric constant, and grinding of the microwave-pretreated coal samples resulted in an 18.18 percent reduction in the 80 percent of passing particle size, or d_{80}, and a 17.1 percent increase in carbon recovery. The microwave-pretreated soft and friable manganese ore samples showed a 47.82 percent reduction in d_{80} during grinding and higher manganese recovery of 42.46 percent during liberation analysis. The microwave pretreatment and milling of hard and banded iron ore reduced the d_{80} by 20.83 percent, but no improvement was observed in mineral liberation. Coal showed better results during treatment at lower energy levels of 180 W for one to three minutes, whereas the minerals needed higher energy of 900 W for five minutes. Particle size analysis indicated rapid size reduction up to an energy input of 25 Wh. This effect diminished with increased energy input.

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Introduction
Comminution is an important unit operation in mineral processing plants for the purposes of size reduction and mineral liberation. But most comminution technologies are energy inefficient and only a small amount of energy is consumed in real size reduction, with the rest wasted. High-grade mineral resources have been exploited on a large scale for the last century, and the upgrading of low-grade resources is now required to fulfill the needs of industry. Pretreatment methodologies for comminution will play a crucial role in the upgrading of low-grade mineral resources. Researchers have studied various pretreatment methods to develop an energy-efficient and techno-economically viable solution to improve mineral liberation and product fineness with minimum energy consumption. Most of these studies were focused on the use of chemical additives, thermal, ultrasonic and microwave treatment, and electric disintegration (Klimpel and Austin, 1982; Norgate and Weller, 1994; Gaete-Garreton, Vargas-Hermandez and Velasquez-Lambert, 2000; Wilson et al., 2006; Kumar et al., 2010; Wang, Shi and Manlapig, 2011; Singh et al., 2012).

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Microwave processing has become a quite popular method for food processing, plastic curing and ceramic sintering (Clark and Sutton, 1996; Lovás et al., 2010; Menezes, Souto and Kiminami, 2012; Chandrasekaran, Ramanathan and Basak, 2013). Selective heating is the main apposite fundamental property of microwave energy for mineral processing. This property can produce stresses in the mineral matter structure due to the differential heating of minerals. Chen et al. (1984) described the general behavior of a number of minerals that were exposed to microwave radiation in air. McGill, Walkiewicz and Smyres (1988) studied the microwave heating of various minerals and chemicals. They measured the effect of microwave treatment on temperature rise and demonstrated the use of microwave energy in oxidation-reduction reactions, mineral liberation, and mercury retorting-vaporization. Walkiewicz, Clark and McGill (1991) investigated the microwave-assisted grinding of iron ore using microwaves with 2.45 GHz frequency at a power level of 3kW. Optical evaluation of the samples showed that rapid microwave heating for 25 seconds induced stress cracking in the iron ore. However, the reduction in grinding energy was not substantial enough for commercialization of the process.

Kingman and Rowson (1998) investigated the effect of microwave heating on the ring-loaded strength of Norwegian ilmenite and reported that the strength of the ore reduced considerably due to microwave treatment and quenching. Harrison and Rowson (1997) investigated the effect of conventional heating and microwave treatment using using microwaves with 2.45 GHz frequency at a power level of 650 W on bornite, chalcocite, chalcopyrite, magnetite and pyrite and reported an increase in surface area during grinding for all materials. Viswanathan (1990) applied microwave energy to coking and noncoking coal samples to observe changes in comminution behavior. Harrison and Rowson (1996) studied the effect of heat treatment on the grindability of coal and observed reductions of 20 to 30 percent in the comparative work index of studied samples. They concluded that microwave heating produces slightly better embrittlement results than conventional heating. Li et al. (2016) studied the effect of microwave treatment on the petrophysical properties of different rank coals and found that microwave treatment can change the internal structure of coal. In the recent past, a number of researchers have reported variation in the efficacy of microwave pretreatment for milling applications, mainly due to variation in material properties (Hartlieb et al., 2016; Batchelor et al., 2015; Bermúdez et al., 2015; Barani et al., 2012; Kim and Ahn, 2012). Researchers are in general agreement that microwave pretreatment affects the comminution and liberation behavior of minerals but the quantified outcomes were not similar and predictive. This was mainly due to irregular variations in material characteristics, such as mineralogy, degree of weathering, structure of the material and grain size. It can therefore be inferred that each material has an intrinsic response range of microwave parameters to produce optimum results, which depends on its properties.

This work was carried out to get a comparative view of the effect of microwave pretreatment on the milling and liberation performance of mineral matters of three different morphologies at commercially feasible process parameters. This can aid in understanding the variation in efficacy of microwave pretreatment due to variation in material properties, which can be helpful to the commercialization of the process.

Materials

The morphology of a mineral matter depends on its composition, grain properties, crystallinity and phase interfaces. Three morphologically different materials — coal, iron ore and manganese ore — were selected for this work to assess the impact of morphological changes on the efficacy of microwave pretreatment.

The results of proximate analyses and other important properties of the samples are listed in Table 1.

Coal. Coal is an aggregate of physically and chemically different macerals and minerals. It is composed of carbon, hydrogen, oxygen and sulfur. Its structure differs significantly from those of the manganese and iron ores. Coal samples of different sizes were collected from coal mines at West Bokaro, India.

Manganese ore. The selected manganese ore has a multimineral system that contains pyrolusite, psilomelane, hematite,

Table 1 — Properties of samples used in the experimental studies (McGill, Walkiewicz and Smyres, 1988; Speight, 2005) (CS = compressive strength, TS = tensile strength, EC = electric conductivity).

Material	Chemical analysis	Important properties	Structure and fracture pattern
Coal	Fixed carbon : 53.13% Volatile material : 17.76% Ash : 29.1% Moisture : 1.39%	CS : 10 to 15 MPa TS : 3 to 7 MPa EC : 0.6 to 10^5 Ωm	Bedded and porous structure Cleats Soft Brittle
Mn ore	Mn : 32.2% Fe (T) : 23.6% Al_2O_3 : 8.2% SiO_2 : 6.7%	CS : 40 to 50 MPa TS : 5 to 10 MPa $EC_{(MnO_2)}$: 3.5×10^{-3} to 10 Ωm $EC_{(Fe_2O_3)}$: 3.5×10^{-3} to 10^7 Ωm $EC_{(SiO_2)}$: 4×10^{10} to 2×10^{14} Ωm	Friable Soft Cleavage planes Micro-cracks
Fe ore	Fe (T) : 43.1% SiO_2 : 35.42% Al_2O_3 : 0.88%	CS : 100 to 150 MPa TS : 10 to 25 MPa $EC_{(Fe_2O_3)}$: 3.5×10^{-3} to 10^7 Ωm $EC_{(SiO_2)}$: 4×10^{10} to 2×10^{14} Ωm	Bedded Hard ores No cleavage planes Micro-cracks

goethite, quartz and kaolinite. The minerals present in the ore have various crystal structures, hardnesses, dielectric constants and thermal properties. Manganese ore samples were collected from Joda, Odisha, India for this study.

Iron ore. Banded hematite jasper (BHJ) ore is the best example of a bi-mineral — hematite and jasper — ore that has minerals of similar crystal structures. The similarity in crystal structure can have an impact on the packing of grains and other physical properties. Samples for this study were collected from Joda, Odisha, India.

Table 2 — Temperatures of coal samples treated at different microwave power settings.

Time (min)	Temperature (°C)		
	Low (180 W)	Medium (540 W)	High (900 W)
1	30	58	118
3	45	142	148
5	68	240	260

Experimental procedure

Sample preparation. The samples of coal, iron ore and manganese ore were collected and crushed into particles sized smaller than 50 mm. These were further crushed into particles sized smaller than 5.6 mm, from which 10 kg of material were taken out using a coning and quartering method for further grinding into particles sized smaller than 3.35 mm. Size analysis of the samples was carried out using 3.35-mm, 1-mm, 0.5-mm and 0.15-mm ASTM standard sieves.

Microwave treatment. Microwave tests were conducted using an LG MC-8047ARH microwave oven (LG Corp., Seoul, South Korea), with dimensions of 530 mm by 295 mm by 550 mm, input rating of 230 V, power rating of 900 W and operating frequency of 2.45 GHz. Energy and treatment time were selected considering the oxidation and sintering effect of microwave energy on coal and ore particles. The oven had a radiation-proof, transparent door and an electronic, programmable panel with options to control the microwave power and heating duration. The samples were thoroughly mixed, and 50-g samples of particles sized 0 to 3.35 mm were placed in an alumina crucible and kept in the microwave oven for durations of one, three and five minutes at energy inputs of 180, 540 and 900 W. As soon as the treatment time was up, the crucible was taken out and the temperature of the sample was measured using a Type K thermocouple with precision of ±5 percent. The sample was cooled and ground in the 500-mL bowl with 225 mL of usable volume of a Fritsch Pulverisette 6 planetary ball mill (Fritsch GmbH, Idar-Oberstein, Germany) for two minutes at 200 rpm using four stainless steel balls with diameter of 40 mm and ball density of 7.9 g/cm^3. Media loss was assumed to be negligible. These parameters were selected considering the optimum size reduction for all three materials. Size distribution and liberation analysis of the samples were carried out to evaluate the effect of treatment.

Characterization studies. The effect of microwave treatment on milling and liberation characteristics was evaluated by the change in particle size distribution and change in the quantity of liberated particles in the samples. Screening was done using 3.35-mm, 1-mm, 0.5-mm and 0.15-mm ASTM standard sieves. The impact of treatment of the particles was measured by comparing the 80 percent of passing particle size, d_{80}, and the mean particle diameter, d_{avg}. Change in d_{80} indicates overall increment in fineness whereas d_{avg} represents effect on generation of superfines, smaller than 150 µm. Fracture and surface characterization were carried out using a conventional microscope. Two grams of ore fines were used to prepare a microscopic sample with resin and hardener in a 9:1 ratio. The hard blocks were further polished and carbon coated for the microscopic studies, which were carried out using an Axioskop 2 image analyzer microscope with Axiovision 4.3 software (Carl Zeiss Microscopy LLC, Thornwood, NY). Liberation studies were carried out using different methods suitable for the different materials.

Sink-float analysis was carried out for coal and iron using liquids with densities of 1.5 g/cm^3 (carbon tetrachloride and benzene) and 2.89 g/cm^3 (bromoform), respectively. The samples were thoroughly mixed and put in the heavy density liquid in a 1:10 ratio and allowed to settle for six hours. Sink and floats were collected separately and thoroughly washed. Chemical analysis was carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES). In the case of the ferruginous manganese ores, because the narrow density difference between manganese and iron minerals is a limiting factor for applying this technique, the required data were generated using a combination of QEMSCAN, or quantitative evaluation of minerals by scanning electron microscopy (FEI Co., Hillsboro, OR), and magnetic separation at fixed process parameters for all of the samples. Magnetic separation was conducted with an induced roll magnetic separator at a constant roll speed of 150 rpm and field strength of 1 T. Magnetic and nonmagnetic fractions were separated and sent for chemical analysis. QEMSCAN analysis could not be performed on the BHJ iron ore and coal samples mainly due to the unavailability of a suitable mineral list and the fine association of mineral particles.

Results and discussion

The potential to use microwave energy in mineral processing depends on the selectivity of a mineral to absorb microwave energy and the transparency of the other minerals. Absorption of microwave energy by any specific material depends on its dielectric properties. When microwave energy is applied, stresses of different magnitudes can be created within the lattice, by both the heating and cooling processes.

Coal. Table 2 shows the coal sample temperatures measured after microwave treatment. Temperature rise is almost proportional to treatment time but has an exponential relationship with energy inputs. Energy input of 180 W caused slow heating of 13.8 °C/min, while 540 W caused rapid heating of 48 °C/min. The studied coal samples attained the maximum temperature of 260 °C after five minutes of heating at an energy input of 900 W, which is almost similar to the temperature rise using 540 W, indicating saturation phenomena. This shows that in these conditions, 180 to 540 W is the optimum microwave energy input to produce the best results. Previous studies had also mentioned that the temperature rise depends on particle size, bed porosity and material properties (Mondal et al., 2010).

Grinding studies. The results of size analysis carried out after the samples were ground with a planetary ball mill are presented in Fig. 1. The graphs show that microwave treatment at 180 W significantly affected the milling characteristics of coal, but the effect was almost insensitive to treatment time. Heating using microwave energy at 540 and 900 W made the coal behavior very complex. The coal samples studied showed improved grinding characteristics only for a short time, and almost no or adverse effects were seen with increased exposure time and energy. Samples treated for one minute at 180 W showed almost 22 percent less d_{avg} and 18.18 percent less d_{80} than the untreated samples during milling. The feed particle size was 0 to 3.35 mm (D_{avg} = 1,300 µm), and the ground sample d_{avg} was 1,137 µm. The lowest size achieved was 880 µm for the sample that was treated at 180 W for five minutes. But treating at 900 W for five minutes increased the d_{avg} by almost 10 percent. This is mainly attributed to hardening of the coal, mostly due to caking properties. The d_{avg} further decreased with exposure time, but the variation was not significant. But for increased energy levels — 540 and 900 W — d_{avg} was smaller than for 180 W and d_{avg} was greater than for the untreated samples. The size distribution indicates that finer particle sizes are more affected than the coarser sizes, and more superfines could be generated. The rapid heating and higher energy inputs created almost no or negative effect on size reduction. It had also been reported in literature that the behavior of coal during microwave treatment is very peculiar and strongly depends on the coal properties (Lester and Kingman, 2004). It is a semicoking coal and microwave heating causes oxidation of the coal surface, and longer exposure time imparts coking properties that make it harder and impart some plasticity also that has an impact on the grinding efficiency.

Liberation analysis. Liberation analysis was carried out on the samples treated using microwave energy of different intensities. It was found that weight of the sinks increased with increased energy intensity. Carbon recovery in the floats increased from 25.5 percent to 48.9 percent. Carbon content in float showed a different trend. It increased almost 5 percent for 180 W energy input but showed a decreasing trend with increased energy inputs. Analysis of these data therefore indicate that microwave treatment can increase the float weight by 7.8 percent, carbon recovery by 17.1 percent and percentage of carbon in product by 8.6 percent for 180 W treatment. These trends were also observed in the ash analysis. It was found that ash content increased in the float, mainly due to lower weight of the floats. The reason behind this could be removal of volatile content during microwave treatment, which increases the porosity and makes it more floatable. Similar phenomena were explained by Borah, Ghosh and Rao (2011), who reviewed the coal devolatilization process. Borah, Ghosh and Rao (2011) also noted that at lower temperatures, the desorption process starts and coal emits moisture and light gasses to form aliphatic tar at 250 °C. The effect of microwave treatment on volatile material was not visible for lower energy inputs but for 900 W it reduced by almost 10 percent. Table 3 shows the chemical analysis of sinks and floats achieved at 1.5 g/cm^3 density separation for the coal samples.

Microscopic analysis. Microscopic studies were carried out to understand the effect of microwave treatment on particle surfaces. It was observed that particles treated with higher microwave energy appear dried and brighter than the particles treated with lower energy. Figure 2 shows the microscopic view of the particle surfaces. The surfaces of large coal particles in the treated samples look porous and very blackish whereas the surfaces in the untreated samples are less porous and the inertinite types of material look brighter than the other parts of

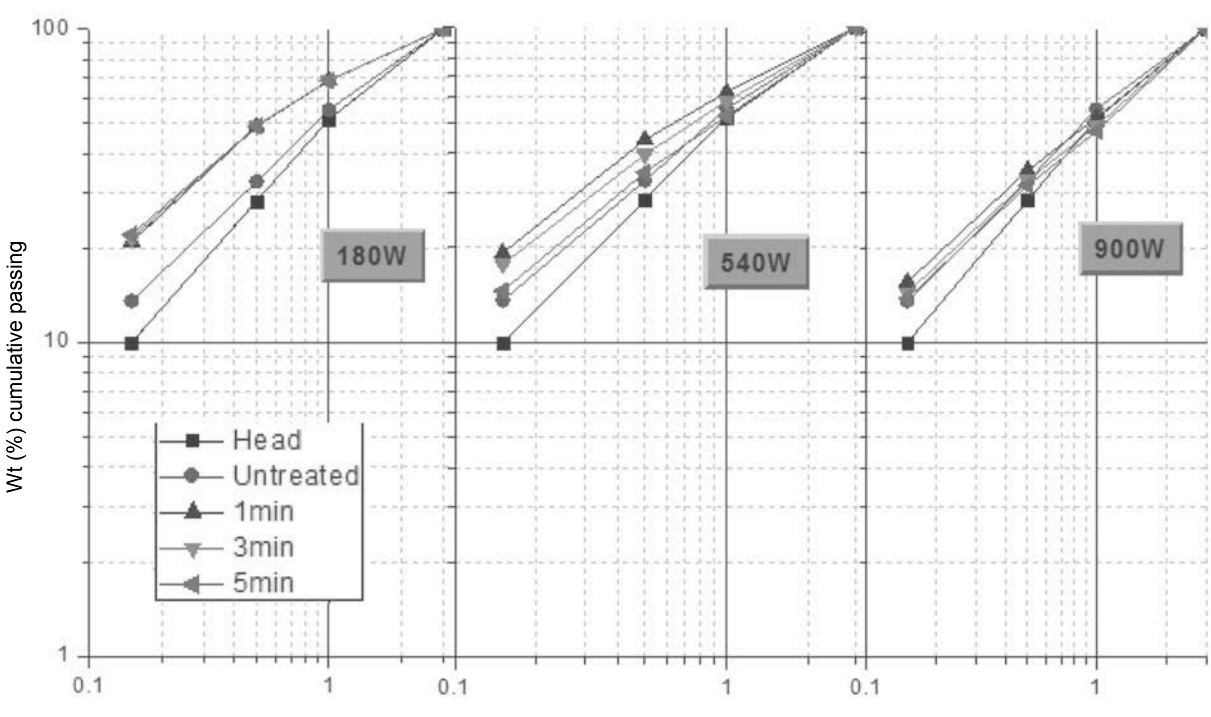

Figure 1 — Effect of microwave treatment on coal milling.

Table 3 — Sink-float analysis of coal samples.

	Carbon in coal							
	Energy (W)	Weight (%)	Carbon (%)	Rec. (%)		Weight (%)	Carbon (%)	Rec. (%)
Sink	0	80.3	37.6	72.5	Float	19.7	58.2	27.5
	180	78.8	35.9	67.8		21.2	63.3	32.2
	540	73.4	35.0	61.1		26.6	61.6	38.9
	900	63.9	33.3	51.1		36.1	56.4	48.9
	Ash in coal							
	Energy (W)	Weight (%)	Ash (%)	Rec. (%)		Weight (%)	Ash (%)	Rec. (%)
Sink	0	80.3	46.5	88.9	Float	19.7	23.8	11.1
	180	78.8	49.3	90.8		21.2	18.5	9.2
	540	73.4	50.2	87.1		26.6	20.5	12.9
	900	63.9	53.1	79.9		36.1	23.6	20.1

coal. This is mainly due to oxidation of the particle surface as a result of temperature rise during treatment. Untreated particles look swelled, but treated particles look more stressed and of relatively different texture. It was also observed that most of the ash grains were superfines, smaller than 15 µm, and were not able to absorb significant microwave energy as a single grain to produce significant effect, which limits the success of microwave treatment for ash liberation.

Manganese ore. This ore is mainly composed of three minerals with significantly different dielectric constants. The dielectric constants of pyrolusite, hematite and quartz are 10^5, 25 and 5, respectively (Telford, Geldart and Sheriff, 1990). The high dielectric constant of pyrolusite mineral imparts semiconductive behavior to this ore. The presence of manganese and iron hydroxides also increases the overall conductivity of the ore and helps to absorb more microwave energy. The two minerals hematite and quartz are very poor conductors of electricity and have low dielectric constant. Table 4 shows the variation in temperature rise due to microwave treatment. Temperature rise is linearly dependent on treatment time but exponentially increases with energy. One minute of exposure at 180 W increases the temperature to 70 °C, and the maximum 720 °C was reached after five minutes of exposure at 900 W. This indicates that microwave energy more rapidly heats manganese ore than the studied coal and iron ore samples.

Table 4 — Temperatures of manganese ore samples treated at different microwave power settings.

Time (min)	Temperature (°C) Low (180 W)	Medium (540 W)	High (900 W)
1	70	202	356
3	120	460	570
5	245	670	720

Grinding studies. The size distributions of the ground samples indicate that manganese ore is very sensitive to microwave treatment. The size distributions of treated and untreated ground samples clearly indicate variation in the fineness

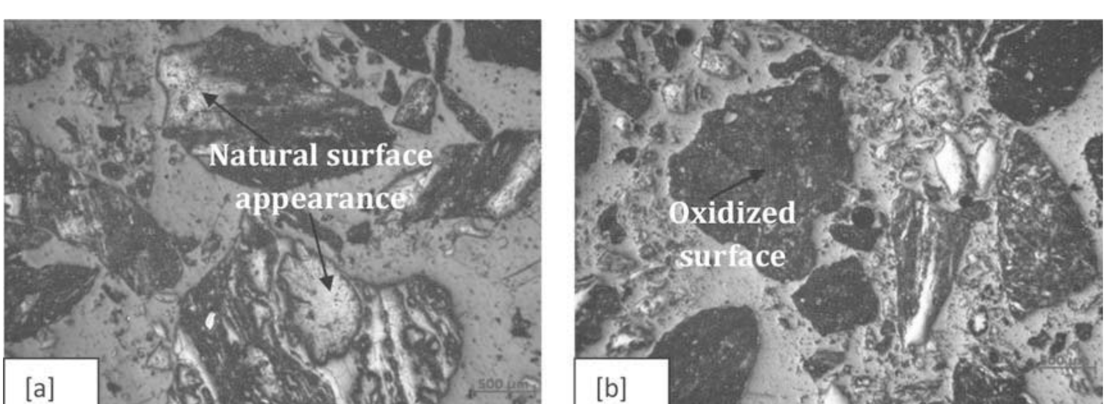

Figure 2 — Microscopic views of coal particles: (a) untreated (b) microwave treated.

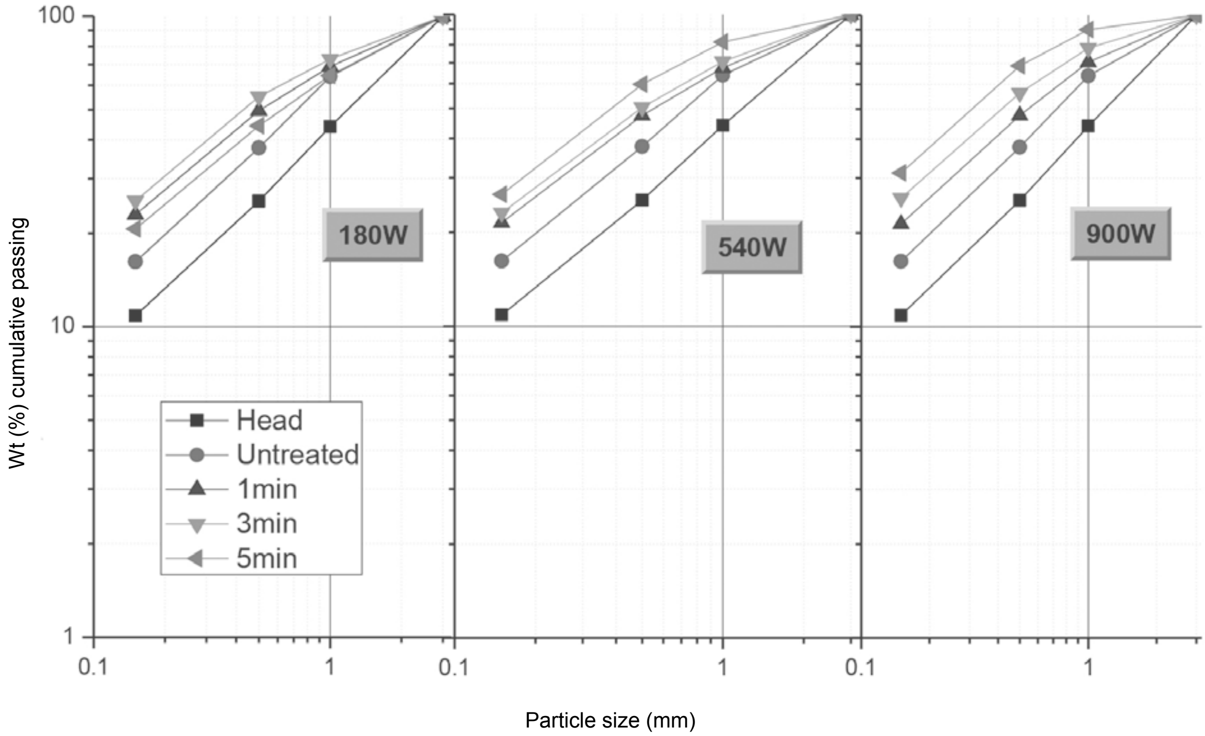

Figure 3 — Effect of microwave treatment on manganese ore milling.

(Fig. 3). This difference in the particle size distributions becomes prominent with increased time and exposed energy intensity. The feed particle size was 0 to 3.35 mm (D_{avg} = 1,314 µm), and the ground sample had d_{avg} of 1,001 µm. The lowest d_{avg} achieved was 506 µm for the sample treated at 900 W for five minutes. Initially, there was a drastic reduction in mean particle size but as the energy input (time × energy) increased, this effect slowed down and a saturation effect appeared. Initially, the size reduction effect was very high and one watt energy was able to reduce the particle size by almost 50 µm, but after 25 W the effect became weaker. This characteristic is a main material property that can give a comparative susceptibility index for microwave treatment to improve grindability. The size distribution curve was skewed toward coarser sizes, and after treatment it skewed toward finer sizes. Microwave treatment can reduce the d_{avg} by 50 percent and the d_{80} by 47.82 percent compared with the untreated samples after five minutes of exposure at 900 W. One minute of exposure at 900 W was able to reduce the d_{avg} by 100 µm.

Liberation analysis. Microwave treatment affects manganese mineral liberation by the selective heating of manganese

Table 5 — Liberation analysis of microwave-treated manganese ore samples.

Sample		Wt (%)	Mn (%)	Mn recovery (%)
Head	Magnetic	66.53	39.37	65.31
	Nonmagnetic	33.47	41.57	34.69
	Total	100.00	40.11	100.00
180 W	Magnetic	51.46	36.68	57.32
	Nonmagnetic	48.54	44.13	42.68
	Total	100.00	40.29	100.00
540 W	Magnetic	61.80	38.91	69.95
	Nonmagnetic	38.20	43.86	30.05
	Total	100.00	40.80	100.00
900 W	Magnetic	60.78	38.28	57.54
	Nonmagnetic	39.22	42.92	42.46
	Total	100.00	40.10	100.00

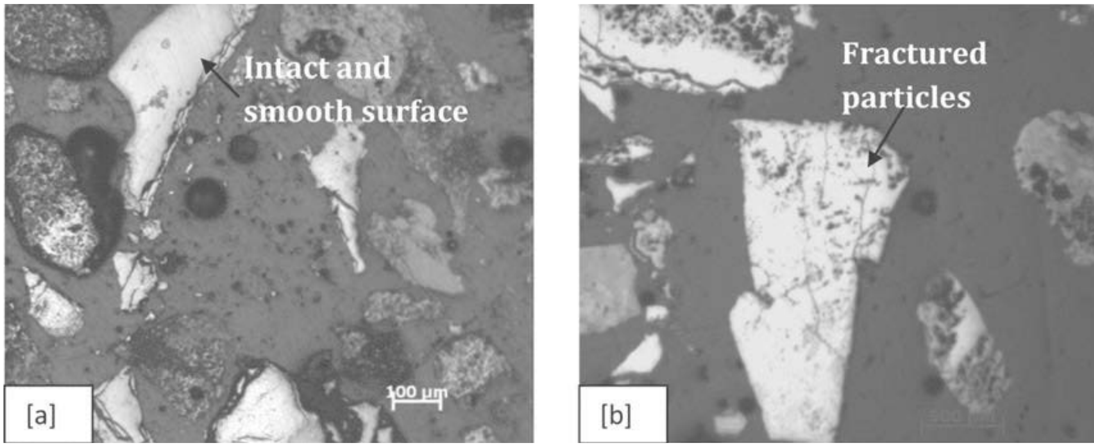

Figure 4 — Microscopic views of manganese ore sample: (a) untreated (b) microwave treated.

minerals and by stress on interfaces that is imparted due to thermal decomposition of the manganese mineral phases ($MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4$). The densities of iron and manganese minerals present in the ore are almost similar, which makes it difficult to measure mineral liberation using sink-float studies, so QEMSCAN mineralogical analysis and magnetic separation were performed. The overall manganese recovery increased from 34.69 percent to 42.46 percent. There was increment in the weight percentage of nonmagnetic fraction, which was mainly due to difference in fines generated due to microwave treatment. The results of chemical analysis of the magnetic and nonmagnetic fractions are presented in Table 5. The variation in yield of the nonmagnetic fraction was not consistent, mainly due to the inconsistent liberation characteristics of ore fines. These data were validated by QEMSCAN analysis also.

Microscopic analysis. Microscopic studies were carried out to understand the effect of microwave treatment on the particle surfaces (Fig. 4). It was observed that the manganese mineral particle surfaces look less bright, which is mainly due to the phase change and decomposition of manganese minerals ($MnO_2 \rightarrow Mn_3O_4$) due to rapid heating. Faria, Jannotti and da Silva Araújo (2012) explained the manganese oxide decomposition phenomena during thermal treatment. Comparison of the treated and untreated samples reveals that the surfaces of the pyrolusite particles are smooth and intact whereas treated surfaces look broken and uneven. The small amount of hydroxides present in the samples got decomposed, and the surfaces of these particles look broken and dry. It also shows increased liberated particles in finer sizes. This indicates the particles became more friable, which enhanced milling characteristics. QEMSCAN analysis of samples was also carried out, and it shows that both the hematite and pyrolusite minerals were liberated in coarser as well as in finer sizes. But it also indicates that finely associated manganese and iron minerals cannot be separated by coarse grinding.

Iron ore. This ore mainly contains quartz and hematite minerals. Hematite and quartz are materials with large differences in their thermal conductivities and dielectric constants. Hematite has thermal conductivity of 11.28 kW/m-K at 30 °C and specific heat capacity of 654.81 J/kg-K at 25 °C. Quartz has thermal conductivity of 7.69 k-W/m-K at 30 °C and specific heat capacity of 740.50 J/kg-K at 25 °C. The volumetric thermal expansion coefficient of quartz and hematite are 45×10^{-6} m^3/K and 25.2×10^{-6} m^3/K at 100 °C, respectively (Telford, Geldart and Sheriff, 1990; McGill, Walkiewicz and Smyres, 1988; Speight, 2005). These properties ultimately affect the temperature rise of the samples, as shown in Table 6. Because iron ore is hard and compact, it quickly becomes heated in the first few minutes, but the temperature does not rise rapidly after the initial climb. The energy input of 180 W was too low for heating. Mondal et al. (2010) studied the effect of particle porosity and particle size on microwave heating and reported that powder compacts with higher porosity and smaller particle sizes interact more effectively with microwaves and are heated more rapidly, which supports the current findings.

Table 6 — Temperatures of iron ore samples treated at different microwave power settings.

Time (min)	Temperature (°C) Low (180 W)	Medium (540 W)	High (900 W)
1	60	80	175
3	70	150	420
5	80	370	510

Grinding studies. The size distribution plot of ground samples is shown in Fig. 5. The feed size was 0 to 3.35 mm (D_{avg} = 1,424 μm). There was a visible effect in the size distributions of treated and untreated samples, but this difference did not increase rapidly with exposure time. The iron ore samples attained the maximum 510 °C temperature after five minutes of exposure time at 900 W. Temperature rise is linearly dependent on time and microwave energy. Milling of samples treated for five minutes at 900 W reduced d_{avg} by 27 percent and d_{80} by 20.83 percent. The d_{avg} of the untreated ground head sample was 1,257 μm. This graph shows that the effect of time is weaker than the effect of microwave energy. The shape of the size distribution curve changes from fine-size skewed to normal size distribution.

Liberation analysis. The liberation of ground iron ore samples was investigated using sink-float analysis. Evaluation

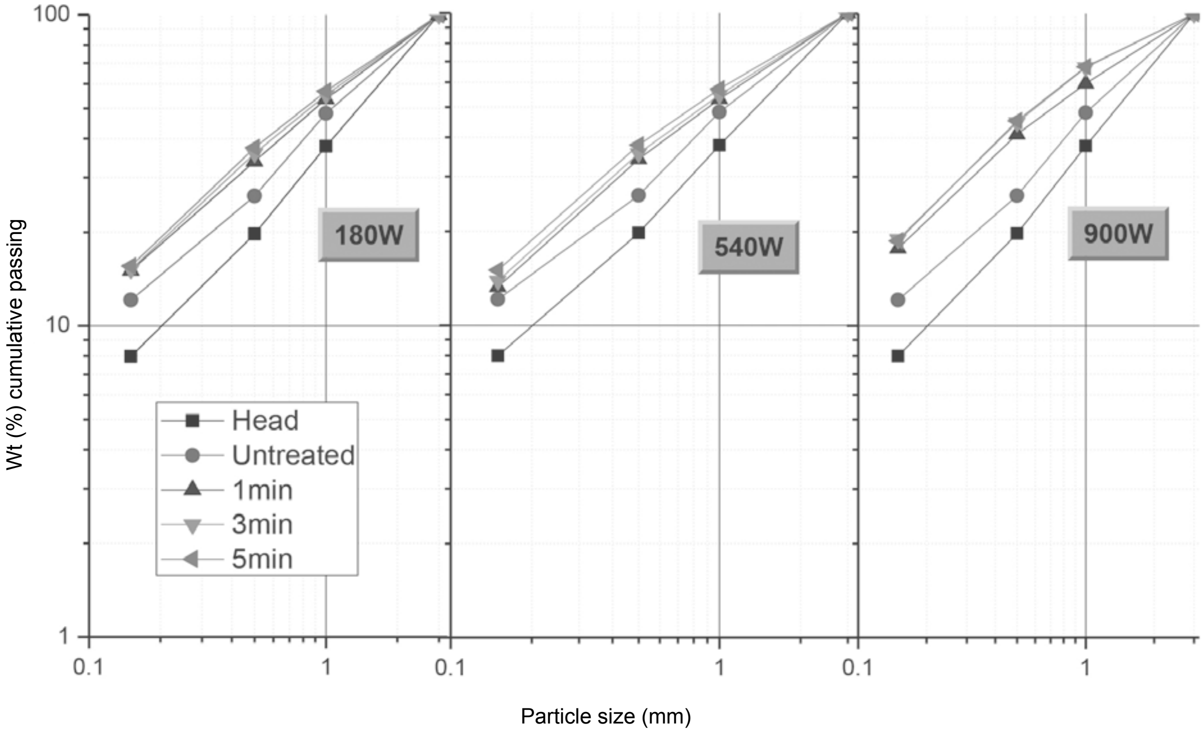

Figure 5 — Size distribution of iron ore samples treated at different microwave energies.

of the data was challenging, mainly due to the narrow differences among the values as well as complex mineral association in finer grain sizes. The distribution of iron and silica (SiO_2) was measured, and it was found that although the weights of floats increased, iron content in the sink also increased, which is contradictory. The main reason behind the increased float weight is liberation of microplaty hematite particles due to microwave treatment. These particles reported in the sink and increased the iron content. Increased input of microwave energy increased the fines, which caused an increase in the float weight, mainly due to particle adherence. Variation in SiO_2 content was mainly due to variation in the iron level as well as due to imparted brittleness in jasper as a result of heating. Table 7 shows the chemical analysis of sink and float products from the microwave-treated iron samples.

Microscopic studies. The micrographs shown in Fig. 6 indicate that microwave heating is effective to initiate preferential fractures at mineral interfaces in these samples. However, these micro-cracks improve liberation of tiny microplaty hematite particles but do not significantly improve the overall liberation of minerals. Figure 6 shows that quartz

Table 7 — Liberation analysis of microwave-treated iron ore samples (R* = Recovery).

	Fe in iron ore								
	Energy	Wt (%)	Fe (%)	R* (%)		Wt (%)	Fe (%)	R* (%)	Head
Sink	0 W	90.1	44.4	98.1	Float	9.9	7.7	1.9	40.78
	180 W	94.2	44.85	99.1		5.9	6.76	0.9	42.62
	540 W	91.2	46.97	98.4		8.8	7.9	1.6	43.52
	900 W	91.6	44.41	98.2		8.4	8.88	1.8	41.43
	SiO_2 in iron ore								
	Energy	Wt (%)	SiO_2 (%)	R* (%)		Wt (%)	SiO_2 (%)	R* (%)	Head
Sink	0 W	90.1	33.44	79.9	Float	9.9	76.63	20.1	37.71
	180 W	94.2	33.16	85.9		5.9	87.86	14.1	36.36
	540 W	91.2	31.43	78.8		8.8	87.07	21.2	36.34
	900 W	91.6	33.07	80.9		8.4	85.34	19.1	37.45

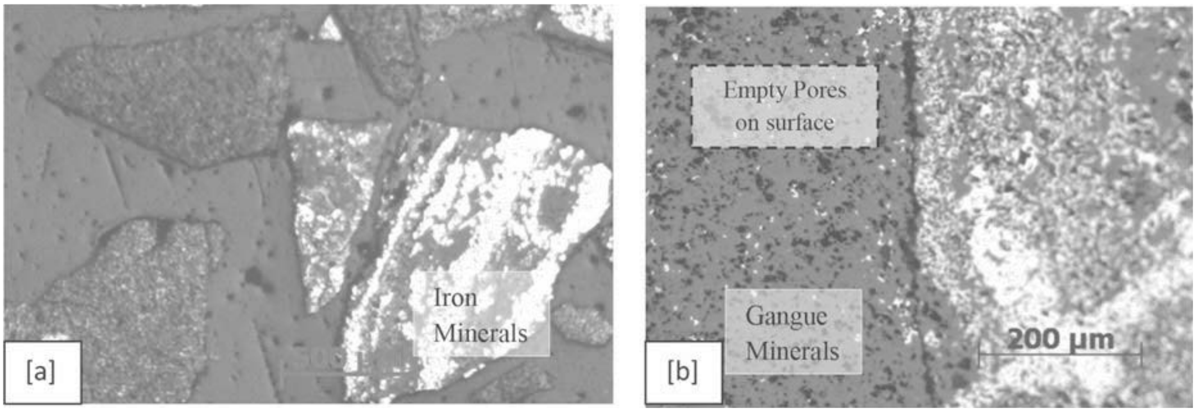

Figure 6 — Microscopic views of BHJ ore: (a) untreated (b) microwave treated.

and hematite are finely associated, and small hematite particles become liberated by microwave treatment but in smaller amounts. The pre-existing fractures were enhanced without significant improvement in liberation. Crack development at the silica and hematite interfaces occurs due to the thermal stresses caused by the difference in the thermal expansion rates of the minerals (Fig. 6).

Comparative analysis

Microwave pretreatment causes a rise in material temperature that dictates the intensity of thermal stresses generated inside the mineral matter. The effect of microwave energy on temperature rise for all three of the different samples is shown in Fig. 7. The graph shows that the temperatures of the samples did not increase significantly up to energy input of 10 Wh. There was a sharp rise in temperature for the 10 to 50 Wh energy range, but after that the increment became constant and this polynomial relationship was similar for all of the studied samples. The polynomial equations fitted between temperature rise and microwave energy for all of the three materials showed regression coefficients of more than 0.95. Temperature rise was lowest for coal due to its low permittivity and porous structure. The highest temperature rise was seen for manganese ore, which has minerals with higher permittivity and thermal conductivity. Analysis of the data reveals that optimum results can be achieved for five minutes of heating at 500 W for the manganese ore and three minutes of heating at 900 W for the BHJ iron ore. The microwave heating characteristics of coal are different from those of the minerals. It showed more dependence on time than microwave energy intensity. It is therefore surmised that the best operating ranges of microwave energy for treatment will be 1 to 30 Wh for coal, 5 to 45 Wh for iron ore and 15 to 40 Wh for manganese ore.

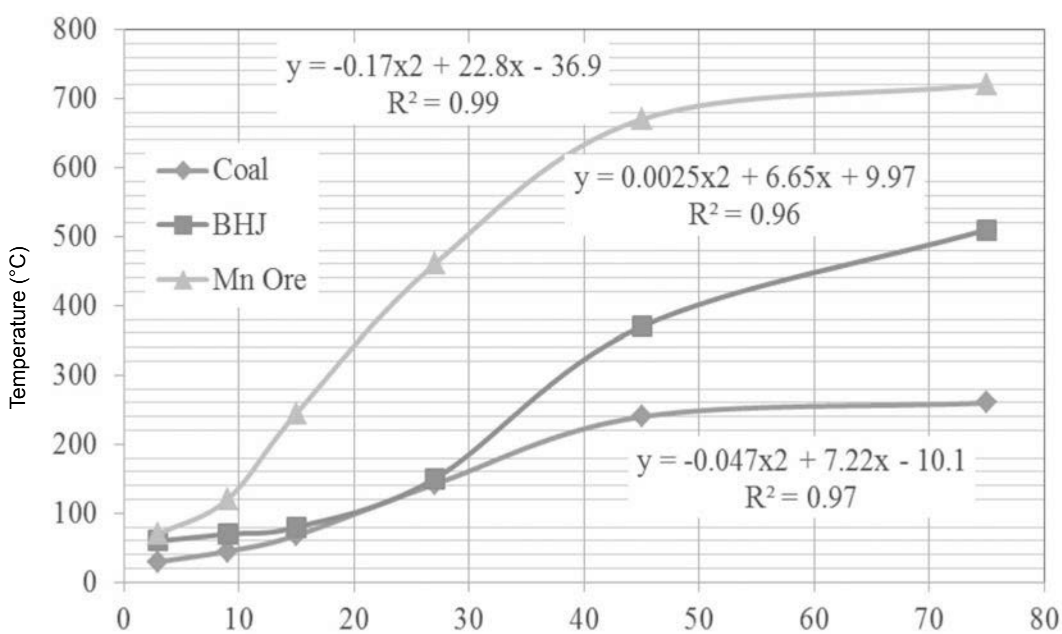

Figure 7 — Relation between input microwave energy and temperature rise.

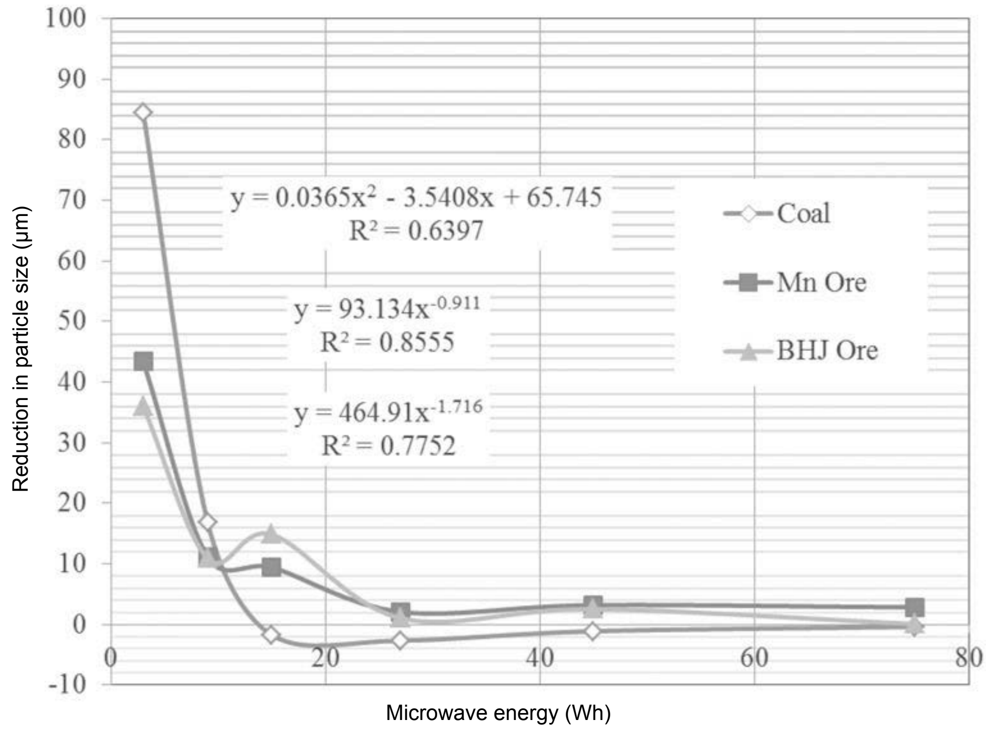

Figure 8 — Relation between input microwave energy and particle size reduction.

The effect of microwave energy on particle size reduction is presented in Fig. 8. This graph shows that the effect on size reduction increased up to a maximum at 25 Wh energy input, and this effect diminished for higher energy inputs. The mineral particles get heated up and possible fracture initiation take place at these energy inputs, so further energy causes excess heating of the material without contributing to fracture initiation. Liberation of moisture and decomposition of hydroxides also take place during this range, but further heating causes anhydrous sintered phases in ore that adversely affect grinding. The highest size-reduction rates observed from the graphs were 84 µm/Wh for coal, 43µm/Wh for manganese ore and and 36 µm/Wh for iron ore. These data indicate that two to three minutes is the optimum exposure time at which these mineral matters achieve the suitable temperature that can help in grinding without the formation of cake or sinter phase. Figure 7 shows that during treatment coal follows a different route than the ores, and it is mainly due to the difference in structure of coal. Volatile material and moisture play important roles during the microwave heating of coal. They partially evaporate when higher energy is applied, and this imparts coking properties that make the coal hard to grind and results in increased d_{80} particle size for higher microwave energy treatment, which indicates negative or no effect of microwave treatment on particle size reduction. Cost benefit analysis based on laboratory data — quantity of sample, microwave energy and particle size — shows that size reduction is not significant enough from the cost economic point of view. The behavior of coal is very complex and after exposure to 15 Wh of energy, size reduction becomes insignificant up to 70 Wh. The relationships between size reduction and microwave energy input for coal, manganese ore and iron ore are:

$$\text{Coal: } Y = 0.0365x^2 - 3.5408x + 65.745 \quad (1)$$

$$\text{Manganese ore: } Y = 93.134x^{-0.911} \quad (2)$$

$$\text{Iron ore: } Y = 464.91x^{-1.716} \quad (3)$$

where Y is reduction in mean particle size in micrometers and X is the input microwave energy in watts. It shows that coal should be treated at low intensity (180 W) for a short time

Table 8 — Comparative analysis of energy savings due to microwave pretreatment.

Material	Particle size, d_{80} (µm)			Energy for milling (kWh/t)			Microwave power, time duration
	Head	Untreated	Treated	$E_{untreated}$	$E_{treated}$	ΔE_{saving}	
Coal	1,900	1,800	1,600	0.06	0.21	0.14	180 W, 5 min
Manganese ore	2,000	1,600	700	0.32	1.85	1.54	900 W, 5 min
Iron ore	2,200	2,000	1,500	0.15	0.63	0.48	900 W, 5 min

whereas ores need more time as well as energy to achieve the saturation level.

These studies indicate that the efficacy of microwave treatment prominently depends on material characteristics and material morphology. Table 8 gives a comparative analysis of energy savings due to grinding of microwave-pretreated materials. Friable manganese responds 10 times better than coal and almost three times better than hard iron ores during the grinding of microwave-treated ore samples. On a laboratory scale, the energy savings are much less relative to the energy supplied to treat samples, which is the main reason for delays in the scale-up and commercialization of microwave pretreatment technology. These challenges can be overcome by the development of an efficient scale-up process. In hard and dense materials, it works more on surface heating phenomena, which limits its success, whereas it can work more efficiently for friable and porous materials. Its application should therefore be explored more for the porous and friable weathered ores generated by sedimentary and hydrothermal processes. Its application should be explored for some other artificially produced porous and friable materials such as metallurgical slag, waste ceramics and other process wastes of the material processing industry.

Conclusions

Microwave treatment improves the grinding characteristics of coal, manganese ore and iron ore, but the magnitude of the impact significantly depends upon the bulk material properties.

The current study revealed that the initial exposure to microwave energy at 25 Wh significantly improved the size reduction of the studied samples but after that it got saturated. Two to three minutes was found to be the optimum exposure time for the ores, but coal requires rapid heating for a short time.

Coal showed an 18.18 percent reduction in d_{80} particle size during the milling of samples treated at 180 W. Grinding of the manganese and iron ore samples showed 47.82 and 20.83 percent reductions in d_{80}, respectively, for samples treated at 900 W for five minutes.

Liberation studies reveal that microwave treatment can lead to a 17.1 percent increase in carbon recovery for coal and 42.46 percent increase in manganese recovery, but the iron ore samples did not show any improvement in mineral liberation.

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