1. Introduction

The reduction of hematite pellets is accompanied by expansion in their volume. About 20% swelling is common and does not adversely affect blast furnace operation in any way. In some cases, pellets exhibit “abnormal” or “catastrophic” swelling/disintegration/degradation. This results in volume expansion more than the normal 20% and results in drastic reduction of the strength of pellets. This catastrophic swelling is a characteristic of pellets and is not observed in sinters or iron ore lumps. It has also been observed in cold-bond briquettes made from pellet-fines. Hence, it is essential to know the exact mechanism and to prevent it as far as possible.

In spite of fact that the swelling of pellets has been rather extensively studied, the exact swelling mechanism is not well understood. Most of the time, catastrophic swelling occurs during the last stage of the reduction process (wustite→iron) when iron of fibre-like morphology (whiskers) is formed. The growing whiskers push neighbouring grains and lead to large-scale swelling. In other types of swelling, there is no formation of whiskers; instead, the whole of the pellet expands and big fissures are created. The occurrence of swelling without the formation of iron whiskers reaches a maximum at about 900°C. At that temperature, CO dissociates to C and CO2 and the C dissolves in the produced iron. As the reduction proceeds, the C reacts with wustite to give CO & CO2 and Fe. The oxidation of dissolved C leads to the formation of bubbles, which exert disruptive force. At high reduction temperature (>900°C), the swelling is less because of low C deposition and greater sintering.

It has been observed that, under certain conditions, the cement-bonded agglomerates containing pellet-fines show a tendency to swell catastrophically when reduced at 900–1,000°C using carbon monoxide as a reducing agent. The swelling does not take place because of the formation of iron whiskers. Instead, the swelling of briquettes is due to the popping up of individual pellet-fines particles during the conversion of wustite to iron. It has been observed that at this stage the reduced iron particles that comprise an individual pellet-fine particle move apart thereby causing swelling. The various factors that affect the swelling of cement-bonded agglomerates are:

1. Effect of Reduction Temperature: The swelling increases and then falls with temperature so that the swelling reaches a maximum at 950–1,000°C.
2. Effect of Degree of Reduction: The catastrophic swelling takes place only during the reduction from wustite to iron.
3. Effect of Raw Material Composition: The swelling of agglomerates is less when the raw material contains a greater proportion of pre-reduced materials. The swelling increases with increase in slag forming oxides, CaO, SiO2, MgO and Al2O3, in the pellets, and for the swelling to take place the ratio of basic oxides to acidic oxides (CaO+MgO/SiO2+Al2O3) should be about one. The briquettes made of pellet-fines swell much more than those made of crushed well sintered Pellet A, even though the pellet-fines comprises approximately 75% Pellet A and 25% Pellet B by

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4. Effect of Particle Size: As the particle size \( d_{50} \) increases the swelling also increases. This is due to the formation of large cracks as well as popping up of large particles. Overall, the volume change is almost proportional to the log of \( d_{50} \) of the raw mix.\(^9\)

5. Effect of Reduction Conditions: The degree of swelling decreases on addition of hydrogen in reducing gas. In the absence of CO, swelling does not take place. There is less swelling in the case of isothermal reduction at 950°C than in the case of non-isothermal reduction wherein the maximum temperature is maintained at 950°C.\(^9\)

6. Effect of Reduction in Steps: The swelling in the case of three-step reduction using reducing gas having different compositions \((N_2:CO:CO_2=60:35:5\) for 3 h, \(60:20:20\) for 3 h and \(60:40:0\) for 4 h) at 950°C is always less than the swelling in the single-step reduction \((N_2:CO:CO_2=60:40:0\) for 5 h) at 950°C for the same type of briquettes.\(^9\)

7. Effect of Cement Content: The briquettes exhibit maximum swelling at 4% cement, thereafter, the swelling decreases. Interestingly, the briquette without any binder (0% cement) does not swell catastrophically. This clearly shows that for catastrophic swelling to take place the presence of cement is essential. In the case of briquettes that have been reduced in steps, there is a shift in the maximum point. Here, the maximum swelling takes place for the briquettes made using 6–8% cement.\(^9\)

8. Effect of Hydration Time: For the swelling to take place hydration of cement, which results in the release of hydrated lime, is not essential. Swelling can also take place in the presence of unhydrated cement.\(^9\)

9. Effect of Cement Composition: Presence of free lime or only lime and silica are not sufficient cause for swelling to take place; instead, the presence of slag-forming oxides (CaO, SiO₂, MgO, Al₂O₃, and FeO) is essential for the swelling to take place.\(^9\)

10. Effect of Alkalis: While the presence of alkali is not essential for swelling to take place, the swelling drastically increases in the presence of alkalis. The presence of alkali can even cause the briquettes made of finely ground raw material to swell.\(^9\)

11. Effect of Binder Type: For the briquettes in which a part (25 weight %) of the cement has been replaced by finely ground CaO, SiO₂ (quartz), Al₂O₃ and MgO are reduced at 950°C in steps \((N_2:CO:CO_2=100:0:0\) for 0.5 h, \(60:35:5\) for 3 h, \(60:20:20\) for 3 h and \(60:40:0\) for 4 h), the tendency to swell is quite low.\(^9\)

12. Effect of Pre-firing: If the cement-bonded briquettes are pre-heated to a temperature above 1250°C in air and cooled to room temperature, such briquettes do not swell catastrophically on reduction at 950°C in \(N_2+CO\) (60–40).\(^9\)

13. Effect of Reduction under Load: Overall, the briquettes reduced under load show a lesser degree of swelling as compared to similar briquettes reduced without any physical constraints. This is not because the briquettes reduced under load have less tendency to swell, but it is because the swelling is restricted by an applied load.\(^9\)

14. Effect of Briquette Size: The swelling of briquettes is independent of the briquette size.\(^9\)

In this paper, various factors that affect the swelling of cement-bonded briquettes prepared using pellet-fines and other wastes from iron and steel plants have been discussed. Based upon the experimental observations a conceptual model to describe the swelling mechanism has been proposed.

2. Materials and Methods

The experiments were conducted on cement-bonded briquettes made using pellet-fines with ordinary Portland cement used as binder. Pellet-fines was a mixture of fines of Pellet A and Pellet B, two commercially available pellets collected by sieving before the pellets were fed to a blast furnace. The fines were generated by the breakage that took place during transportation and handling. Even though the chemical composition of the pellet-fines is an average of those of Pellets A and B, structurally it is different, since it is mostly the weak-under-fired or over-fired–pellets that break.

Detailed descriptions of the materials used and the experimental procedure followed are given in previously published papers.\(^8,9\) Additional experimental techniques employed are outlined below:

2.1. X-ray Diffraction Analysis of Powdered Sample

The material to be analysed was dried and ground to \(-75\mu m\) and diffraction patterns were obtained employing a X-ray diffractometer using Ni filtered Cu Kα radiation at 40 kV and 50 mA.

2.2. High Temperature X-ray Diffraction Analysis

\textit{In situ} high-temperature X-ray diffraction (HT-XRD) studies were carried out using an automatic diffractometer. The basic units in this system were: a powder diffractometer with a vertical goniometer, a graphite monochromator, a proportional counter for reflected beam and a generator. The heating of the sample was done in a high-temperature attachment. The temperature of the sample was measured with a Type R thermocouple placed close to the sample. The specimens, made by grinding the cured samples into a thin wafer (10 mmX7 mmX0.7 mm), were heated in a flowing nitrogen environment. The temperature was ramped at a rate of 8.3°C/min. Cu Kα (50 kV, 30 mA) radiation was employed. The samples were scanned at room temperature and at every 100°C at a rate of 1.2°C/min.

2.3. Scanning Electron Microscopic (SEM) Examination

A test piece of the sample to be observed was fixed into an epoxy resin mould, ground and polished. The moulded specimen was then fixed on an aluminium mount and coated with a thin layer of gold-palladium alloy using a sputter coater. The coated specimen was then examined under a scanning electron microscope. The Energy Dispersive X-ray Analysis (EDXA) was also done on the sample to obtain chemical mapping and line mapping of the sample.
2.4. Melting Point

The melting point of samples was determined using a melting-point-measuring microscope. The sample to be studied was ground to fine powder and a small cuboid (length=2 mm, breadth=2 mm, height=3 mm) was made using the powder and optimum amount of water. The pellet was placed inside the furnace on top of an alumina plate. The temperature at which the pellet shrunk by 10% of its height was defined as the softening point (SP) and the temperature at which the height fell to 33% was defined as the melting point (MP).

3. Experimental Results and Discussion

3.1. Cracking of Grains on Transformation from Hematite $\rightarrow$ Magnetite $\rightarrow$ Wustite

Pellet-fines particles are normally the weak—under-fired or over-fired—pellets that have broken. These pellet-fines particles contain significant areas of defect. Figure 1(a) shows an optical micrograph of pellet-fines particle containing large portions of magnetite (dark grey) along with hematite (light grey). As the reduction proceeds the oxygen diffusing outward follows the path of maximum defects. The transformation of hematite to magnetite is accompanied by volume increase. This generates stresses leading to the cracking of grains (Fig. 1(b)).

Most probably, the cracking of grains is accelerated by the presence of cement in the briquettes. In the first step, the cement coating the pellet-fines particles dehydrates to calcium disilicate and calcium oxide. At high temperatures, these react with hematite to form a thin layer of calcium ferrite (CF) and calcium silicoferrite ($\text{C}_2\text{SF}_3$). High temperature XRD of pellet-fines (75%)–cement (25%) briquette samples have shown the formation of these phases. The formation of these phases at the surface promotes the “injection” of foreign oxides into the iron oxide grains, which leads to the creation of defects in the crystal structure. Along these defects, the reduction begins initially, resulting in the disintegration of the iron oxide grains. Finally, the whole pellet-fines particle fragments on reduction to magnetite (Fig. 1(c)). When the magnetite is reduced to wustite, the cracks become wider (Fig. 1(d)) due to the shrinking of structure during magnetite to wustite transformation.

3.2. Slag Formation

Figure 2 shows the effect of temperature on a hydrated cement sample. When the hydrated cement is heated in the nitrogen environment, the dehydration of CSH gel starts at about 100°C. With an increase in temperature, the degree of dehydration also increases, so that at about 950°C all the CSH gel is converted to $\text{C}_2\text{S}$ and $\text{CaO}$. The portlandite ($\text{Ca(OH)}_2$) crystals start losing water at about 500°C and convert to $\text{CaO}$.

When the pellet-fines (75%)–cement (25%) briquette is heated in the nitrogen environment, the hydrated cement dissociates to $\text{C}_2\text{S}$ and $\text{CaO}$. A part of $\text{C}_2\text{S}$ reacts with $\text{CaO}$ and $\text{Fe}_2\text{O}_3$ to form calcium silicoferrite ($\text{C}_2\text{SF}_3$) and the rest of the $\text{C}_2\text{S}$ remains unreacted. $\text{CaO}$ also reacts with $\text{Fe}_2\text{O}_3$ to form $\text{CaO}$–$\text{Fe}_2\text{O}_3$ (Fig. 3). Figure 4 is a SEM micrograph of a heated briquette sample showing very limited reaction between $\text{C}_2\text{S}$, olivine and hematite.

In the magnetite stage, there is almost no reaction between $\text{Fe}_2\text{O}_3$ and other oxides (Fig. 5).

Figure 6 shows the effect of reduction on the formation of...
of various phases. When the magnetite converts to wustite the reaction between the wustite, CaO, C$_2$S and olivine takes place. The reaction between these leads to the formation of (Ca, Fe, Mg)$_2$SiO$_4$. CF remains largely unreduced and does not undergo any transformation.

Normally, the melting point of slag is rather high (above 1300°C). With proper proportions of CaO, SiO$_2$, FeO, MgO and Al$_2$O$_3$, a slag having a lower melting point may be formed. Experiments have shown that the melting point is minimal at 1150°C, when the ratio of cement to pellet-fines is 40/60 by weight (Fig. 7). It is quite possible to achieve this ratio at the interface of cement and pellet-fines particle. Figure 7 also shows that the temperature difference between the softening point and melting point is minimal at 40/60 cement/pellet-fines ratio. Visually, it has been observed that at that ratio the viscosity of the melt is also min-

Fig. 2. High-temperature XRD of hydrated cement sample showing the effect of temperature in nitrogen environment.

Fig. 3. High-temperature XRD of cured pellet-fines (75%)-cement (25%) briquette sample showing the effect of temperature in nitrogen environment.

Fig. 4. SEM of centre of a briquette after 0.5 h reduction showing the presence of unreacted dehydrated cement (C$_2$S) and olivine along with hematite.

Fig. 5. SEM of a portion inside a briquette after 0.5 h reduction showing the presence of unreacted dehydrated cement (C$_2$S) and olivine along with magnetite.
Figure 8 shows a region of briquette that seems to have been quenched. The figure shows spherical iron grains surrounded by slag. This indirectly proves the formation of liquid slag during the reduction of wustite. Firstly, the spherical shape of iron can only occur when it is reduced in a bath of molten slag. Secondly, the filling of slag in the interstice of the iron grains can only take place when the slag is in a molten state. As Fig. 7 shows, the minimum melting point for the CaO–MgO–FeO–SiO$_2$–Al$_2$O$_3$ system is 1150°C. Since the reduction experiments take place at 950°C, it is assumed that the reduction of wustite provides the additional heat, which is able to increase the temperature substantially at the microscopic level. This increase in temperature at the microscopic level is not recorded by the thermocouple placed inside the briquette but is sufficient to melt the slag.

Figure 9 is a Back Scatter Electron image of a particle having only CaO, SiO$_2$ and FeO. In this particle, the CaO–SiO$_2$ and FeO rich regions also separate very distinctly. It is quite possible that the region contained only the CaO–SiO$_2$–FeO phase in a molten state. On cooling, the FeO phase separated from the CaO–SiO$_2$ phase. Since the viscosities of these two phases are similar, they separated in a dispersed manner.

Figures 10 and 11 are the SEM images of partially reduced briquettes showing the slag having frozen into three distinct layers: (a) MgO–SiO$_2$ rich core, (b) CaO–SiO$_2$ rich middle shell, and (c) FeO rich outermost shell. The “flow-
lines” present throughout the inner structure indicate a possibility of the particle being in a liquid state earlier. One possible explanation for the formation of this kind of structure is that at the wustite state CaO–SiO2-MgO–FeO reacts together to form (Ca, Fe, Mg)2SiO4. Due to the reduction of wustite around it, a substantial amount of heat is liberated. This heat melts the phase forming a liquid slag. On cooling, the individual components MgO–SiO2, CaO–SiO2 and FeO phases separate out. MgO–SiO2 (olivine) forms the inner core. Around this core CaO–SiO2 and FeO form the shells. The CaO–SiO2 and FeO phases do not separate very well and form only dispersed phases.

In order to calculate the amount of slag that can theoretically form, simple mass balance can be applied. On reduction, a briquette containing 6.5 weight percent cement would contain–88.47 weight percent wustite and 11.53 weight percent other oxides. It has been observed that the slag having the lowest melting point forms when the ratio of pellet-fines to cement is 60/40. Under such conditions the composition of slag would be FeO: 55.82, SiO2: 12.24, MgO: 2.35, CaO: 27.49, Al2O3: 2.10 weight percent. Hence, 11.53 weight percent other oxides can react with wustite in the ratio 44.18/55.82 (other oxides/wustite) to form 26 weight percent slag. In practice, however, the amount of slag formed at an instance of time would be much less than this, since not all of it would be produced at the same time. It may still be expected that the amount of slag present at the wustite-iron boundary would be substantial.

Figure 12 shows the optical micrographs of the pellet-fines and cement interface. It shows that the formation of such CaO–SiO2–MgO–FeO phases is very wide spread. Figure 13 shows that the molten slag may coalesce to spread over a large region. On further reduction, the wustite transforms to iron.
Other phases like CF and (Ca, Fe, Mg)$_2$SiO$_4$ also lose FeO. As a result, CF transforms to CaO and iron and (Ca, Fe, Mg)$_2$SiO$_4$ transforms to (Ca, Mg)$_2$SiO$_4$. The removal of FeO again raises the melting point of the slag and it crystallises out as (Ca, Mg)$_2$SiO$_4$. Figure 14 shows the SEM of the region from which all the FeO has been reduced. The iron particles formed are spherical in nature and the CaO–MgO–SiO$_2$ region in the middle has a homogeneous distribution. In some regions where the MgO is in excess MgO–SiO$_2$ phase forms the core and the CaO–MgO–SiO$_2$ phase forms the shell (Fig. 15).

3.3. Formation of Iron Carbide

Figure 6 shows the high-temperature XRD of pellet-fines (75%)-cement (25%) briquette reduced at 950°C using N$_2$–CO (60 : 40). The XRD shows the formation and subsequent disappearance of Fe$_3$C. It can be seen that as the reduction proceeds, the hematite reduces to magnetite and then to wustite. On further reduction Fe$_3$C is formed. With the passage of time, Fe$_3$C again oxidises forming Fe. The steps may be written as:

\[
3\text{FeO} + 5\text{CO} = \text{Fe}_3\text{C} + 4\text{CO}_2 \\
\text{Fe}_3\text{C} + \text{FeO} = 4\text{Fe} + \text{CO} \\
\text{Fe}_3\text{C} + \text{CO}_2 = 3\text{Fe} + 2\text{CO}
\]

Figure 16 is the room-temperature XRD of pellet-fines (75%)-cement (25%) briquette reduced at different temperatures, using N$_2$–CO (60 : 40) and then quenched to room temperature. At 700–800°C, the iron carbide is rather stable. From the literature, it is known that at high temperatures it is not formed. Hence, around 950°C there is a formation of metastable Fe$_3$C.

High-temperature XRD of pellet-fines shows that the formation of Fe$_3$C does not take place in the case of pellet-
fines. The high-temperature XRD of cement-bonded (6.5 weight percent) briquette shows the formation of less Fe₃C compared to the formation in cement-bonded (25 weight percent) briquette. This shows that the cement acts as a catalyst for the formation of metastable Fe₃C.

Figure 17 shows the optical micrograph of reduced briquette exposed to air for a short duration while it was still hot. The micrograph shows “bubbling” of the iron particles. It seems as if generation of gas pressure inside liquid iron drops has caused the blowing up of the drops. As a result, the iron drops have formed bubbles. The generation of gas pressure inside the iron drops is probably due to the oxidation of Fe₃C to Fe with the release of CO/CO₂. The CO/CO₂ may have exerted a pressure resulting in the formation of iron bubbles. In the same way, a reduction-oxidation reaction between Fe₃C and FeO can also generate high gas pressure, although at a lower rate.

In another experiment, when the hot reduced briquette was quenched in water, C₂H₂ gas was generated. This was probably due to the reaction between Fe₃C and H₂O. This experiment also shows the formation of Fe₃C.

3.4. Proposed Model to Describe Swelling of the Cement-bonded Briquettes

In the absence of a well-proven theory, a model to describe the swelling mechanism may only be surmised. It is proposed that the swelling takes place in the following steps:

- Disintegration of pellet-fines particles. On reduction from hematite to magnetite, the weak pellet-fines particles develop cracks and disintegrate to smaller and detached particles. On further reduction to wustite, the particles disintegrate even further, as a result of which the wustite particles are much smaller and fragmented. At this stage, the wustite particles are still close to each other and a rough outline of the original particle may still be there.
- Formation of liquid slag. The CaO, SiO₂, FeO, MgO and Al₂O₃ react together to form a phase having a low melting point. Due to the heat released during the reduction of wustite to iron, the phase melts to form liquid slag having a low viscosity. This liquid slag acts as a lubricant.
- Generation of high gas pressure due to formation and oxidation of metastable iron carbide. The moving apart of iron particles is due to the generation of high gas pressure inside wustite particles that pushes the reduced iron particles out. The gas pressure is generated due to the formation and subsequent oxidation of metastable iron carbide, Fe₃C. In the first stage the iron carbide is formed and later this iron carbide oxidises back to iron and CO/CO₂ by taking oxygen from wustite or carbon dioxide.

Swelling does not take place in any of the pellets because:

- the structure is rather strong and does not get fragmented;
- there is no formation of iron carbide; and
- there is no formation of molten slag.

Based on this conceptual model, some of the observations may be explained:

1. Effect of Reduction Temperature: The swelling takes place in the short temperature range 900–1000°C because at a lower temperature the iron carbide oxidises at a far lower rate. Hence, high gas pressure is not generated. At the higher temperature, iron carbide is not formed.
2. Effect of Degree of Reduction: The swelling does not
Effect of Reduction in Steps: The swelling in three-step reduction is partly proven by the fact that when the briquettes are reduced in three stages the cement bonding breaks at low temperatures. In the presence of cement, there is a formation of a slag having high melting point. This slag binds all the oxides, as a result of which it is not available to form a slag having low melting point. Also, the slag increases the strength of the pellet-fines structure by forming additional slag bonds. The third reason is that pre-heating leads to the oxidation of magnetite and sintering of hematite grains leading to better structure.

Effect of Reduction under Load: There is a tendency to swell, but the external load prevents this swelling from taking place.

Effect of Briquette Size: The briquette size does not affect the swelling, because the generation of high temperature is at the microscopic level and is not affected by the size of briquette.

Conclusions

From the work carried out, it may be concluded that:

1. The pellet-fines having weak structure disintegrate during reduction from hematite to magnetite to wustite.
2. The CaO, SiO$_2$, FeO, MgO and Al$_2$O$_3$ react together to form a phase having a low melting point. Due to the heat released during the reduction of wustite to iron, the phase melts to form liquid slag having a low viscosity.
3. In the presence of cement, there is a formation of metastable iron carbide at 950°C. Later, a redox reaction between Fe$_3$C and FeO can take place resulting in the formation of Fe and CO$_2$/CO.
4. A model has been proposed to explain the swelling of cement-bonded briquettes.
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