Studies on the Cement-Bonded Briquettes of Iron and Steel Plant By-products as Burden Material for Blast Furnaces

Maneesh Singh
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Division of Process Metallurgy
Luleå University of Technology
SE-971 87, Luleå
Sweden

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SUMMARY

During the various stages of iron and steel production a number of iron bearing by-products are generated. Since these by-products cannot be recycled back in fine form, they need to be agglomerated. The traditional way to recycle them back to the blast furnace has been the balling and sintering process. In recent years, this process has come under attack because of its adverse environmental impacts, resulting in closure of all the sintering plants in Sweden. Cold-bond agglomeration process, if perfected, offers an alternative process for recycling the by-products.

The aim of the investigation is to study the properties of cement-bonded agglomerates prepared using iron and steel plant by-products at room temperature and when subjected to high-temperature reduction. The effect of various processing parameters on the properties of cement-bonded briquettes has been studied. This thesis presents the results of the work done to study the following:

Optimisation of parameters for briquetting process. It has been found that the room-temperature properties of briquettes depend upon various processing parameters like solid / water ratio, vibration time, briquetting force, compression time and particle size distribution of the raw material. The optimum values of these are interrelated and depend upon the composition of the briquettes.

Strength of briquettes when reduced at high temperature. The study has shown that the strength of briquettes after heating in nitrogen environment and after reduction depends upon a number of factors. The composition and the physical and chemical characteristics play a major role in determining the strength. The strength of briquettes falls with increase in swelling tendency on reduction of the pellets used. The decrease in strength is also less if the raw material contains pre-reduced materials, flaky particles and materials like cutting slags, which can act as a skeleton in the briquettes. The strength of briquettes – cured, heated in nitrogen environment and reduced – increases with decreasing particle size of the raw material and increases almost linearly with increase in cement content.

The strength of briquettes depends upon the reduction / heating conditions. The strength of briquettes falls drastically as the temperature drops to 700°C, but falls rather slowly beyond that. The decrease in strength is greater in the case of reduced briquettes than in the case of heated briquettes due to the combined effect of destruction of binding phase (CSH gel) and phase transformations of iron oxides. With increase in the degree of reduction (up to 10%), the briquettes rapidly lose their strength. Beyond this, the strength is not affected by the degree of reduction. For the briquettes that are made of coarse raw material, the decrease in strength on reduction under load is less than the decrease in strength on reduction allowing free swelling.

Catastrophic swelling of cement-bonded briquettes. Under certain reducing conditions, the cement-bonded briquettes exhibit a tendency to swell catastrophically. Maximum swelling takes place when the briquettes are reduced at 950°C using carbon monoxide. The swelling is reduced by the presence of hydrogen in the reducing gas.

The presence of cement is essential for swelling to take place, but beyond 4 weight percent the increase in cement content again leads to a decline in swelling. Thus, swelling may be decreased either by replacing cement with some other binder or by increasing the cement content to more than 10 weight percent. All the individual oxide components of the cement – CaO, SiO₂, MgO and Al₂O₃ – should be present in the proper proportions for swelling to take place. Removal or addition of any of these oxides may decrease it.
For the catastrophic swelling to take place, the composition of the briquette plays an important role. Swelling takes place when the briquettes are made using pellets containing a greater amount of slag forming oxides, CaO, SiO₂, MgO and Al₂O₃ with cement as binder. Even though the briquettes made of crushed pellets may not swell, the briquettes made of pellet-fines of the same pellet type swell. This is because it is mostly the under-fired and weaker pellets that break and end up as pellet-fines particles. Incorporating a high percentage of pre-reduced and flaky material can reduce the swelling.

The physical attributes of the raw material also affect the swelling behaviour. The swelling of briquettes increases with the increase in average particle size of the raw material. The swelling is almost proportional to the log of d₅₀ of the raw mix. Thus, using finely ground raw material may decrease the swelling.

The swelling takes place during the transformation of wustite to iron and is not due to the formation of iron whiskers; instead, it is due to the movement of iron particles away from each other in a bath of molten slag. It has been proposed that it takes place in three steps: (a) cracking of weak pellet-fines particles during reduction to form dispersed grains of wustite; (b) formation of molten slag due to reaction between CaO, SiO₂, FeO, MgO and Al₂O₃; and (c) generation of gas pressure due to formation and subsequent oxidation of Fe₃C.

Study of reactions involved in the reduction process. The reactions taking place at different temperatures, reduction potential and chemical composition have been studied. It has been observed that at high temperature dehydrated cement, olivine and wustite react to form a phase having roughly the composition (Ca,Mg,Fe)₂SiO₄. The properties of this phase depend upon the pellet-fines / cement ratio. It is possible to have a composition with a rather low melting point, 1150°C. This phase can melt locally due to heat released by the reduction of wustite in the adjoined region to form a liquid slag phase. This slag reduces at high reduction potential to form (Ca,Mg)₂SiO₄ and Fe.

It has also been observed that the formation of Fe₃C is catalysed by the presence of dehydrated cement. It is possible to form metastable Fe₃C at 950°C. With time, Fe₃C takes oxygen from wustite to oxidise to Fe and CO/CO₂.

Testing of briquettes in a pilot blast furnace. Effect of some parameters – composition, particle size of raw material, cement content and coke content – on the behaviour of briquettes reduced in a pilot blast furnace has been studied. It has been observed that the strength of briquettes can be increased by increasing the percentage of pre-reduced and flaky components, increasing the cement content, decreasing the particle size of the raw material and decreasing the coke content. Some of the weak briquettes get crushed under the load of burden material on top of them.

The briquettes do not have any tendency to swell catastrophically when tested in the pilot blast furnace. Optical microscopic study of the samples recovered from the blast furnace shows that the briquettes experience the first two steps of swelling – disintegration of pellet-fines particles and formation of liquid slag – but do not experience the third step – generation of high gas pressure. Hence, the briquettes do not swell catastrophically.

The briquettes recovered from pilot blast furnace have a big core of wustite even after descending quite low in the furnace. There are three reasons for this: (a) larger size of the briquettes as compared to pellets; (b) formation of CaO-SiO₂-MgO-Al₂O₃-FeO slag that reduces at high reduction potential, and (c) covering of the wustite grains by the molten slag.

Keywords:
Blast furnace, by-products, cement-bonded briquettes, iron and steel, reduction, strength, swelling.
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LIST OF PAPERS

This thesis is based on the following papers:


2. Maneesh Singh and Bo Björkman, Strength of cement-bonded briquettes, (Submitted).


6. Maneesh Singh and Bo Björkman, Testing of cement-bonded briquettes under laboratory and blast furnace conditions, (Manuscript).

Related publications not included in this thesis:


3. Maneesh Singh and Bo Björkman, Reduction of cement-bonded briquettes, (Manuscript).
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PAPER 6. Testing of cement-bonded briquettes under laboratory and blast furnace conditions.
CHAPTER 1
INTRODUCTION

1. COLD-BOND AGGLOMERATION PROCESS

Stringent regulations restricting emissions of industrial pollutants and the increasing costs of primary sources of materials have made it imperative that recycling of the by-products from plants be maximized.

During the various stages of iron and steel production, a number of iron-bearing by-products are generated. Since these by-products cannot be directly recycled in their fine form, they need to be agglomerated. The traditional way to recycle them back to the blast furnace has been the balling and sintering process. In recent years, this process has come under attack because of its adverse environmental impacts, resulting in closure of all the sintering plants in Sweden. Hence, there is a need for a technically viable, economically attractive and environmentally safe way for agglomerating iron-rich steel plant by-products.

For agglomerates to be considered suitable as feed material for a furnace, they should have sufficient strength for handling, transportation and outside storage and complete reducibility of iron-containing elements without degradation or excessive swelling. The process for producing these agglomerates should be robust enough to tolerate a variety of materials in various proportions; it must be economically feasible, even for relatively small-scale operations, and should generate little or no pollution.

The cold-bond agglomeration process offers one such means. In this process, various steel plant by-products, carbonaceous material and other necessary ingredients can be agglomerated, using a binder, into a form suitable for charging into a furnace. In the furnace, the metallic oxides in the agglomerates are reduced to metals, and the carbon units act as a fuel and reducing agent, thereby substituting the more expensive metallurgical coke. The additives required as binders either burn off without interfering with the reactions (organic binders) or are compatible with the blast furnace reactions (lime-silica, Portland cement) [1-14].

2. CEMENT-BONDED AGGLOMERATION PROCESS

2.1. The Portland Cement as Binder

Portland cement is the most commonly used binder for cold-briquetting iron-rich fines. The main benefits of its use are: easy availability and use, low cost, good room-temperature strength development and near neutral effects on blast furnace reactions. It has been fairly well studied and found suitable for various applications.
Portland cements consist of calcium silicates (C\textsubscript{2}S\textsuperscript{1}, C\textsubscript{3}S, etc.), calcium aluminates (CA, C\textsubscript{3}A, C\textsubscript{12}A\textsubscript{7}, etc.), calcium ferrites (CF, C\textsubscript{2}F, etc.) and calcium aluminoferrites (as solid solution in the series C\textsubscript{6}A\textsubscript{2}F\textsubscript{2}-C\textsubscript{6}AF\textsubscript{2}, which is generally represented as C\textsubscript{4}AF). Of these phases, alite (C\textsubscript{3}S), belite (β-C\textsubscript{2}S), tricalcium aluminate (C\textsubscript{3}A) and calcium aluminoferrite (C\textsubscript{4}AF) are the most important phases that impart strength to hydrated cement samples [15-17].

On hydration of ordinary Portland cement (OPC), the phases that are formed can be broadly classified into four kinds: (a) C-S-H gel; (b) hydrated calcium aluminates; (c) AFt (hydrated aluminoferrite trisulphate, ettringite) and (d) AFm (hydrated aluminoferrite monosulfate). Calcium silicates (C\textsubscript{3}S and β-C\textsubscript{2}S) react with water to form calcium silicate hydrates of variable composition and structure (classified under a general term CSH gel). The structure of CSH gel depends, among other factors, on C/S, S/H, time of hydration, pH of slurry and presence of other compounds / impurities. Hydration reactions can be expressed as [15-18]:

\[
\begin{align*}
\text{C}_3\text{S} + x\text{H} &\rightarrow \text{C}_3\text{S}\text{H}_{(x+y-3)} + (3-y)\text{CH} \\
\text{C}_2\text{S} + x\text{H} &\rightarrow \text{C}_2\text{S}\text{H}_{(x+y-2)} + (2-y)\text{CH}
\end{align*}
\]

C\textsubscript{3}A in general has lower strength compared to silicates. It hydrates according to the equation:

\[
\begin{align*}
2\text{C}_3\text{A} + 21\text{H} &\rightarrow \text{C}_4\text{AH}_{13} \text{ (hexagonal)} + \text{C}_2\text{AH}_8 \text{ (hexagonal)} \\
\text{C}_4\text{AH}_{13} + \text{C}_2\text{AH}_8 &\rightarrow 2\text{C}_3\text{AH}_6 \text{ (cubic)} + 9\text{H}
\end{align*}
\]

In the presence of CH, C\textsubscript{4}AH\textsubscript{13} and C\textsubscript{3}AH\textsubscript{6} can coexist.

The ferrite phase, which exists as a solid solution of C\textsubscript{2}F and hypothetical C\textsubscript{2}A between the series C\textsubscript{6}A\textsubscript{2}F-C\textsubscript{6}AF\textsubscript{2} is often approximated as C\textsubscript{4}AF, and it reacts similarly in some ways to C\textsubscript{3}A.

\[
\begin{align*}
\text{C}_4\text{AF} + 16\text{H} &\rightarrow 2\text{C}_4(\text{A,F})\text{H}_8 \\
\text{C}_4\text{AF} + 16\text{H} &\rightarrow \text{C}_d(\text{A,F})\text{H}_{13} + (\text{A,F})\text{H}_3
\end{align*}
\]

### 2.2. Raw material preparation

This involves the selection and pre-treatment of the raw material. In this stage, the raw materials are selected based on their chemical, physical and mineralogical composition [2,19,20].

### 2.3. Grinding

This is done in order to bring about homogenization and proper particle size distribution. The raw mixture is optimally ground so as to obtain a continuous particle size distribution. Such a material satisfies the conditions for the ‘ Fuller Curve’ and has coarse, fine and very fine particles in the desired proportions [6,19,21-34].

### 2.4. Mixing

In this stage, the raw material to be agglomerated is mixed with the desired quantity of cement. Proper mixing leads to homogenization of the material and ensures an increased number of bond points, thereby enhancing the mechanical strength of the agglomerates after curing.

The amount of cement used is an important parameter controlling the agglomeration process. The strength of briquettes – cured and reduced – increases almost linearly with increase in cement content. There is a linear relationship between the strength of briquettes after curing and after reduction. The increased strength is due to the stronger bonding by the cement [1,2,11,24,35,36].

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\(1\) The following notation has been used throughout the text:

A: Al\textsubscript{2}O\textsubscript{3}   C: CaO   F: Fe\textsubscript{2}O\textsubscript{3}   H: H\textsubscript{2}O   M: MgO   S: SiO\textsubscript{2}   W: Wustite
While the increase in cement content increases the strength, it also increases the amount of slag formed, water inside the blast furnace and the cost of production. Normally, a blast furnace uses less than 10% cement-bonded agglomerates as iron-ore burden material, and these agglomerates contain less than 10% cement as binder. This leads to an increase of less than 15 kg slag per tonne of hot metal. In Sweden, the blast furnaces produce about 170-200 kg of slag per tonne of hot metal. Hence, there is an increase of less than 8% slag [2,37]. When the blast furnace operates on high-quality iron ore/pellets, this additional slag formation may not be a disadvantage. On the contrary, it may improve the performance by making the movement of burden material smoother.

When the amount of cement increases, the amount of moisture also increases. Inside the blast furnace most of the free moisture escapes from the top part of the shaft and may not adversely affect its operation, except for increasing the fuel demand. On the other hand, the bound water present in the briquettes is released at high temperature. A substantial part of it may be released in the thermal reserve zone [38,39].

### 2.5. Briquetting / Pelletizing

Before agglomerating, an optimum amount of water is added to the concentrate and all of it is properly blended to form a thick homogeneous slurry. This paste is then compacted using dies and a press system or by using standard disk / drum pelletizers. The room-temperature strength of a briquette made using steel plant by-products and cement depends upon various processing parameters [1,2,11,23,24,40-44].

### 2.6. Curing / Autoclaving

The curing of green agglomerates is very much dependent on the agglomeration process and the type of binder used. Strength development, in the case of calcium-silicate-based binders (like cement, lime + silica, granulated blast furnace slag), is due to the formation of hydrated calcium silicate gel, which forms a skeleton-like solid material after hydrating. The strength development is very fast during the initial days and then it approaches the final strength asymptotically. Hence, it can generally be divided into two steps: Primary Curing and Secondary Curing. The strength development is crucial during the first two days, since agglomerates are weakest then; hence, in the Primary Curing the agglomerates are kept in special humid chambers without being subjected to movements. The Secondary Curing is usually done under normal atmospheric conditions in storage areas where the agglomerates are left undisturbed until they attain the targeted strength values [11,23,24,40,45].

Instead of curing, autoclaving can be used for fast development of strength; but this is normally not a preferred method because of higher production cost and lower strength development [4].

The factors that may affect the properties of the agglomerates produced are: (a) composition of concentrate; (b) particle size distribution of concentrate; (c) amount of cement used; (d) method of curing; and (e) presence of additives in the binder (like gypsum) [35,36,46,47].

### 3. ADVANTAGES OF THE CEMENT-BONDED AGGLOMERATION PROCESS

The use of the cold-bond agglomeration process has a number of benefits. Some of them are:

1. Recyling of By-products: The closure of sintering plants in many countries has made the disposal of by-product fines a liability. This process allows these materials to be recycled back into furnaces [2,7,48].
2. **Good Strength Characteristics:** Cement-bonded agglomerates have good low-temperature mechanical (compression strength, abrasion resistance, etc.) properties. Also, the high-temperature strength is proportional to the amount of cement added; hence, agglomerates having acceptable high-temperature strengths can be prepared [38,39,49].

3. **Prevention of Emission of Toxic Gases:** The sintering process for agglomeration of dusts results in large-scale emission of NO\textsubscript{x} and SO\textsubscript{x}. This problem does not arise in the cold-bond agglomeration process.

4. **Control of Properties of Agglomerates:** It gives greater freedom to manipulate both the mechanical and metallurgical properties of the agglomerates. This is done by including the desired additives along with the other major ingredients and controlling the process parameters. Such possibilities are limited in induration or sintering process because of the reactions taking place at high temperatures and the oxidizing environment [43].

5. **Addition of Carbonaceous Materials:** Carbonaceous materials can be included in the agglomerates themselves. This improves the reduction kinetics (reduction rate and reducibility) owing to the presence of a larger number of reaction sites available simultaneously and due to shorter diffusion. It also allows recycling of cheaper carbonaceous materials present in the dust or as coke breeze to be included in the agglomerates and used in place of costlier metallurgical coke. The drawback of the addition of carbon is that it usually lowers the strength; hence, most of the time, agglomerates contain less than 10% carbon [4,48,50-63].

6. **Improved Reduction Kinetics:** Apart from the improvement in kinetics brought about by the presence of carbon in agglomerates, the kinetics is also affected by the presence of free lime, other metal oxides and better physical features of the cold-bond agglomerates. Free lime and metal oxides are able to react directly with the open wustite lattice and influence the reduction properties [6].

7. **Economical:** Compared to other processes, the cold-bond agglomeration process is more economical due to lower capital investments, operating costs, feasibility of small-scale production, cheaper process and lower energy requirements. Also, Portland cement is a relatively cheap commercial product, of which only small quantities are required (4-8% of total weight); hence, it proves economically attractive [1,12,51].

8. **Energy Saving:** The energy required for producing iron using cold-bond agglomerates is less than that required for indurated pellets or sintered material [1].

9. **No Deleterious Influence on Blast Furnace Chemistry:** Addition of cement as binder results in incorporation of additional amounts of silica and calcium oxide. Neither of these has a large influence on the reduction chemistry and both are removed along with rest of the slag.

### 4. DISADVANTAGES OF THE CEMENT-BONDED AGGLOMERATION PROCESS

In spite of a number of advantages offered by the use of cold-bonded agglomerates there are some major disadvantages, as a result of which their use has been rather limited.

1. **Low Temperature Degradation:** Most of the cold-bond agglomerates disintegrate and crumble to powder between 500 and 1000°C. For the agglomerates, prepared using cement and heated in nitrogen environment, strength diminishes with increase in temperature. This is due to the gradual decomposition of calcium silicate hydrate (CSH gel). On being subjected to high-temperature reduction, the fall in the strength of agglomerates is much more significant due to the decomposition of the binding matrix combined with the phase transformations in the iron oxide particles. The strength of briquettes decreases as the temperature rises, and at 700°C, less than 20% of the original strength remains. The maximum decrease in strength takes place during the initial stages of reduction, and beyond 10% reduction, the strength of briquettes is low [63-69].
2. **Harmful Effects of Additional Moisture:** The water of crystallization may result in as much as 2-3% bound water and about 9% free moisture content. In comparison to the conventional pellets, this means that about 18% extra weight, including cement and water, must be transported. A part of this water is released at elevated temperatures and exerts an influence on the temperature distribution inside the furnace, thereby affecting blast furnace efficiency [70].

3. **Additional Formation of Slag:** The cementitious binder in the agglomerates ends up as slag. The formation of this additional molten slag requires some energy [37].

5. **BLAST FURNACE TRIALS**

Portland cement-bonded agglomerates have been in regular use in a number of plants including those of USS Gary No. 8, Gary (Indiana, USA); SSAB Tunnplåt, Luleå (Sweden); SSAB, Oxelösund (Sweden); Nippon Steel Corporation, Nagoya (Japan); Bethlehem Steel and McLouth Steel Corporation, Trenton (Michigan, USA) [2,11,64,71-73].

1. **Fuel Rate:** Since the agglomerates may contain a significant proportion of pre-reduced materials, like cuttings, mill scale, and LD converter dust, the total fuel rate decreases. Incorporating flue dust and coke fines in the agglomerates can enable a further decrease in the consumption of coke [2,37,71].

2. **Control of Feed Material:** Certain ingredients like manganese ore, etc. can be easily mixed with the other charge materials and fed to the blast furnace [1].

3. **Problems in Burden Distribution:** Different plant operators report different experiences on charging cement-bonded agglomerates to the furnace, but the common observation has been that the increase in cement-bonded agglomerate percentage leads to increase in the instability of the furnace. This difference may be due to the differences in the composition of agglomerates, the quality of agglomerates and the plant parameters. Generally, it has been reported that the burden movement and distribution within the blast furnace depend upon the amount of cement-bonded agglomerates in the burden. Most of the blast furnaces perform without any apparent problem on use of up to 5% cement-bonded agglomerates as iron-ore burden material. As the amount increases, the movement becomes more erratic and the blast furnace has a tendency to hang and slip. The reported upper limit of agglomerate addition varies between 10 and 15%. This is probably due to the disintegration of briquettes inside the blast furnace [2,3,73,39].

4. **Changes in the Temperature Profile inside the Furnace:** Cold-bond agglomerates contain water; hence, their addition may lead to a delay in temperature rise in the upper shaft of the blast furnace. When cold-bond agglomerates are used instead of indurated pellets, the gas temperature in the blast furnace tends to fall and the low-temperature thermal reserve zone of 500-700°C tends to elongate. This leads to a delay in reduction. However, it may be possible to keep the gas temperature in the blast furnace almost constant by increasing the fuel ratio and by controlling the burden distribution [11,70].

5. **Increase in Gas Pressure:** The pressure drop increases with increase in agglomerate addition. This is probably caused by the reduction in bed permeability due to the increase in amount of fines resulting from the disintegration of agglomerates [2,37,71].

6. **Increase in Flue Dust:** At a high rate of agglomerate addition, the amount of blast furnace flue dust may increase. This again is the result of disintegration of the agglomerates inside the furnace; but at a lower charge rate (up to 5%), this increase has not been observed [2,37,71].
6. SWELLING OF INDURATED PELLETS

The reduction of indurated pellets is accompanied by expansion in their volume. About 20% swelling is common and does not adversely affect blast furnace operation in any way. This swelling is mainly a result of the phase transformation from hematite (hexagonal) → magnetite (cubic). In some cases, there is volume increase during conversion of magnetite to wustite. This increase in volume is often attributed to the release of the remnant stresses generated during the conversion of hematite to magnetite, during conversion of magnetite to the weaker wustite structure [74-78].

In some cases, pellets exhibit “abnormal” or “catastrophic” swelling / disintegration / degradation. This results in volume expansion more than the normal 20% and in drastic reduction of the strength of pellets. This catastrophic swelling is a characteristic of pellets and is not observed either in sinters or in iron ore lumps.

Most of the time, catastrophic swelling occurs during the last stage of the reduction process (wustite → iron) when iron of fibre-like (whiskers) morphology is formed. The growing whiskers push neighbouring grains and lead to large-scale swelling [79]. The causes of abnormal swelling are many and varied. The various causes of swelling that have been studied include:

Properties of pellets:
- Induration time and temperature [80].
- Size distribution of ground ore.
- Presence of alkalis [81-84].
- Amount and composition of slag [76,77,85-89].
- Porosity of pellets [90].
- Strength of pellets [90].

Reducing conditions:
- Reduction temperature [75,91-93]
- Reduction time.
- Reduction potential.
- Presence of CO or H₂ in reducing gas.
- Flow rate of reducing gas.
- Change of gas composition with time.
- Impurities in reducing gas [94,95].
- Isothermal / non-isothermal reduction [92,96].
- Thermal treatment.

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. When the pellet is reduced with CO at low temperatures, CO dissociates to C and CO₂. At low temperatures (about 700°C), C either deposits inside the pellet and / or reacts with iron to form iron carbides (Fe₃C or Fe₂C). As reduction temperature increases instead of depositing as free C, the C dissolves in the produced iron. As the reduction proceeds, the C reacts with wustite to give CO and CO₂ and Fe. The oxidation of dissolved C leads to the formation of bubbles, which exert a disruptive force. At high reduction temperature (>900°C), the swelling is less because of low C deposition and greater sintering [97-102].

7. SWELLING OF COLD-BONDED AGGLOMERATES

Abnormal swelling has also been observed in cement- or lime-bonded agglomerates made from high-grade magnetite ore. In all the cases, the swelling took place due to the nucleation and growth of iron whiskers. It has been proposed that the cause and mechanism of swelling of cement-bonded agglomerates and that of the indurated pellets is the same. Hence, various parameters affect both in roughly the same way [103-112].
8. NEED FOR FURTHER STUDY

A significant amount of research work has been done in order to improve the performance of the cold-bonded agglomerates. Most of the effort has been directed towards improving the strength of agglomerates at room temperature. Some work has also been carried out to improve the strength of agglomerates subjected to high temperature and reduction. In spite of this, there is still a need for detailed study of the parameters that affect the strength at high temperature and reduction.

Even though the swelling of cement-bonded agglomerates has been noted over the past three decades, no in-depth work has been carried out. Hence, there is a strong need to study the swelling phenomenon of cement-bonded agglomerates in detail.

In spite of all the investigation carried out to perfect the production and use of cement-bonded agglomerates, the work is far from over. Work needs to be done to develop a robust process for producing cement-bonded agglomerates that would have sufficient strength at room temperature to withstand stresses during handling and transportation. Even more important is the development of a process for producing agglomerates that would have optimal qualities under blast furnace conditions.

9. AIM OF THE PROJECT

The aim of the study is to understand the properties of cold-bond agglomerates at room temperature and when subjected to high temperature reduction. The effect of various processing parameters on the properties of agglomerates has being studied. The study has been carried out with the requirements of the steel industry in mind. The results will help the steel industry to recycle its by-products back into the blast furnace more efficiently.

10. THE SCOPE OF WORK

The present work has been carried out to study the following (Figure 1):

10.1. Effect of Processing Parameters on the Room Temperature Properties of Briquettes

From the time briquettes are manufactured in a briquetting plant to the time they are charged into a blast furnace, they undergo a number of unit operations. These unit operations subject them to various stresses that may lead to their disintegration. Hence, the briquettes should be strong enough to withstand the stresses experienced during the handling steps. The strength of briquettes depends upon their processing parameters like cement / water ratio, briquetting force and particle size distribution of raw material. Investigation has been carried out to find the parameters on which the properties of the cured briquettes depend.

10.2. Strength of Briquettes

When the briquettes are put into the blast furnace, the high temperature and the reducing condition of the blast furnace transforms the iron oxide particles and dehydrates the hydrated cement; as a result, the briquettes lose their strength. It is essential that the briquettes do not lose too much strength too rapidly, because that would cause them to crumble. This would in turn lead to a high amount of dust in the stack gases and a decrease in the permeability of the bed, thereby affecting the flow of gas. The study has been undertaken to investigate the effect of temperature and reducing condition on the strength of briquettes. The effect of various parameters like particle size of the raw material, cement content, pellet type and coke content on briquette strength after high-temperature reduction has been investigated.
10.3. Swelling of Briquettes

The cement-bonded briquettes have been observed to show a tendency towards catastrophic swelling under certain reducing conditions. Catastrophic swelling in briquettes can lead to their mechanical failure inside the furnace, resulting in hanging and slipping of the blast furnace. In order to prevent the abnormal swelling, an understanding of the factors that cause it is essential. The effect of various parameters like temperature, reduction degree, particle size of the raw material, cement content, composition of the raw material and pellet type on the catastrophic swelling of briquettes has been investigated. Based on the experimental results, a model has been proposed to explain the swelling mechanism.

10.4. Reactions taking Place in Briquettes

During heating and reduction, a number of reactions take place in the briquettes. As the briquette gets hot, the hydrated cement dissociates to calcium silicate and calcium oxide. These react with iron oxides to form a series of phases. These reactions in turn affect the performance of the briquettes. In order to understand and control the reduction and the swelling of briquettes, an understanding of the briquette chemistry is important. The effect of temperature, reduction potential and cement content on the reactions taking place has been studied.

10.5. Behaviour of Briquettes in a Pilot Blast Furnace

A blast furnace is a very complex system that cannot be replicated in the laboratory. Most of the laboratory tests consider only a small aspect of the actual blast furnace operation. Hence, to understand the actual performance, the briquettes need to be tested in a real blast furnace. The pilot-scale experimental blast furnace is a powerful tool for studying the behaviour of the briquettes in actual plant conditions, because its characteristics closely approximate an actual blast furnace. In order to study the effect of various parameters on the performance of cement-bonded briquettes, some briquettes have been tested in a pilot blast furnace.
Figure 1. Cold-bond agglomeration process and the reported areas of research.
CHAPTER 2
MATERIALS AND METHODS

1. MATERIALS

1.1. Raw Materials

Nine raw materials received from SSAB Merox AB were used for the study. They were:

- Pellet-fines
- Cutting slag (steel-work)
- Cutting slag (rolling)
- Grinding fines
- Blasting dust
- LD converter dust
- Mill scale
- Slag handling scrap
- Manganese slag

One of the materials, pellet-fines, was a mixture of fines of Pellet A and Pellet B, two commercially available pellets. The generation of fines took place due to breakage during transportation and handling. Structurally pellet-fines is different from either Pellet A or Pellet B since it is mostly the weak – under-fired or over-fired – pellets that break.

The remaining materials were different iron-rich slags, sludges and dusts generated at SSAB Oxelösund AB.

Even though Manganese slag is not a by-product, it has also been included in the composition. This is because SSAB Merox also adds it during the production of its briquettes, since manganese is required in hot metal during the steelmaking process.

Particle Size Distribution: Figures 1-8 show that all the raw materials have a wide range of particle size distribution. Only blasting-dust and LD dust have a relatively short range of distribution and are rather fine. In the case of pellet-fines, while most of the material (86.67%) is greater than 1190 µm size fraction, a significantly large portion (7.23%) is in the form of dust (-74 µm). This is because of the friable nature of the pellet-fines, which results in the generation of fines due to abrasion.

Figure 1. Particle size distribution of cutting slag (steel-work). Figure 2. Particle size distribution of cutting slag (rolling).
Chapter 2

Materials and Methods

Figure 3. Particle size distribution of blasting dust.

Figure 4. Particle size distribution of LD converter dust.

Figure 5. Particle size distribution of manganese slag.

Figure 6. Particle size distribution of mill scale.

Figure 7. Particle size distribution of slag handling scrap.

Figure 8. Particle size distribution of pellet-fines.
Table 1. Chemical analysis of various raw materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manganese slag</th>
<th>Slag handling scrap</th>
<th>Pellet-fines</th>
<th>LD converter dust</th>
<th>Cutting slag (steel-work)</th>
<th>Cutting slag (rolling)</th>
<th>Mill scale</th>
<th>Blasting dust</th>
<th>Cement</th>
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<td>Fe</td>
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<td>64.49</td>
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<td>76.86</td>
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<td>85.61</td>
<td>-</td>
<td>12.31</td>
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<td>31.91</td>
<td>-</td>
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<td>0.47</td>
<td>53.00</td>
<td>-</td>
<td>0.05</td>
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<td>22.68</td>
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<td>57.90</td>
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<td>18.83</td>
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<td>Fe_{x}O_{y}</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MnO</td>
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<td>1.14</td>
<td>0.75</td>
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<td>0.04</td>
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<td>4.36</td>
<td>3.34</td>
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<td>SiO_{2}</td>
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<td>0.04</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
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<td>0.03</td>
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<tr>
<td>C</td>
<td>-</td>
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<td>-</td>
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<td>0.10</td>
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<td>97.63</td>
<td>99.36</td>
<td>101.66</td>
<td>102.83</td>
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Chemical Analysis: Table 1 shows the chemical analysis of the materials. Except for Manganese slag, all other by-products contained 58-87% iron in various oxide forms. The other major components were CaO, SiO_{2}, MgO and Al_{2}O_{3}. The main constituent, iron, was present in form of Fe_{2}O_{3}, Fe_{3}O_{4}, FeO and Fe. The manganese slag contained about 50% MnO and the other oxides constituted the rest. The various oxides, which were present in form of a number of phases, made the materials quite complex in nature.

1.2. Cement

Ordinary Portland cement (Standard Portland Cement, Type P, Cementa) was used as a binder. Table 1 gives the chemical composition of the cement used.

1.3. Sand

Cen-standard sand conforming to EN 196-1 and supplied by Normensand, Backum (Germany) was used for the experiments.

1.4. Reagents

Laboratory-grade iron oxide (Fe_{2}O_{3}), aluminium oxide (Al_{2}O_{3}), calcium hydroxide (Ca(OH)_{2}), quartz (SiO_{2}), and magnesium oxide (MgO) supplied by Fluka, Kebo Lab, Carl Roth GmbH & Co. and Riedel-deHaen were used.
Table 2. Chemical composition of pellets.

<table>
<thead>
<tr>
<th></th>
<th>A Wt.%</th>
<th>B Wt.%</th>
<th>C Wt.%</th>
<th>D Wt.%</th>
<th>E Wt.%</th>
<th>F Wt.%</th>
<th>G Wt.%</th>
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<tbody>
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<td>Fe₂O₃</td>
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<td>FeO</td>
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<td>Al₂O₃</td>
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<td>0.23</td>
<td>0.22</td>
<td>0.21</td>
<td>0.20</td>
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</table>

Table 3. Composition of briquettes.

<table>
<thead>
<tr>
<th></th>
<th>Pellet-fines</th>
<th>Cutting slag (steel-work)</th>
<th>Cutting slag (rolling)</th>
<th>Cutting fines</th>
<th>Grinding fines</th>
<th>Blasting dust</th>
<th>LD converter dust</th>
<th>Mill scale</th>
<th>Slag handling scrap</th>
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<th>Cement</th>
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<tr>
<td></td>
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<td>Wt.%</td>
<td>Wt.%</td>
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<td>Wt.%</td>
<td>Wt.%</td>
<td>Wt.%</td>
<td>Wt.%</td>
<td>Wt.%</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.5</td>
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</tr>
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<td>Wt.%</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

1.5. Indurated Pellets

Pellet A was used as a reference. Seven other types of pellets, Pellets B-H, were also used for some experiments. Of these, only Pellet A and Pellet B are commercially available and the rest are in experimental stages of development. Table 2 shows the chemical analysis of various types of pellets used for the experiments.

2. COMPOSITION OF BRIQUETTE

Mainly three different compositions were tested. The composition of the briquettes is given in Table 3.

- **Mix A**: Pellet-fines + ordinary Portland cement (6.5 weight%). This system was designed to be easily understood.
• **Mix B**: All the by-product is roughly in the proportion generated in a typical integrated steel plant + ordinary Portland cement (6.5 weight%). This was based upon the recipe developed by SSAB Merox AB and the idea was to consume as much of the by-products generated by SSAB Oxeösund as possible.

• **Mix C**: Sand + ordinary Portland cement (6.5 weight%). This was to understand the behaviour of hydrated cement at high temperature without any interference from the iron oxide phases.

3. **EXPERIMENTAL PROCEDURE**

3.1. **Preparation of Briquettes**

900 g of Mix A or Mix B was ground in a steel ball mill. 150 g (for Mix A and Mix B) or 100 g (for Mix C) of this mixture and optimum quantity of water (7.5 ml for Mix C and 10-15 ml for Mix A and Mix B, depending upon the composition and particle size distribution of the raw mixture) were then put in a steel trough and mixed for about a minute, so as to obtain a mouldable paste.

The plastic paste was placed in a cylindrical steel mould measuring 4.2 cm in diameter and compacted first by vibration for a fixed period (1.0 min.) (using a vibrating machine, Retsch Vibro) and subsequently by compression under fixed load (1.5 tons) for fixed time (1.0 min.) (using a laboratory scale press, Carver Laboratory Press, Model C). The green briquette thus obtained was cured for 28 days in a high-humidity chamber. The cured briquettes were dried overnight in an oven maintained at 105°C.

3.2. **Isothermal Reduction of Briquettes**

The schematic diagram of the reduction set-up is shown in the Figure 9. The reduction set-up consisted of two parts: the gas supply and the heating furnace. The gases were supplied from cylinders. The supply of these two gases was controlled using needle valves and flow meters. The gases in the required proportions were mixed in a gas mixer consisting of a tube containing glass beads.

The heating furnace consisted of a Kanthal wire-wound tube furnace (length: 100 cm, diameter: 12.5 cm). A stainless steel tube (length: 135 cm, outer diameter: 6.5 cm) closed at the bottom end was placed inside this furnace. A K-type thermocouple placed inside the furnace near the briquette monitored the furnace temperature. The gas mixture, either only nitrogen or a mixture of nitrogen and carbon monoxide (N₂:CO = 60:40) at a flow rate of 10 l/min. entered from the bottom and was burnt at the top by means of an off-gas burner.

For isothermal reduction, the furnace was heated until the desired temperature was reached and then the flow of reducing gas mixture was introduced. A briquette, placed in a high-temperature steel basket, was then lowered into the furnace and suspended from a balance placed above. The briquette was suspended in the region where the error was within ±5°C of the desired temperature. Figure 10 shows the temperature profile of the furnace. As an example, when a briquette was considered reduced at 950°C, the temperature in the space between the briquette and the steel wall was 955°C. A thermocouple implanted inside the briquette, axially midway and radially 7 mm from the surface, registered a linear rise in temperature up to 850°C in almost 11 min. It reached 940°C in 24 min., 950°C in 35 min. and finally stabilised at 954°C in 150 min (Figure 11). After the desired time had elapsed, the briquette was raised to the mouth of the furnace and cooled in a flowing-nitrogen environment.
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Figure 9. Schematic diagram and photograph of the experimental set-up.

Figure 10. Temperature profile of the furnace.  

Figure 11. Heating rate inside a briquette.

For isothermal reduction with non-isothermal heating, the briquette was lowered into the furnace at room temperature and heated in a nitrogen environment till the desired temperature was reached. Figure 12 shows the heating rate of the furnace. Thereafter, the reducing gas was passed through the furnace for the desired time. After reduction, the briquette was allowed to cool overnight inside the furnace in a flowing nitrogen environment.

3.3. Isothermal Reduction under Load

A high-temperature steel crucible with small holes at the bottom was used. A layer of alumina balls (diameter 10 mm) was laid at the bottom of this crucible. A briquette was then placed over the layer of alumina balls and in the centre of the crucible. The space between the briquette and the wall was then filled with alumina balls and a layer of alumina balls was placed over the briquette. 650 g (arbitrarily decided) of stainless steel balls (diameter 10 mm) was then placed over the briquette to apply a constant load (Figure 13). The crucible containing the briquette was placed inside the hot furnace and reducing gas was blown from the bottom. Figure 14 shows a typical briquette reduced under load.
3.4. Pilot Plant Tests

Some briquettes were also tested in a pilot blast furnace owned by LKAB and located at the premises of MEFOS, Luleå. The pilot plant has the following specifications: hearth diameter = 1.2 m, height = 14 m, volume = 8.2 m³, production = 36 tonnes/24 h, blast temperature = 1200°C, coke / coal consumption = 510 kg/tonne hot metal (Figure 15).

The briquette to be tested was put in a steel basket and surrounded by commercially available Pellet A (Figure 16). Just prior to the quenching of the furnace, the baskets were introduced into the furnace from the top at regular intervals. The furnace was then quenched by flushing nitrogen from the top. Within minutes, the reducing gases were removed and the reduction stopped. After cooling for about ten days, the furnace was dissected by first removing the furnace top and then removing the burden material layer-by-layer from stockline down to the hearth. The position and nature of baskets found inside the quenched furnace was recorded (Figure 17).
Figure 15. Schematic diagram of LKAB’s pilot blast furnace.

Figure 16. Photograph of sample-baskets that were put into the pilot blast furnace prior to quenching. The basket in the middle contains two briquettes surrounded by Pellet A.

Figure 17. Schematic diagram showing the position in the pilot blast furnace from which the briquettes were excavated to study the effect of various parameters.
3.5. Simulated Blast Furnace Tests

The simulated blast furnace tests were carried out at LKAB’s CK-laboratory at Malmberget, Sweden. Figure 18 shows the schematic diagram of the reduction setup. It consists of two parts: the gas supply unit and the heating furnace. The gas supply of individual gases was from the gas cylinders and was regulated by computer-controlled differential pressure transducers. The reduction equipment consisted of an electric furnace with an inner diameter of 12.5 cm in which a vertical reduction tube was suspended from a load cell place above the furnace. The load cell was connected to a computer that continuously recorded the weight of the reduction setup.

The reduction tube had a double wall for preheating of the reduction gas in the space between the walls. The reducing gas entered from above, passed between the walls of the two tubes and entered from the bottom of the inner tube. The gas reached the reducing zone through a perforated base. A test briquette was placed above the alumina pellets that covered the perforated base. The spent gas left the reduction tube from the top. A thermocouple placed beside the briquette measured and monitored the temperature inside the furnace. Figure 19 shows the temperature and gas flow profile of the experiment.

For the sake of comparison, isothermal tests were also conducted in the setup. Here, the briquettes were heated in nitrogen environment till the briquettes attained 950°C. Reducing gas N₂+CO (60:40) was then introduced (Figure 20).

3.6. Compression Strength Testing at Room Temperature

The briquettes were tested for compression strength using a Tonindustrie Testing Machine, Model - Seger. The load at which the briquettes suddenly failed was recorded. An average value of three briquettes per test was accepted. Strength of pellets was tested by crushing three pellets at a time.
Figure 19. Temperature and gas-flow profile for reduction under simulated blast furnace conditions tested in LKAB’s CK Lab at Malmberget.

Figure 20. Temperature and gas-flow profile for reduction under isothermal condition tested in LKAB’s CK Lab at Malmberget.

3.7. Degree of Reduction

The degree of reduction was calculated according to the formula:

\[
\text{Degree of reduction} = \frac{\text{Total loss in weight} - \text{Loss in weight due to the removal of moisture}}{\text{Total possible loss in weight due to oxygen removal}}
\]

Total loss in weight was obtained by recording the change in weight of briquettes during reduction. Loss in weight due to the removal of moisture was obtained by recording the weight of similar briquettes heated in a nitrogen environment. Total possible loss in weight due to oxygen removal was obtained from TGA and crosschecked using the chemical analysis of individual components. An average value of three briquettes per test was accepted. A variation within ±10% of the mean value was accepted.
3.8. Volume Measurements

The bulk volume of briquettes and pellets was calculated under the assumption that they were perfectly cylindrical and spherical, respectively. The diameter and the length were measured using callipers. After reduction, the briquettes and pellets often distorted. Even in this case, the diameter and length were measured at several places and an average of the readings was taken. This method of measuring the volume gave only rough values; hence, they should be taken only qualitatively.

3.9. Chemical Analysis

Chemical analysis was carried out at LKAB’s laboratory using an Inductively Coupled Plasma (ICP) Spectrometer.

3.10. Particle Size Analysis

Approximately 100 g of dried material was dry-sieved to various size fractions using a set of U.S. Standard Sieves conforming to ASTM. In this thesis, the particle size has been reported as d_{50}, which is a cumulative fifty percent finer than the value.

3.11. X-ray Diffraction Analysis of Powdered Sample

The material to be analysed was dried and ground to -75 µm and diffraction patterns were obtained employing a Siemens D5000 X-ray Diffractometer using Ni filtered Cu Kα radiation at 40 kV and 50 mA.

3.12. High-Temperature X-ray Diffraction Analysis

In situ high-temperature X-ray diffraction (HT-XRD) studies were carried out using an automatic diffractometer (Philips PW-1710). The basic units in this system were: a Philips powder diffractometer with a vertical goniometer (PW 1050/25), a graphite monochromator (PW 1752/00), a proportional counter for reflected beam (PW 1711/10) and a generator (PW 1730/25). The heating of the sample was done in an Anton Paar 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 mm X 7 mm X 0.7 mm), were heated in a flowing nitrogen environment. The temperature was ramped at a rate of 8.3°C/min. Cu Kα (50kV, 30mA) radiation was employed. The samples were scanned at room temperature and at every 100°C at a rate of 1.2°C/min.

3.13. Optical Microscopic Examination

A test piece of the sample to be observed was cast in a cold-mounting epoxy resin mould under vacuum. The moulded sample was then ground and polished using standard techniques. The polished sample was then observed using a Nikon Eclipse E600 Pol optical microscope.


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 Bal-tec MCS 010 sputter coater. The coated specimen was then examined under a Philips XL 30 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.
3.15. Melting Point

The melting point of samples was determined using a Leitz 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 an 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).

3.16. Thermal Analysis

The sample materials were dried and ground to -75 μm. The TG and DTA analysis were carried out on the samples using a Netzch STA 409 C thermoanalyser. Inert environment inside the furnace was maintained by argon gas flowing at a rate of 10 cc/min. The furnace was ramped at an average rate of 10°/min.

3.17. Porosity and Pore Size Measurements

The porosity and pore size distribution of the samples were measured by mercury porosimetry using a Micromeritics Pore Sizer 9305. The standard methods for low-pressure and high-pressure measurements were employed.

While considerable effort has been made to prepare and test the briquettes in a reproducible way, there are some inherent uncertainties that could not be eliminated. These uncertainties arise due to errors that are often unavoidable with this kind of experimental work. The errors are introduced right from the first stage of briquette preparation to the last stage of testing. For example, during the preparation stage the errors arise due to the segregation caused by the wide particle size distribution, inherent differences between any cement-bonded material and differences in the characteristics of the different batches of the raw materials used. During the testing of briquettes, errors arise due to a number of reasons including inaccurate temperature control of the furnace, position of briquette inside the furnace, heat transfer to and in the briquette, carbon deposition inside the furnace resulting in a changed gas composition and distortion of briquettes upon reduction. Therefore, while best efforts have been made to interpret the results rationally keeping in mind the sources of errors, some differences in the interpretation are inevitable.
CHAPTER 3
RESULTS AND DISCUSSION

1. STRENGTH OF CEMENT-BONDED BRIQUETTES (PAPERS I AND II)

From the time the cement-bonded briquettes are produced in a briquetting plant to the time they are put into a blast furnace, the briquettes go through a number of handling and transportation operations. During all these unit operations, the briquettes are subjected to a number of external forces that cause them to break. For briquettes to be considered acceptable by blast furnace operators, the briquettes should have sufficient strength to withstand all such external loads.

The room temperature strength of briquettes is due to the cementitious binder (CSH gel) holding the individual particles together. Hence, for the briquettes to have acceptable strength the aggregates should be well compacted and should have a maximum number of point-to-point contacts. This can be brought about by controlling various processing parameters. The parameters include:

1. **Water / solid ratio.** An optimum amount of water is required to provide correct balance between lubrication and porosity (Figure 1).

2. **Vibration time.** A certain minimum vibration time is required to aid in settling the particles. Beyond a certain time, vibration only results in cracking.

3. **Briquetting load.** Optimum load is required for proper compaction, but excessive load may lead to the cracking of friable particles, thereby resulting in low strength (Figure 2).

4. **Compression time.** Increase in compression time initially aids proper compaction, but beyond that, it may either be useless or result in poor strength because of cracking of friable particles.

5. **Particle size distribution of the raw material.** The strength of cured briquettes increases with fineness because of the greater degree of compaction in the case of finely ground material and because of the elimination of larger friable pellet-fines particles that are prone to cracking.

6. **Amount of coke.** The strength of cured briquettes decreases with increase in coke content because (a) coke is hydrophobic in nature; as a result the bonding between the cement matrix and coke particles is not strong; and (b) coke particles are soft and friable and prone to rupturing under load.

7. **Composition of raw material.** The strength increases with increase in pre-reduced and flaky / angular particles because they provide skeleton-like structures to hold the briquette together and because pellet-fines are relatively more friable.

Since all these factors are inter-dependent, the optimum conditions need to be found a case-to-case basis.
In the blast furnace, the briquettes are subjected to severe degrading conditions and a high-temperature reducing environment. Along with that, as the briquettes descend in the stack the crushing load also increases due to the presence of overlying burden material. Under such severe conditions, the briquettes tend to fail. The failure of briquettes may result in erratic movement of the burden material, decrease in the gas permeability inside the furnace and increase in dust in stack gas. Hence, the briquettes should be strong enough so as not to crumble inside the furnace.

Inside the blast furnace, the briquette moves down the stack, the temperature slowly increases. With the increase in temperature, the dehydration of cementitious binder also progressively increases. Hence, it has been observed that there is almost a linear decrease in strength of sand-cement briquette with increasing temperature. Similarly, there is a near linear decrease in the strength of briquettes made of pellet-fines + cement.

Inside the blast furnace, the briquettes are also subjected to a reducing environment, resulting in transformations in the iron oxide based aggregates. The changes in the structure of aggregates coupled with the loss of binding phases result in drastic loss of strength (Figure 3).

Inside the blast furnace, the following factors may affect the behaviour of briquettes:

1. **Cement content.** Increase in cement content results in increase in the net strength of the briquettes (Figure 4). Hence, when recovered from pilot blast furnace, the briquettes containing more cement show better strength characteristics.

2. **Particle size of the raw material.** With the decrease in particle size, the compactness of the briquette increases resulting in higher strength (Figure 5). Examination of the briquettes recovered from the pilot blast furnace shows that the briquettes made of finely ground raw material retain their shape. On the other hand, the briquettes made of coarsely ground material get crushed under the load of the burden on top of them (Figure 6).
Figure 3. Effect of temperature on the compression strength of briquettes made of Mix A and Mix B reduced isothermally for 1 h in N$_2$+CO (60:40).

Figure 4. Effect of cement content on the compression strength of the Mix A briquettes, (a) after curing; (b) after heating in N$_2$ environment; and (c) after reducing in N$_2$+CO (60:40) environment. (Time: 1 h, Temperature: 950°C)

Figure 5. Effect of particle size on the strength of briquettes (a) after curing; (b) after reducing in N$_2$+CO (60:40) at 950°C for 1 h; and (c) after reducing in N$_2$+CO (60:40) at 950°C for 3 h. (Mix A: Pellet-fines + cement; Mix B: Pellet-fines + pre-reduced by-products + cement)

Figure 6. Photograph of cross sections of briquettes recovered from the pilot blast furnace, (a) $d_{50} < 74 \mu m$, and (b) $d_{50} = 2465 \mu m$. 

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3. **Amount of pre-reduced component.** Increase in the percentage of the pre-reduced components improves the strength characteristics, since the reduction potential inside the blast furnace increases slowly and the pre-reduced material starts transforming later. The angular and flaky components also act as a skeleton to hold the briquette together (Figure 3). When recovered from the pilot blast furnace, the briquettes containing pre-reduced material retained their strength to a greater degree than the briquettes containing only pellet-fines.

4. **Coke content.** The presence of coke decreases the strength, since the coke itself is soft and friable. It also increases the reduction rate of the briquettes. Observation of briquettes recovered from the pilot blast furnace corroborates this.

5. **Presence of load.** As the briquettes move down the stack, two opposing factors affect their behaviour. On one hand, the load of burden material may help the briquettes to retain more strength (Figure 7); on the other, the same load may crush the briquettes. The briquettes recovered from pilot blast furnace showed that the briquettes kept in steel baskets without any surrounding pellets tend to break more than the briquettes surrounded by pellets. In both the cases, weak briquettes may distort and have the edges broken in the lower portion of stack under the load of burden.

6. **Type of crushed pellets.** Some pellets are more prone to swelling on reduction when made into cement-bonded briquettes. Inclusion of such aggregates may result in a decrease in strength on reduction at high temperature (Figure 8).

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**Figure 7.** Compression strength of briquettes (a) after curing, (b) after reduction under load, and (c) after reduction hanging free in a basket.

**Figure 8.** Effect of tendency of a briquette to swell, given by volume expansion after 5 h reduction, on the strength of briquette after 1 h reduction. (Reduction temperature: 950°C, N₂:CO=60:40)
2. SWELLING OF CEMENT-BONDED BRIQUETTES (PAPERS III AND IV)

Inside a blast furnace, some pellets have a tendency to swell catastrophically. Normally, this happens in the thermal reserve zone where the temperature is about 950°C. If that happens, then pellets lose their strength drastically, resulting in the erratic movement of burden leading to hanging and slipping.

When cement-bonded briquettes are reduced in laboratory, under certain conditions they also tend to swell catastrophically. It has been observed that the briquettes swell abnormally under the following conditions:

1. Reduction temperature. The swelling reaches a maximum when the briquettes are reduced isothermally at 950°C. They do not swell abnormally below 900°C and above 1000°C (Figure 9).
2. Particle size of raw material. The swelling increases with increase in the particle size of the raw material (Figure 10).
3. Degree of reduction. The abnormal swelling takes place during the reduction of wustite to iron.
4. Composition. The swelling increases with the increase in the pellet-fines content.
5. Cement content. The swelling does not take place in the absence of cement and reaches a maximum when the cement content is 4-6 weight percent (Figure 11).
6. Reduction condition. The swelling does not take place in the absence of carbon monoxide and decreases in the presence of hydrogen.
7. Briquette size. Briquette size has no effect on the swelling.

**Figure 9.** Effect of temperature on the volume expansion of briquettes made of Mix A after reduction for 5 h in N₂:CO.

**Figure 10.** Effect of particle size on the volume of briquettes reduced for 3 h at 950°C in N₂:CO.
Figure 11. Effect of cement content on the swelling of briquettes on reduction. (Reduction time = 5 h, reduction temperature = 950°C, N₂:CO=60:40)

Figure 12. Swelling of briquettes (a) after reduction with free swelling for 5 h at 950°C in N₂+CO (60:40); (b) after reduction under load for 5 h at 950°C in N₂+CO (60:40); and (c) after reduction in pilot plant.

8. **Pellet-type.** Even when the pellets do not have any tendency to swell catastrophically, cement-bonded briquettes made of crushed pellets may swell catastrophically. Normally, the swelling increases with increase in the content of slag forming oxides in the pellets. It also increases with the basicity till the basicity is 1.2. The briquettes made of pellet-fines swell more than the briquettes made of crushed pellets, since the pellet-fines are the weaker – over-fired or under-fired – pellets that break during transportation and handling.

9. **Composition of cement.** For the swelling to take place, all the components of the cement – CaO, MgO, SiO₂ and Al₂O₃ – are essential. These oxides should be present in the right proportion, excess or absence of any one can reduce the degree of swelling.

10. **Alkalis.** Presence of alkalis is not essential for swelling to take place, but the degree of swelling increases in their presence.

11. **Coke content.** The swelling increases with increase in the coke content, probably due to increased reduction rate and presence of ash.

12. **Reduction under load.** The swelling decreases when the briquettes are reduced under load, not because the briquettes do not have a tendency to swell, but because the load prevents the swelling from taking place.

The briquettes recovered from the pilot blast furnace do not show any tendency to swell catastrophically (Figure 12). Overall, the swelling of briquettes when reduced in pilot blast furnace diminishes with decrease in the particle size of the raw material (Figure 12), increase in the content of pre-reduced components, under the influence of burden load and decrease in coke content. The swelling is not due to the popping of individual particles, as is the case with briquettes reduced isothermally; it is due, instead, to the widening of the cracks between the individual pellet-fines particles.
Overall, the performance – strength, swelling, reduction, etc. – of briquettes at room temperature and after high-temperature reduction depends upon a number of processing parameters. All these parameters are often interdependent. The individual parameter may also affect the performance in a contradictory manner. Figure 13 shows the effect of cement content on the behaviour of the briquettes. With increase in the cement content, on one hand

- the strength of briquettes increases,
- the degree of catastrophic swelling decreases;

but on the other,

- the slag formation increases,
- the amount of moisture released increases, and
- the reduction rate decreases.

The coke content has almost opposite effects on the performance (Figure 14). With the increase in coke content

- the reduction rate increases,

but

- the strength decreases,
- the swelling increases,
- the amount of slag obtained from the briquette increases but net amount of slag will remain unchanged since the coke in briquette will replace coke in the furnace.

Hence, various parameters need to be optimised, based not only on the performance of briquettes but also on the blast furnace operation.
3. SWELLING MECHANISM IN CEMENT-BONDED BRIQUETTES (PAPERS V AND VI)

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

Step 1. Disintegration of Pellet-fines Particles 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 15a shows an optical micrograph of pellet-fines particle containing large portions of magnetite (dark grey) along with hematite (light grey). The transformation of hematite to magnetite is accompanied by volume increase. This generates stresses leading to the cracking of grains (Figure 15b). 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 (Figure 15c). On further reduction to wustite, the particles disintegrate even further, as a result of which the wustite particles are much smaller and fragmented (Figure 15d).

Figure 15. Optical micrograph of pellet-fines particles showing the different stages in cracking of hematite grains during reduction at 950°C in N₂+CO (60:40) environment: (a) cured (grey particles are pellet-fines particles); (b) conversion to magnetite; (c) magnetite; and (d) wustite.
Step 2. Formation of Liquid Slag. At the hematite stage there is only a partial reaction between C₂S, olivine and Fe₂O₃ (Figure 16b). Similarly, at magnetite stage, too, the reaction is rather limited (Figure 16c). When the magnetite converts to wustite, the reaction between the wustite, CaO, C₂S and olivine takes place (Figures 16d-16e). The reaction between these leads to the formation of (Ca,Fe,Mg)₂SiO₄. When the wustite begins to reduce to iron, liquid slag is formed (Figures 16f and 17b). Normally, the melting point of slag is rather high (above 1300°C), but with proper proportions of CaO, SiO₂, FeO, MgO and Al₂O₃, 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.

Figure 16. Photograph and Secondary Electron micrographs of cross section of briquette B1 reduced for 0.5 h at 950°C in N₂+CO (60:40). (b) SEM from Position A; (c) SEM from Position B; and (d) SEM from Position C; (e) and (f) SEM from Position D.
Figure 17. Photograph and Secondary Electron micrographs of cross section of briquette B1 reduced for 3 h at 950°C in N₂+CO (60:40) (b) SEM from Position E; (c) SEM from Position F; and (d) SEM from Position G.

Figure 18. Secondary Electron image showing the separation of MgO-SiO₂, CaO-SiO₂ and FeO phases. Magnesium silicate forms the core. Around it, the CaO-SiO₂-FeO forms the slag layer and the excess FeO forms the outermost shell.

Figure 18 shows the freezing of the slag into three distinct layers: (a) MgO-SiO₂ rich core, (b) FeO-CaO-SiO₂ rich middle shell, and (c) FeO rich outermost shell. 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. 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 sufficient to melt the slag. Theoretical calculations using simple mass balance have shown that a briquette containing 6.5 weight percent cement can form up to 26 weight percent slag at the wustite stage. Even though the amount of slag formed at an instance of time would be much less than this, since not all of it would be
Figure 19. High-temperature XRD of cured pellet-fines (75%) + cement (25%) briquette sample showing the phase transformations during reduction at 950°C in the N₂+CO (60:40) environment.

![X-ray Diffraction Pattern]

produced at the same time, the amount may still be substantial. This liquid slag can act as a lubricant. Figures 17c-17d show that as the reduction of (Ca,Fe,Mg)₂SiO₄ to (Ca,Mg)₂SiO₄ takes place, the (Ca,Mg)₂SiO₄ again solidifies.

**Step 3. 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 (Figure 19). 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.

\[
\begin{align*}
3\text{FeO} + 5\text{CO} & = \text{Fe}_3\text{C} + 4\text{CO}_2 \\
\text{Fe}_3\text{C} + \text{FeO} & = 4\text{Fe} + \text{CO} \\
\text{Fe}_3\text{C} + \text{CO}_2 & = 3\text{Fe} + 2\text{CO}
\end{align*}
\]

Figure 20 shows “bubbling” of the iron particles when the reduced briquette was exposed to air for a short duration while it was still hot. It seems as if generation of gas pressure inside liquid iron drops has caused the drops to blow up. 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. In the same way, a reduction-oxidation reaction between Fe₃C and FeO can also generate high gas pressure, although at a lower rate.

Even though the briquettes excavated from the pilot blast furnace were not swollen, the optical microscopic examination of the briquettes shows some similarity to the briquettes reduced in the laboratory. In both cases, the pellet-fines particles disintegrate to small wustite disjointed grains. The difference is that while in the laboratory-tested briquettes almost all the particles disintegrate, in the pilot plant tested briquettes a substantial amount of particles do not disintegrate. In both the cases, wustite reacts with CaO, SiO₂, MgO and Al₂O₃ to form liquid slag. The difference comes in the final stage; in the case of briquettes tested in pilot blast furnace, the iron particles do not move away but remained closely together; hence, there was no swelling.
Figure 20. Secondary Electron image of reduced briquette showing bubbling of iron due to oxidation of iron carbide.

The difference in the behaviour of the briquettes when tested in the laboratory and when tested in the pilot plant may be because the laboratory tests do not replicate the actual conditions inside a blast furnace. In the laboratory, all the experiments are carried out in the isothermal condition (950°C) using a fixed environment (N₂:CO=60:40) as stipulated by the reduction test ISO 4695. This test is intended to simulate the reserve zone of a typical blast furnace. On the other hand, the conditions inside the pilot blast furnace are different in many ways. Two important differences are:

- In the pilot plant, the reduction takes place under non-isothermal conditions. Basically, there are four zones inside the furnace – drying, reserve, cohesive and dripping zones. The reserve zone has a temperature range of 800-1100°C, retention time of approximately 2 h 30 min and the temperature gradient of 2°C/min. The earlier experiments have shown that the swelling takes place only in the range of 900-1000°C and since in the pilot plant the briquettes stay in this temperature range for only a short time, they may not swell.

- In the pilot plant, hydrogen is present inside the furnace. Experiments have shown that the briquettes have less tendency to swell in the presence of hydrogen.

The conditions inside the pilot plant are very close to those of an actual blast furnace. Still, the conditions inside vary from blast furnace to blast furnace depending upon the design and operation. Larger blast furnaces normally have larger isothermal reserve zones having a temperature of about 950°C. Under such conditions, there may be a possibility for the briquettes to swell.
CHAPTER 4

CONCLUSIONS

In an iron and steel plant different types of iron rich by-products are generated at different stages of production. Traditionally these by-products are sintered and subsequently used as burden material for blast furnace. Cold bonded agglomeration is an alternative for the sintering process. In spite of being in use for the last one and half decades the cement-bonded briquettes suffer from certain technical problems which restrict their use.

It has been found that the room temperature properties of briquettes depend upon various processing parameters like solid/water ratio, vibration time, briquetting force, compression time, particle size distribution of the raw material and coke content. The optimum values of these are inter-related and also depend upon the composition of the briquettes.

One of the major problems is the loss of strength on exposure to high temperature. This happens because of the destruction of the cement matrix. This fall in strength becomes even more severe during the reduction process when the iron oxide particles undergo phase transformations. As a result a briquette reduced to over 10% overall reduction retains only about 10% of its original strength, this strength is rather low when compared to those of indurated pellet which retains about 25% of its strength. To some extent the strength may be increased by controlling the composition, i.e. by increasing the percentage of pre-reduced and flaky particles. Another way of improving the strength of briquettes is by increasing the fineness of the raw material. When the raw material is ground fine the compaction of the briquette increases and at the same time the number of contact points also increases, this results in higher strength. The strength can also be increased by increasing the cement content; but the additional cement increases the cost of production, the amount of slag generated and the amount of moisture released.

Under certain conditions the cement bonded briquettes show tendency of catastrophic swelling. This happens especially during the reduction of wustite to iron at 950°C using CO as the reducing gas. The briquettes that contain coarse pellet-fines particles are specially prone to swelling since the pellet-fines contains a large percentage of under-fired and weak fraction of the pellets. The swelling and the strength of briquettes are closely related. The briquettes that tend to swell also lose their strength more. This swelling can be controlled by finely grinding the raw material, increasing the cement content, adding calcium oxide / magnesia / silica or alumina to the cement.

A simple conceptual model has been proposed to describe the swelling mechanism. The model is based on three premises:

- Pellet-fines contain a significant proportion of under-fired and weak pellet particles that disintegrate to very small particles of wustite on step-wise reduction of hematite.
- The calcium silicate from cement reacts with magnesia from olivine, alumina from cement and pellet-fines and wustite to produce a slag having low melting point. The molten slag covers the iron oxide particles.
- At about 950°C carbon monoxide in reducing gas reacts with wustite to form metastable iron carbide.

During the reduction of a cement-bonded briquette a thin layer of molten slag envelops the disintegrated pellet-fines particle which has been reduced to wustite. The carbon monoxide reacts with wustite to form iron carbide. The iron carbide oxidises to iron and carbon monoxide by taking oxygen from wustite or carbon dioxide. The carbon monoxide thus generated builds up a pressure inside the fragmented particle. This pressure then pushes out the iron particles. Since there is liquid slag present, hence, there is sufficient lubrication for the particles to move out. This outward movement of particles leads to swelling.
Investigation of the briquettes recovered from pilot blast furnace shows that the performance of briquettes can be increased by increasing the percentage of pre-reduced and flaky components, increasing the cement content, decreasing the particle size of the raw material and decreasing the coke content. The recovered briquettes do not have any tendency to swell catastrophically. It has been observed that the briquettes experience the first two steps of swelling – disintegration of pellet-fines particles and formation of liquid slag – but do not experience the third step – generation of high gas pressure.
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PAPER I

COLD BOND AGGLOMERATES OF IRON AND STEEL PLANT BY-PRODUCTS AS BURDEN MATERIAL FOR BLAST FURNACES

Maneesh Singh and Bo Björkman
Division of Process Metallurgy
Luleå University of Technology
97187 - Luleå, Sweden
{Maneesh.Singh, Bo.Bjorkman}@km.luth.se

Abstract

During various steps in the production of steel from the raw iron ore pellets a wide variety of by-products are generated. These by-products are in form of sludges, slags or fine powder and are generally rich in iron oxides. Hence, they have the potential of being recycled back to the blast furnace after having being agglomerated. For agglomerates to be considered suitable as feed material for a blast furnace, they should have sufficient room temperature strength and complete reducibility of iron containing elements without degradation or excessive swelling. Cold bond agglomeration process offers an economically attractive and environmentally safe method for achieving this. In this process, various necessary ingredients are agglomerated using a binder into a form suitable for charging into a blast furnace.

The paper presents results of the experiments carried out to study the effect of various parameters on the behaviour of briquettes prepared using iron and steel plant by-products and ordinary Portland cement (OPC). The room temperature properties of the briquettes have been found to depend upon various parameters like: the particle size distribution, composition of the raw materials and processing conditions. The properties of briquettes subjected to high temperature under reducing environment depend upon the temperature of reduction, particle size distribution and composition of the raw material.

1. INTRODUCTION

The implementation of stringent regulations for the suppression of pollutants from industries and increasing costs of primary sources of materials have made it imperative that as much as possible the by-products from plants be recycled.

Steel industry generates a wide variety of by-products rich in iron, which have the potential of being recycled back to the blast furnace. Since these by-products generally have fine particle size, they cannot be, as such recycled back to the furnace, hence, need to be agglomerated. The traditional way of recycling them back to the blast furnace has been the balling-sintering process. In recent years this process has come under attack because of its adverse environmental impacts, resulting in closure of all the sintering plants in Sweden. Hence, there is a need for a technically viable, economical attractive and environmentally safe way of recycling the steel plant by-products.

For agglomerates to be considered suitable as feed material for a blast furnace, they should have sufficient strength for handling, transportation & outside storage and complete reducibility of iron containing elements without degradation or excessive swelling. The process producing these agglomerates should be robust enough to tolerate a variety of materials in various proportions, must be economically feasible even for relatively small-scale operations and should generate little or no pollution.
Cold bond agglomeration process, if perfected, may offer an attractive method for recycling the by-products. In this process various steel plant by-products, carbonaceous material and other necessary ingredients can be agglomerated using a binder into a form suitable for charging into a blast furnace. In the furnace the metallic oxides in the agglomerates are reduced to metals. The carbon units, if present, act as fuel and reducing agent, thereby, substituting the more expensive metallurgical coke. The additives used as binders either burn off without interfering with the reactions (organic binders) or are not very harmful for the blast furnace reactions (lime-silica, Portland cement). [1-14]

Compared to sintering process, the cold bond process has a number of advantages, like: (a) saving on energy costs, (b) better manipulation of agglomerate properties, (c) almost negligible pollution, (d) low requirement of capital investment. It also has a few disadvantages, like: (a) failure of agglomerates at high temperature under reducing conditions, (b) possibility of temperature imbalance inside blast furnace due to the presence of moisture in the briquettes, and (c) additional requirement of energy for converting calcium silicates from the binders to molten slag. These technical problems are the major causes for its poor acceptance.

The paper describes the results of the investigation carried out to study the properties of cold bond agglomerates prepared using iron & steel plant by-products, at room temperature and when subjected to high temperature reduction.

2. MATERIALS AND METHODS

2.1. Materials

Eight by-products received from SSAB Merox AB were used for the study. They were:

- Pellet fines
- Cutting slag (steel-work)
- Cutting slag (rolling)
- Grinding fines
- Blasting dust
- LD converter dust
- Mill scale
- Slag handling scrap
- Manganese slag

Manganese slag was also included in the composition. Even though it is not a by-product the reason for its addition is that the manganese in hot metal is required during the steel making process.

The chemical and mineralogical compositions of all these raw materials were analysed using chemical methods and XRD, respectively. Except for Manganese slag, all other by-products contained 58-87 % iron in various oxide forms. The other major components were CaO, SiO₂, MgO and Al₂O₃. The main constituent, iron, was present in form of Fe₂O₃, Fe₃O₄, FeO and Fe. The Manganese slag contained about 50 % MnO and the other oxides constituted the rest. The various oxides, which were present in form of a number of phases, made the materials quite complex in nature.

The particle size analysis, carried out using U.S. Standard Sieves, showed a wide range of distribution for all the by-products. While most of the materials ranged from very fine (-200 mesh, 75 μm) to quite coarse (+9.5 mm); blasting dust and LD dust had only fine fractions.

Two sets of compositions were used for the study:

- Mix A: Pellet fines + ordinary Portland cement (6.5 weight %).
- Mix B: All the earlier mentioned by-products in the proportion generated in the integrated steel plant + ordinary Portland cement (6.5 weight %).

2.2. Preparation of Briquettes

The desired quantities of the raw materials were taken and ground / mixed in steel ball mill for a predetermined time. 150 g of this mixture and optimum quantity of water (10-15 ml, depending upon the composition and particle size distribution of the raw mixture) were then taken in a steel trough and mixed for about a minute so as to obtain a mouldable paste.
The plastic paste was put in a cylindrical steel mould of 4.2 cm diameter and compacted first by vibration for known period of time (0-2.0 min.) (using a vibrating machine, Retsch Vibro) and subsequently by compression under predetermined load (0.5-2.5 tons) for varied time (0.5-2.5 min.) (using a laboratory scale press, Carver Laboratory Press, Model C). The green briquette thus obtained was cured for 28 days in a high humidity chamber.

2.3. Testing of Briquettes at Room Temperature

The cured briquettes were tested for compression strength using Tonindustrie Testing Machine, Model - Seger.

2.4. Testing of Briquettes after Reduction

The heating furnace used for testing the briquettes was a Kanthal wound tube furnace (length: 100 cm, diameter: 12.5 cm). A stainless steel tube (length: 135 cm, outer diameter: 10.5 cm) having flanges at both the ends was placed inside this furnace. The gas mixture entered from one end and left from the other. A K-type thermocouple placed inside the furnace near the briquettes and a Eurotherm 2132 controller were used to maintain the desired temperature. The off-gas was burnt in a gas burner.

Three briquettes were placed at a time on a stainless steel crucible and placed in the middle zone of the horizontal furnace. The furnace was switched on and the temperature of the briquettes raised to the desired level. During this stage flow of nitrogen was maintained. During the constant temperature period the briquettes were heated for 3 h either in the nitrogen environment or in the reducing environment of $N_2 + CO$ (3:2) mixture. A flow rate of 5 l/min. was maintained. At the end of the soaking period the furnace was shut down and the briquettes were allowed to cool inside the furnace itself in the nitrogen environment.

3. RESULTS AND DISCUSSION

3.1. Effect of Water / Solid Ratio

Solid-water pastes of varied consistency were prepared using 150 g of finely ground Mix B and varied amount of water. The pastes were then briquetted using the earlier mentioned technique (vibration time: 1 min., compression load: 1.5 ton, compression time: 1 min.).

A strong correlation between the water/solid ratio and the compression strength was observed (Figure 1). An optimum amount of water was required to provide correct balance between lubrication and porosity, but there was no fixed ratio which gave the best result. Similar experiments showed that the optimum ratio depended on various factors like:

- Particle size distribution of the material – the amount of water required decreased with increase in coarseness.
- Composition of material – amount of water desired increased with increase in Pellet fines content.
- Other processing conditions, like: time taken for making the paste, vibration time, etc.

3.2. Effect of Vibration Time

The briquettes were prepared by vibration for varied time (0-2.0 min.) and subsequent compaction at the fixed pressure of 1.5 tons for the fixed time (1 min.).

The strength of the briquettes increased with increase in vibration time, but beyond 1.5 min the curve tended to reach a plateau (Figure 2). This might be because initially the increase in vibration time aided in particle packing but beyond a certain limit vibration did not increase the packing. In fact very long vibration times resulted in poor quality briquettes because excessive vibration led to cracking.
Figure 1. Effect of water/solid ratio on the compression strength of the briquettes. (Particle size: $d_{50} = 44 \, \mu m$)

Figure 2. Effect of vibration time on the compression strength of the briquettes. (Particle size: Mix A: $d_{50} = 733 \, \mu m$, Mix B: $d_{50} = 580 \, \mu m$)

Figure 3. Effect of briquetting force on the compression strength of the briquettes. (Particle size: Mix A: $d_{50} = 733 \, \mu m$, Mix B: $d_{50} = 580 \, \mu m$)

Figure 4. Effect of compression time on the compression strength of the briquettes. (Particle size: Mix A: $d_{50} = 733 \, \mu m$, Mix B: $d_{50} = 580 \, \mu m$)
3.3. Effect of Briquetting Force

For the preparation of briquettes the wet pastes were vibrated for the fixed time (1 min.) and later pressed under different loads (0.5-2.5 tons) but for the same time (1 min.). It was observed that for the Mix A with an increase in compression load during briquetting the compression strength values fell (Figure 3). The fall in strength was attributed to the friable nature of the Pellet fines particles. The bigger Pellet fines particles ruptured relatively more easily under the applied load, thereby, giving net lower strength of the briquettes. The ruptured could be seen even with the naked eyes. On the other hand, the briquettes of Mix B attained highest strength when prepared under compression load of 1.5 ton. Probably this was due to the presence of harder components like cutting slags and mill scales.

3.4. Effect of Compression Time

The briquettes were prepared by vibrating the solid - water pastes placed inside the mould for a fixed time (1 min.) and compressing at a constant load of 1.5 tons for varied time (0.5-2.5 min.). The briquettes showed slight fall in strength with increasing compression time (Figure 4). This could have been because more number of the bigger Pellet fine particles ruptured under the applied load.

3.5. Effect of Particle Size Distribution

Solid mixtures having different particle size distribution but same composition were prepared by grinding 900 g of Mix A and Mix B compositions in steel ball mill for varied time (1.0 min.-2 h). One set of material was also mixed for 30 min. in a small porcelain jar just by rotating the material (without balls). The differently ground samples were briquetted in the normal fashion (vibration time: 1 min., compression load: 1.5 ton, compression time: 1 min.).

Figure 5 is the plots of log (Cumulative Undersize, wt. %) versus log (Particle Size, micron) for the dry mixes of Mix A ground for different time periods. In the figure, a significant section of the curves are parallel and have a gradient of 0.38. Mix B too showed similar grinding characteristics. In both the cases, the ground materials satisfied the Andreasen’s equation according to which the best packing of powder having continuous size distribution would take place when the gradient would have values between 0.33-0.5. [15]

In both the cases (Mix A and Mix B) the strength of briquettes decreased with the increase in coarseness (Figure 6). This could have been because of the greater degree of compaction in the case of finely ground material and because of the elimination of larger fragile Pellet fines particles which were prone to rupturing.

3.6. Effect of Autoclaving Time

Four sets of raw mixes: Mix A Fine (d50 = 30 µm), Mix A Coarse (d50 = 830 µm), Mix B Fine (d50 = 44 µm) and Mix B Coarse (d50 = 549 µm) were prepared. These were briquetted in the normal fashion (vibration time: 1 min., compression load: 1.5 ton, compression time: 1 min.).

These green briquettes were cured for a day in a high humidity chamber and then autoclaved at 180°C for varying time (0.5-8.0 h). One set of briquettes was also cured for 28 days and tested as reference.

It was observed that the autoclaving did not give the same strength as the 28 days curing process. It was also seen that the autoclaving time, between 0.5-8.0 h had almost no effect on the strength of the briquettes (Figure 7).

The XRD pattern of a 28-days cured briquette showed the presence of poorly crystalline calcium silicate hydrate phase (CSH-gel) formed due to the hydration of tricalcium silicate (3CaO.SiO2) and dicalcium silicate (β-2CaO.SiO2) phases of the Portland cement. On the other hand the XRD pattern of an autoclaved briquette did not show any peak of the CSH-gel, this was because the hydration reaction during autoclaving was too fast to allow crystallisation of the gel.
Figure 5. Particle size distribution of Mix A ground for different time.

Figure 6. Effect of particle size on the compression strength of the briquettes.

Figure 7. Effect of autoclaving time on the compression strength of the briquettes.
3.7. Effect of Temperature

Figures 8 and 9 show the effect of temperature on the strength of briquettes. In all the cases, the strength of briquettes fell with the increase in temperature. The briquettes made of Mix A showed some increase in strength at higher temperatures. This was especially more in the case of Mix A Fine. Compared to the briquettes made of finely ground materials, the briquettes made of coarse materials lost more strength. This was probably due to the lesser degree of sintering taking place in the coarsely ground material because of the lesser number of contact points.

The fall in strength of briquettes was more when the briquettes were heated in the reducing environment compared to when they were heated in the nitrogen environment. This was because in the reducing environment the loss of strength was both due to the destruction of binding phases and due to the phase transformations taking place in the iron oxide particles.

In both, fine and coarse materials, the loss of strength was more in the case of Mix A as compared to the Mix B. The reason could have been that the Mix B contained more of pre-reduced materials and also some reduced iron. These particles acted like a skeleton holding other particles together and also lowered the net degree of transformations taking place. Also particles in Mix B were more angular and flaky, as a result there was more interlocking of particles giving the briquettes some additional strength.

It was also observed that there was not much loss of strength beyond 700°C. This could have been because by 700°C the CSH gel had already got destroyed. It might also have been due to the fact that the reduction degree did not increase with the increase in temperature because the large briquette size made the kinetics of reaction diffusion controlled and not rate controlled.
4. CONCLUSIONS

From the investigation carried out it may be concluded that:

1. The room temperature strength of a briquette made using steel plant by-products and cement depends upon the processing parameters like:
   - Water / solid ratio.
   - Vibration time.
   - Briquetting load.
   - Compression time.
   - Particle size distribution.

2. The optimum values of these in turn depend upon the composition of the briquettes.

3. Other processing conditions being the same, the strength of a briquette prepared by autoclaving is less than that prepared by curing for 28 days.

4. The strength of a briquette falls drastically with temperature, but it does not fall at the same rate beyond 700°C.

5. The fall in strength is more in the case of reducing environment compared to the inert environment. This is because while in the case of nitrogen the loss of strength is only due to the loss of binding phases, in the case of reducing environment it is also due to the phase transformations in the iron oxide particles.

6. The loss of strength is lesser in the case of finely ground material, due to the greater degree of sintering taking place.

7. The loss of strength is lesser in the case of Mix B compared to the Mix A because of the presence of prereduced materials, flaky particles and materials like cutting slags which can act as a skeleton in the briquettes.

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REFERENCES


PAPER II

Maneesh Singh and Bo Björkman, Strength of cement-bonded briquettes, (Submitted).
STRENGTH OF CEMENT-BONDED BRIQUETTES

Maneesh Singh and Bo Björkman

Division of Process Metallurgy
Luleå University of Technology
971 87, Luleå, Sweden

Abstract

The cold-bond agglomeration process is being increasingly used as a means of recycling iron-rich steel plant by-products back to the blast furnace. Even though more and more plants are adopting this process, the use of cold-bonded agglomerates as burden material for the blast furnace is restricted to about 5% of the total burden material. This is because the cold-bonded agglomerates may lose their strength inside the furnace due to the dissociation of binder at high temperatures. This failure may result in generation of fines, resulting in low bed permeability and higher dust content in stack gases. This paper describes the effect of temperature, degree of reduction, particle size of the raw material (d$_{50}$), cement content, pellet-type and reduction under load on the compression strength and microstructure of cement-bonded briquettes comprising iron and steel plant by-products.

Key Words:
Cement-bonded agglomerates, particle size, reduction, strength, temperature.

1. INTRODUCTION

The steel industry generates a wide variety of by-products rich in iron. These by-products need to be recycled back to the blast furnace. The traditional way has been the sintering process, but in recent years the cold-bond agglomeration process is often being used. In this process, various iron-rich steel plant by-products are mixed together with a binder and agglomerated. The cured agglomerates are then used as burden material for the blast furnace.

Portland cement bonded briquettes have been in regular use in a number of plants including SSAB Tumplåt AB, Luleå and SSAB, Oxelösund AB (Sweden) (Berglund and Eriksson, 1993; de Bruin and Sundqvist, 1998). A common observation among the plant operators has been that addition of cold-bonded briquettes up to 5% of the burden material does not pose any major problem, but at higher percentages the blast furnace starts operating in an erratic manner (Wargo et al., 1991). This is probably due to the disintegration of briquettes inside the blast furnace. This disintegration of briquettes may be lessened by controlling different parameters like (a) quantity and type of binder; (b) composition of the raw material; (c) particle size of raw material; and (d) curing technique.

The main components of ordinary Portland cement are alite (tricalcium silicate, 3CaO.SiO$_2$) and belite (basically dicalcium silicate, $\beta$-2CaO.SiO$_2$). On hydration they form CaO-SiO$_2$-H$_2$O gel (CSH gel, calcium silicate hydrates of variable composition and structure) and portlandite (calcium hydroxide, Ca(OH)$_2$). In a cement-bonded agglomerate the different particles are bound together by the CSH gel. The overall strength of an agglomerate is dependent upon the bond strength between individual particles, which in turn depends upon various factors like: type of solid, type and amount of binder and shape and size distribution of solid (Lea, 1988).
The greater the number of contact points between the solid particles, the greater the strength of the agglomerate will be. This can be achieved by increasing the particle packing. In an ideally packed system, comprising particles of discrete sizes, the size and number of the next smallest particles should be such that they just fit in the gaps between the largest particles, and so on for subsequent particle sizes. In order to obtain the best particle packing, Andreasen proposed an empirical equation (Dinger and Funk, 1992):

\[
\frac{\text{CPFT}}{100} = \left( \frac{D}{D_L} \right)^n
\]

where
- CPFT = Cumulative percent finer than
- D = particle size
- \(D_L\) = largest particle size
- n = distribution modulus

This equation produces straight lines of CPFT versus D plots on log-log axes which meet the similarity conditions. From the experiments it has been found that for the best packing of particles, n should be between 0.33 and 0.5. The Fuller curve is the specific case of this equation where n = 0.5.

From the work done on agglomeration of “blue dust” (naturally occurring iron ore fines in India) using Portland cement binder it has been found that the optimum compaction density is achieved when the coarse, medium and fine (arbitrarily defined) particles are present in almost equal proportions (Dutta et al., 1997). It has also been shown that for a cold-bonded briquette / pellet to have optimum properties, the particle size distribution of the solids should be as close to the Fuller curve as possible. To reach the desired particle size distribution suitable for cold bonding feed, 80% of the feed must be finer than 200-250 microns (Hassler, 1975; Hassler and Kihlstedt, 1981).

The strength of cold-bond agglomerates depends upon the cement content. With an increase in the cement content the strength of briquettes after curing and after reduction increases. There is a linear correlation between the strength of agglomerates after drying and after reduction (Takahashi et al., 1993).

On heating, the disintegration of briquettes takes place when the CSH gel loses its water of hydration at about 700°C. The behaviour of a cement-based structure on exposure to high temperature depends upon a number of factors: (a) amount of moisture; (b) type of aggregate; (c) porosity of the aggregate; (d) pre-load condition; and (e) confinement of sample (Jahren, 1989; Dias et al. 1990; Castillo and Durrani, 1990; Bazat and Kaplan, 1996; Terro and Hamoush, 1997). When the cement-bonded iron ore agglomerates are heated in a nitrogen environment, the strength of agglomerates falls almost linearly with temperature till 850°C. When they are heated in a reducing environment, the strength falls drastically to less than 15% of the original strength at 650°C and falls slowly thereafter (Takahashi et al., 1993).

When the destruction of binding phase is coupled with the transformation of the aggregate, then the fall in strength is more drastic. The strength of cement-bonded iron ore agglomerates decreases drastically with the reduction degree to 10% reduction degree. At that reduction degree, the agglomerates have less than 20% of their after-curing strength. Beyond that degree of reduction, the strength falls rather slowly (Takahashi et al., 1993).

The use of cement-bonded agglomerates as blast furnace burden material is a common practice, but more research work needs to be carried out to improve their performance even further. The loss of strength of cement-bonded briquettes may be a factor that can limit the use of this material in blast furnace burden. This paper discusses the influence of temperature, degree of reduction, particle size of raw mixture, cement content, pellet-type and reduction under load on the strength of cement-bonded briquettes made of steel plant by-products. The knowledge gained from the laboratory investigation may aid plant operators in developing briquettes that have sufficient strength at room temperature and would not fail inside a blast furnace.
2. MATERIALS AND METHODS

2.1. Raw Materials

Nine raw materials received from SSAB Merox AB were used for the study. One of the materials, pellet-fines, was a mixture of fines of Pellet A and Pellet B, two commercially available pellets. During the transportation and handling the weaker pellets break, these broken pellet segments are removed as pellet-fines by sieving before the pellets are charged into blast furnace. The remaining materials were different iron rich slags, sludges and dusts generated at SSAB Oxelösund AB.

Even though Manganese slag is not a by-product it has also been included in the composition. This is because SSAB Merox also adds it during the production of its briquettes, since manganese in hot metal is required during the steelmaking process.

Ordinary Portland cement (Standard Portland Cement, Type P, Cementa) was used as a binder. Cen-standard sand conforming to EN 196-1 was supplied by Normensand, Backum (Germany).

The particle size analysis, carried out using U.S. Standard Sieves, showed a wide range of distribution for all the by-products. While most of the materials ranged from very fine (-200 mesh, 75 µm) to quite coarse (+9.5 mm), blasting dust and LD dust had only fine fractions.

Table 1 gives the chemical analysis of various raw materials, and Table 2 gives the composition of the briquettes.

2.2. Preparation of Briquettes

900 g of Mix A or Mix B was ground in a steel ball mill. 150 g (for Mix A & Mix B) or 100 g (for Mix C) of this mixture and optimum quantity of water (7.5 ml for Mix C and 10-15 ml for Mix A and Mix B, depending upon the composition and particle size distribution of the raw mixture) were then put in a steel trough and mixed for about a minute, so as to obtain a mouldable paste.

The plastic paste was put in a cylindrical steel mould of 4.2 cm diameter and compacted first by vibration for fixed period of time (1.0 min.) (using a vibrating machine, Retsch Vibro) and subsequently by compression under fixed load (1.5 tons) for fixed time (1.0 min.) (using a laboratory scale press, Carver Laboratory Press, Model C). The green briquette thus obtained was cured for 28 days in a high humidity chamber. The cured briquettes were dried overnight in an oven maintained at 105°C.

2.3. Reduction of Briquettes

The schematic diagram of the reduction set-up is shown in the Figure 1. The reduction set-up consisted of two parts: the gas supply and the heating furnace. The gases were supplied from cylinders. The supply of these two gases was controlled using needle valves and flow meters. The gases in the required proportions were mixed in a gas mixer consisting of a tube containing glass beads.

The heating furnace consisted of a Kanthal wire wound tube furnace (length: 100 cm, diameter: 12.5 cm). A stainless steel tube (length: 135 cm, outer diameter: 6.5 cm) closed at the bottom end was placed inside this furnace. A K-type thermocouple placed inside the furnace near the briquette monitored the furnace temperature. The gas mixture, either only nitrogen or a mixture of nitrogen and carbon monoxide (N₂:CO = 60:40) at a flow rate of 10 l/min. entered from the bottom and was burnt at the top by means of an off-gas burner.

For isothermal reduction, the furnace was heated until the desired temperature was reached and then the flow of reducing gas mixture was introduced. A briquette, placed in a high-temperature steel basket, was then lowered into the furnace and suspended from a balance placed above. The briquette was suspended in the region where the error was within ±5°C of the desired temperature. As an example, when a briquette was considered reduced at 950°C, the temperature in the space between the briquette and the steel wall was 955°C. A thermocouple implanted inside the briquette, axially midway and
Table 1. Chemical analysis of various raw materials.

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Table 2. Composition of briquettes.

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<tr>
<td>Sand</td>
<td>93.5</td>
<td>6.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Paper 2: Strength of Cement-bonded Briquettes
radially 7 mm from the surface, registered a linear rise in temperature up to 850°C in almost 11 min. It reached 940°C in 24 min., 950°C in 35 min. and finally stabilised at 954°C in 150 min. After the desired time had elapsed, the briquette was raised to the mouth of the furnace and cooled in a flowing-nitrogen environment.

For isothermal reduction with non-isothermal heating, the briquette was lowered into the furnace at room temperature and heated in nitrogen environment till the desired temperature was reached. Thereafter, the reducing gas was passed through the furnace for the desired time. After the reduction, the briquette was allowed to cool overnight inside the furnace in flowing-nitrogen environment.

2.4. Reduction under Load

A high-temperature steel crucible with small holes at the bottom was used. A layer of alumina balls (diameter 10 mm) was laid at the bottom of this crucible. A briquette was then placed over the layer of alumina balls and in the centre of the crucible. The space between the briquette and the wall was then filled with alumina balls and a layer of alumina balls was placed over the briquette. 650 g (arbitrarily decided) of stainless steel balls (diameter 10 mm) was then put over the briquette to apply a constant load (Figure 2). The crucible containing the briquette was placed inside the hot furnace and reducing gas was blown from the bottom.

2.5. Compression Strength Testing of Briquettes and Pellets at Room Temperature

The briquettes were tested for compression strength using a Tonindustrie Testing Machine, Model - Seger. The load at which the briquettes suddenly failed was recorded. An average value of three briquettes per test was accepted. Strength of pellets was tested by crushing three pellets at a time.

2.6. Degree of Reduction

The degree of reduction was calculated according to the formula:

\[
\text{Degree of reduction} = \frac{\text{Total loss in weight} - \text{Loss in weight due to removal of moisture}}{\text{Total possible loss in weight due to oxygen removal}}
\]

Total loss in weight was obtained by recording the change of weight of briquettes during reduction. Loss in weight due to the removal of moisture was obtained by recording the weight of similar briquettes heated in a nitrogen environment. Total possible loss in weight due to oxygen removal was obtained from TGA and cross-checked using the chemical analysis of individual components. An average value of three briquettes per test was accepted. A variation within ±10% of the mean value was accepted.
2.7. Chemical Analysis

Chemical analysis was carried out at LKAB’s laboratory using an Inductively Coupled Plasma (ICP) Spectrometer.

2.8. Optical Microscopic Examination

A test piece of the sample to be observed was cast in a cold-mounting epoxy resin mould under vacuum. The moulded sample was then ground and polished using standard techniques. The polished sample was then observed using a Nikon Eclipse E600 Pol optical microscope.

2.9. Particle Size Analysis

Approximately 100 g of dried material was dry-sieved to various size fractions using a set of U.S. Standard Sieves conforming to ASTM. In this paper the particle size has been reported as $d_{50}$, which is the cumulative fifty percent finer than the value.

2.10. Volume Measurements

The bulk volume of briquettes and pellets was calculated under the assumption that they were perfectly cylindrical and spherical, respectively. The diameter and the length were measured using callipers. After reduction, the briquettes and pellets often distorted. Even in this case the diameter and length were measured at several places and an average of the readings was taken. This method of measuring the volume gave only rough values; hence, they should be taken only qualitatively.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature

In the first set, three compositions – Mix A, Mix B and Mix C (all having 6.5 weight % cement) – were used for the study. Two different types of briquettes were made from Mix A and Mix B. In one case, the raw materials were ground for a short time (about 5 min.) and in the other for a long time (almost 3 h). Hence, the raw materials had different particle size distribution. The briquettes were then prepared in the standard way.

<table>
<thead>
<tr>
<th>Mix</th>
<th>d$_{50}$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A-fine</td>
<td>&lt;74</td>
</tr>
<tr>
<td>Mix A-coarse</td>
<td>1743</td>
</tr>
<tr>
<td>Mix B-fine</td>
<td>&lt;74</td>
</tr>
<tr>
<td>Mix B-coarse</td>
<td>1198</td>
</tr>
<tr>
<td>Mix C</td>
<td>586</td>
</tr>
</tbody>
</table>

In the second set, briquettes having varied amount of cement were made using raw mixture prepared by inter-grinding cement and pellet-fines for 2 h.

As can be seen from Figure 3, the strength of briquettes made of Mix C (sand-cement) decreases almost linearly with temperature. This loss of strength is not dependent upon the type of environment (neutral or reducing), since both the aggregates (quartz sand) and hydrated cement, are unaffected by the type of environment. The strength of briquettes at 800°C is about 20% of the original. This compares well with the data reported by others working on normal or high-strength concrete containing different amounts of cement content (Jahren, 1989; Dias et al. 1990; Castillo and Durrani, 1990; Bazat and Kaplan, 1996; Terro and Hamoush, 1997). Hence, it may be assumed that beyond 800°C, whatever be the cement content, the decrease in strength would follow a similar trend.
Figure 3. Effect of temperature on the compression strength of plain concrete (Bazant and Kaplan, 1996; Terro and Hamoush, 1997) and briquettes made of Mix C. (Air: Air Cooled, Quen.: Quenched, Furn.: Furnace Cooled.)

Figure 4. Effect of temperature on the compression strength of briquettes made of Mix A heated non-isothermally. (Strength of briquettes after curing: Mix A-fine = 44.56 kN, Mix A-coarse = 42.63 kN)

Figure 5. Effect of temperature on the compression strength of briquettes made of Mix B heated non-isothermally. (Strength of briquettes after curing: Mix B-fine = 57.54 kN, Mix B-coarse = 44.56 kN.)

Figures 4-5 show the effect of temperature on the strength of briquettes made of Mix A and Mix B when heated non-isothermally. The briquettes were heated to the required temperature in a nitrogen environment and then maintained at the set temperature for 1 h either in a nitrogen environment or in a reducing (nitrogen + carbon monoxide) environment. The figures show a progressive decline in strength with temperature for both Mix A and Mix B. The loss of strength is much greater for the briquettes undergoing reduction than for the briquettes that have been heated in nitrogen. These observations corroborate the observations made for cement-bonded pellets (Takahashi et al., 1993). The figures also show that the briquettes made of finely ground material do not lose strength to the same extent as those made of coarse material. This may be due to better packing and a larger number of contact points. In coarse materials, the loss of strength is larger in the case of Mix A compared to the Mix B. The reason may be that Mix B contains more pre-reduced materials, flaky particles and cutting slags, which lower the degree of swelling and increase interlocking of particles. The figures also show that the loss of strength in the case of Pellet A is not as great.
Figure 6 shows the effect of temperature on the strength of briquettes heated isothermally in nitrogen. It can be seen that the strength increases at 500-700°C and then decreases. This may be due to the reaction between the calcium silicates from cement and iron oxide. Figure 7 shows the effect of temperature on the strength of briquettes after reduction for 1 h. As is to be expected, the strength decreases with increasing temperature.

Figure 8 shows the optical micrographs of the briquettes made respectively of Mix A-coarse raw material after curing, heating in a nitrogen environment and after reduction for 5 h. In the case of a cured briquette, binding gel (CSH gel) joins the large particles and completely envelops the smaller ones. On heating in a nitrogen environment, this gel becomes rather rough and grainy. This may be due to the dehydration of the binding CSH gel. On dehydration, the gel converts to crystalline C₃S, which does not hold together; hence, the matrix has no strength. On reduction, not only does the gel dehydrate to C₃S, the pellet-fine particles also undergo transformations. At the first stage, due to the hematite-to-magnetite transformation, the interconnected hematite grains separate from each other. At the next stage, magnetite-to-wustite, the wustite phase reacts with C₃S, MgO from olivine and Al₂O₃ from cement to form slag, which has a relatively low melting point. On further reduction, the iron precipitates out along with (Ca,Mg)₂SiO₄. Due to all these phase transformations taking place in the matrix and the aggregates, the briquettes lose their strength.

Comparative study of the optical micrographs of reduced Mix A-coarse briquette (Figure 8), Mix A-fine briquette and Pellet A (Figure 9) show that, in the case of Mix A-coarse, the individual hematite particles break into small wustite grains and then disperse further during the formation of iron; on the other hand, in the Mix A-fine briquettes, this dispersion is far more restricted. Finally, in the case of Pellet A, the wustite grains are far larger and laminar in shape. During the reduction to iron, the reduction takes place in a topographical way without further disintegration. This formation of interlocked iron grains imparts higher strength to the reduced Pellet A. In fact, at a high degree of reduction, the strength of Pellet A may even increase due to the sintering of iron particles.
Figure 8. Optical micrographs of briquette ($d_{50} = 2465 \, \mu m$), (a) cured (grey particles are hematite), (b) heated in $N_2$ environment for 1 h at 950°C (grey particles are hematite), (c) reduced in $N_2$+CO for 3 h at 950°C (centre) (grey particles are wustite, black particles are calcium silicate), and (d) reduced in $N_2$+CO for 3 h at 950°C (periphery) (grey particles are iron, black particles are calcium silicate).

Figure 9. Optical micrographs of Pellet A reduced in $N_2$+CO for 3 h at 950°C, (a) reduced (centre), and (b) reduced (periphery) (grey particles are wustite and white particles are iron).
3.2. Effect of Degree of Reduction

Four sets of briquettes, of the types presented above, were tested for strength after being reduced to different degrees. Pellet A was also reduced at 950°C in flowing nitrogen + carbon monoxide environment for varying periods.

Figure 10 shows the effect of calculated degree of reduction on the strength of briquettes and pellets. For all the five cases beyond 10% reduction the strength of briquettes is low. Also, there is almost no change in the strength with increase in reduction degree. This behaviour of briquettes is similar to that reported for cement-bonded pellets (Takahashi et al., 1993). It can be seen that, on reduction, Pellet A retains about 25% of its original strength. The briquettes made of Mix A-fine and Mix B-fine retain almost 10% of the strength obtained after curing. On the other hand, the strengths of Mix A-coarse and Mix B-coarse fall to almost zero. These differences may be due to the fact that the briquettes made of finely ground material retain their compactness, which gives them better strength as compared to those made of coarse materials.

Observation of polished samples under the optical microscope shows that the briquettes that have undergone as low as 10% overall reduction do not have any binding phase left. Additionally, the phase transformation from hematite to magnetite leads to a further decrease in the strength.

3.3. Effect of Particle Size (d50)

Solid mixtures having different size distributions but the same composition were prepared by grinding 900 grams of Mix A (6.5% cement content) and Mix B (6.5% cement content) compositions in a steel ball mill for varying periods (1.0 min. to 2 h). One set of material was also mixed for 30 min. in a small porcelain jar by simply rotating the material (without balls). It was noted that in the plots of log (Cumulative Undersize, wt.%) versus log (Particle Size, micron) for the dry mixes of Mix A and Mix B ground for different time periods, a significant section of the curves are parallel and have a gradient of 0.38. In both the cases, the ground materials satisfied Andreasen’s equation for best packing (Singh and Björkman, 1999). The differently ground samples were briquetted in the normal fashion.
Figure 12. Effect of particle size on the strength of briquettes of Mix B (a) after curing; (b) after heating in N₂ environment at 950°C for 3 h; and (c) after reducing in N₂+CO (60:40) environment at 950°C for 3 h.

Figure 13. Effect of particle size on the strength of briquettes of Mix A (a) after curing; (b) after reducing in N₂+CO (60:40) environment at 950°C for 1 h; and (c) after reducing in N₂+CO (60:40) environment at 950°C for 3 h.

Figure 11 shows the effect of particle size on the room-temperature strength of briquettes. The figure shows that for both the cases (Mix A and Mix B) the strength of briquettes increases with the increase in fineness. This may be explained by the fact that, with increasing fineness, there is increase in the degree of compaction, increase in the number of contact points and elimination of larger friable pellet-fines particles that are more prone to rupturing under load.

Figure 12 shows the effect of particle size on the strength of briquettes heated in a nitrogen environment for 3 h. Relative increase in strength of briquettes with increase in fineness may be attributed to better compaction of the material and a greater number of contact points.

Figures 12 and 13 show that reduced briquettes retain only a fraction of their original strength. Figure 13 also shows that, for a lower degree of reduction, the strength of briquettes increases with increasing fineness, but for a higher degree of reduction, the difference is not so large. At a high degree of reduction, the strength of briquettes becomes so low that the testing machine is not sensitive enough to register the strength. Manual testing indicates that the briquettes made of finely ground material are stronger (i.e., the briquettes feel stronger to the touch). The strength of briquettes declines with increasing coarseness for two reasons:

- The briquettes made of coarse material have a larger number of voids and fewer contact points.
- The briquettes made of coarse material show abnormal swelling on reduction. Up to 30% swelling of agglomerates is considered acceptable, but some briquettes swell more than this. In fact, it has been observed that the degree of swelling is proportional to the log of d₅₀ of the raw material. Hence, while the briquettes made of finely ground material retain their compactness, those made of coarse material swell and tend to fall apart.

Figures 11 & 13 also give some idea about the reproducibility of the experiments. For these experiments, the briquettes were prepared and reduced over a period of one year. For the cured briquettes (Figure 11), the strength varies within ±15% of the mean value. This kind of variation is quite common for any cement-bonded agglomerate. On reduction (Figure 13), the briquettes lose their strength drastically, but in this case, too, the strength varies within ±15% of the mean value.

From the study it is clear that the strength of cement-bonded briquettes may be increased by using finely ground raw material. This can be achieved either by grinding the raw material in a mill or by sieving the raw material and using only the fine fraction.
3.4. Effect of Cement Content

Raw mixtures having different compositions were prepared by mixing pellet-fines and varied amounts of cement in a porcelain jar. Two different sets of raw mix were prepared. In one set, coarse pellet-fines was used and in the other finely ground pellet-fines was used. Briquettes were then prepared using these mixtures in the normal way. Compression strength of briquettes was tested after curing, heating in a nitrogen environment and after reduction in nitrogen + carbon monoxide (60:40) at 950°C for 1 h.

As is to be expected, the strength of briquettes increases with increasing cement content (Figures 14 and 15). This is probably due to the increase in the binding of material and decrease in particle size ($d_{50}$). For the same cement content, the briquettes prepared using finely ground material are stronger. This may be because (a) there are many contact points, (b) there are fewer voids; and (c) the large pellet-fine particles tend to rupture relatively easily under the load due to their friable nature.

As can be seen in Figures 14 and 15 the compression strength of heated briquettes is far less than the strength of cured briquettes, but the strength of the heated briquettes increases with an increase in cement content. In fact, there is almost a linear relation between the strength of cured briquettes and those heated for 1 h. By regression analysis it is seen that:

- Strength of Heated Coarse Briquette (kN) = $0.176 \times $ Strength of Cured Coarse Briquette + 3.865 kN
- Strength of Heated Fine Briquette (kN) = $0.123 \times $ Strength of Cured Fine Briquette + 14.373 kN

When the briquettes that break during the strength testing are examined, it can be seen that in the case of cured briquettes, a large number of big pellet fines particles are ruptured, but in the case of heated briquettes, none of the pellet-fines particles are cracked. All the large particles dislodge completely, showing that the bonding between the matrix and the particles is the weakest.

The strength of reduced briquettes is far less than the strength of briquettes heated in a nitrogen environment (Figures 14 and 15). Like that of the cured and heated briquettes, the strength of the reduced briquettes also increases with an increase in cement content. By regression analysis it can be seen that:
Figure 16. Compression strength of briquettes (a) after curing; (b) after reduction under load; and (c) after reduction with free swelling.

- Strength of Reduced Coarse Briquette (kN) = 0.047 × Strength of Cured Coarse Briquette – 0.346 kN
- Strength of Reduced Fine Briquette (kN) = 0.225 × Strength of Cured Fine Briquette – 2.407 kN

The linear relationship between the cement content and the strength of briquettes – after curing and after reduction – is similar to that observed for the cement-bonded pellets (Takahashi et al., 1993).

Optical microscope examination of the briquettes shows that the pellet-fine particles in the briquette containing 2% cement on reduction initially sever to pieces and then disperses. This results in poor strength. On the other hand, even though the pellet-fine particles in the briquette containing 25% cement break to pieces, the pieces are not so free to disseminate. This, along with presence of non-swelling dicalcium silicate particles (from dehydration of cement gel), prevents abnormal swelling of the briquettes. Hence, the strength is higher in the case of briquettes containing more cement.

While the increase in cement content helps by increasing the strength of briquettes, it adversely affects the production cost of briquettes. To some extent, increased addition may also affect the blast furnace operation. The lime part of the cement may be compensated by the lower addition of limestone, but the silica part has to end up as molten slag. The increased energy requirement has to be calculated taking into account savings due to lesser decarbonation of limestone and addition due to more generation of molten slag. Additional cement will also increase the amount of moisture content in the furnace. It has been seen that with increase in cement content from 2 to 25 weight percent the amount of bound water increases from 1.7 to 5.2 weight percent. The free water may vaporise at the top part of the shaft and escape along with the shaft gas. The bound water may be released only at the lower part of the furnace and may contribute to smoother furnace operation.

3.6. Effect of Reduction under Load

Two sets of Mix B briquettes were prepared. Mix B-fine had a $d_{50} < 70 \mu m$ and Mix B-Coarse had a $d_{50} = 2194 \mu m$. The briquettes were tested for compression strength after curing, after reduction at 950°C with free swelling and after reduction at 950°C under load.

Figure 16 shows the strength of Mix B briquettes after curing and after reduction. It can be seen that in the case of Mix B-fine, where there is no swelling on reduction, there is no effect of reduction under load. On the other hand, in the case of Mix B-Coarse, the strength of briquettes reduced under load is...
much more than the strength of briquettes reduced with free swelling. This may be due to the fact that, under load, the briquettes are not free to swell, as a result of which the briquettes remain rather compact. Since Mix B-fine does not show any swelling tendency, the strength is not affected, and since Mix B-Coarse shows acute swelling, its strength increases on the prevention of swelling.

The decline in strength of cold-bonded briquettes with increase in reduction temperature is almost a direct result of dissociation of water containing binding matrix. In the actual blast furnace, the temperature increases with the depth from the stock line of the blast furnace. Hence, it may be assumed that the briquettes would slowly lose their strength and by the time temperature reaches 950°C (general temperature of the thermal reserve zone) the briquette would have fallen quite low in the stack. By this time, the briquettes would have also been reduced by at least 20%, thereby retaining only a fraction of the original strength. Lower down in the stack, two opposing factors may affect the behaviour of the briquettes. On one hand, the load of burden material may help the briquettes to retain more strength; on the other hand, the same load may crush the briquettes. Trials carried out in a pilot blast furnace owned by LKAB and located at Mefos, Luleå (Tottie, 1998; Dahlstedt et al. 1999) showed that the briquettes retain their shape until they have reached the lower region of the stack. This implies that in spite of a sharp decline in strength on reduction, the briquettes retain enough strength to remain somewhat intact.

3.7. Effect of Pellet-type

Eight different types of pellets (Pellet A-H) were used. Table 3 gives the chemical composition of the pellets. In each case, 1870 g of pellets were ground with 130 g of cement (6.5% cement) for 3 minutes in a rod mill. The raw materials were then briquetted in the normal way.

Figure 17 shows the strength of various types of briquettes after curing and after reduction. The figure shows that there is no correlation between the strength of the briquette after curing and strength of the briquette after one hour of reduction at 950°C in an N₂+CO (60:40) environment.

Figure 18 shows the tendency of a briquette to swell on the strength of briquettes. Since the briquettes do not swell to an appreciable extent after 1 h of reduction, the degree of swelling after 5 h of reduction has been measured. The briquettes hardly retain any strength after 5 h of reduction; hence, strength after 1 h has been taken. The figure clearly shows that the decline in the strength of briquettes after reduction increases with the increase in the tendency to swell.

### Table 3. Chemical composition of pellets.

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>94.84</td>
<td>94.77</td>
<td>95.22</td>
<td>95.18</td>
<td>96.10</td>
<td>95.97</td>
<td>95.77</td>
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</tr>
<tr>
<td>FeO</td>
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<td>0.37</td>
<td>0.39</td>
<td>0.82</td>
<td>0.36</td>
<td>0.51</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.40</td>
<td>1.09</td>
<td>1.29</td>
<td>0.36</td>
<td>0.25</td>
<td>1.33</td>
<td>1.22</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.95</td>
<td>2.15</td>
<td>1.44</td>
<td>1.38</td>
<td>1.81</td>
<td>1.90</td>
<td>1.33</td>
<td>1.31</td>
</tr>
<tr>
<td>MgO</td>
<td>1.44</td>
<td>1.47</td>
<td>0.92</td>
<td>0.31</td>
<td>0.31</td>
<td>0.43</td>
<td>0.35</td>
<td>0.76</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.36</td>
<td>0.23</td>
<td>0.33</td>
<td>0.32</td>
<td>0.28</td>
<td>0.27</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.09</td>
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<td>0.05</td>
<td>0.00</td>
<td>0.05</td>
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<td>0.07</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.025</td>
<td>0.049</td>
<td>0.021</td>
<td>0.025</td>
<td>0.023</td>
<td>0.020</td>
<td>0.031</td>
<td>0.026</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.021</td>
<td>0.062</td>
<td>0.018</td>
<td>0.018</td>
<td>0.016</td>
<td>0.016</td>
<td>0.018</td>
<td>0.016</td>
</tr>
</tbody>
</table>
Figure 17. Effect of pellet-type on the strength after curing and after reduction for 1 h at 950°C using N\textsubscript{2}+CO (60:40).

Figure 18. Effect of tendency of a briquette to swell, given by volume expansion after 5 h reduction, on the strength of briquette after 1 h reduction. (Reduction temperature: 950°C, N\textsubscript{2}:CO=60:40)

4. CONCLUSIONS

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

1. The strength of briquettes decreases drastically with temperature to 700°C, but declines rather slowly beyond that. The decrease in strength is greater in the case of reduced briquettes than in the case of heated briquettes. The loss of strength is due to the combined effect of destruction of binding phase (CSH gel) and phase transformations of iron oxides.

2. The loss of strength is less in the case of briquettes made of Mix B compared to those made of Mix A because of the presence of pre-reduced materials, flaky particles and materials such as cutting slags, which can act as skeleton in the briquettes.

3. With increase in the degree of reduction (up to 10%), the briquettes rapidly lose their strength. Beyond this, the strength is not affected by the degree of reduction.

4. The strength of briquettes - cured, heated in nitrogen environment and reduced – increases with decreasing particle size of the raw material.

5. The strength of briquettes - cured, heated in nitrogen environment and reduced – increases almost linearly with increase in cement content. There is a linear relationship between the strength of briquettes after curing and after heating or after reducing.

6. For the briquettes that are made of coarse raw material the decline in strength on reduction under load is less than the decline in strength on reduction allowing free swelling.

7. The strength of briquettes decreases with increase in swelling tendency. The swelling tendency itself is dependent upon the type of pellets used for the preparation of briquettes.

ACKNOWLEDGEMENTS

This work was carried out within MiMeR (Minerals and Metals Recycling Research Centre) at the Luleå University of Technology, Sweden. It was partly financed by VINNOVA (the Swedish Agency for Innovation Systems) and a number of Swedish metallurgical industries. For their suggestions and overall support, the authors are grateful to their colleagues at MiMeR.
REFERENCES


PAPER III

Maneesh Singh and Bo Björkman, Swelling behaviour of cement-bonded briquettes – Part 1, ISIJ International (In press).
Cement-bonded agglomerates of by-products generated in iron and steel plants are commonly used as burden material for blast furnaces. It has been observed that under certain conditions the briquettes containing pellet-fines show a tendency to swell catastrophically when reduced at 900-1000°C using carbon monoxide as reducing agent. This swelling is dependent upon a number of factors like: reducing temperature, composition of briquettes, particle size of raw material, amount of cement and composition of reducing gas. The optical micrographs do not show the formation of iron whiskers as the cause of swelling; instead, the reduced iron particles seem to move apart, thereby causing swelling. This paper describes the effect of various parameters that cause the abnormal swelling of briquettes.

Key Words:
Cement-bonded agglomerates, blast furnace, swelling, reduction, pilot-plant.

1. INTRODUCTION

The reduction of hematite pellets is accompanied by expansion in their volume. About 20% swelling is common and does not adversely effect blast furnace operation in any way. On the contrary, the swelling promotes the reduction process, due to increase in porosity. This swelling is caused mainly due to the phase transformation from hematite (hexagonal) $\rightarrow$ magnetite (cubic). In some cases, there is volume increase during conversion of magnetite to wustite. The exact mechanism for this expansion is not clear, but it is often attributed to the release of the remnant stresses, generated during the conversion of hematite to magnetite, during conversion of magnetite to the weaker wustite structure $^{1,2)}$.

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 either in sinters or in 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 $^{1,3)}$.

Most of the time, catastrophic swelling occurs during the last stage of the reduction process (wustite $\rightarrow$ iron) when iron of fibre-like (whiskers) morphology 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 degree of swelling of indurated or cold-bonded pellets and briquettes depends upon the mechanism of reduction, which in turn depends upon the:
- Reduction temperature;
- Reducing gas composition.

Different researchers have reported differently about the effect of temperature on the swelling behaviour of pellets. These contradictory observations may be due to differences in the quality of pellets, the test conditions and the mechanism of swelling.
When the pellets show catastrophic swelling due to the formation of iron whiskers, the swelling generally increases with increase in temperature. This may be because at low temperature the metallic iron is formed uniformly over the surfaces of the wustite grains, giving a shell-like growth of iron. On the other hand, at high temperature, the nucleation takes place at favoured sites on wustite grain and continues to grow from these points as nodules or angular projection. The transition from shell-like to nodular iron growth occurs in the temperature range 850-900°C, and marks the onset of abnormal swelling.

The occurrence of swelling without the formation of iron whiskers reaches a maximum at about 900°C. When the pellet is reduced with CO at low temperatures, CO dissociates to C and CO₂. At low temperatures (about 700°C), C either deposits inside the pellet and/or reacts with iron to form iron carbides (Fe₃C or Fe₂C). As reduction temperature increases instead of depositing as free C, 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.

The swelling of pellets increases almost linearly with the increase in porosity of indurated pellets. This is because high porosity creates weak bonding, thereby allowing easier formation of iron whiskers.

The steel industry generates a wide variety of by-products rich in iron. The traditional way of recycling these by-products back to the blast furnace has been the sintering process; but in recent years, the cold-bond agglomeration process is becoming popular. In this process, various iron-rich steel-plant by-products are mixed together with a binder and agglomerated. The cured agglomerates are then used as burden material for the blast furnace. Such cement-bonded briquettes have been in regular use in a number of plants including SSAB Tunnplåt AB, Luleå and SSAB, Oxelösund AB (Sweden). A common observation among the plant operators has been that addition of cold-bonded briquettes comprising up to 5% of the burden material does not pose any major problem, but at higher percentages, the blast furnace starts operating in an erratic manner. This is attributed to the disintegration of briquettes inside the blast furnace. The destruction of cementitious phase is the major cause for the disintegration of cement-bonded agglomerates; but it is suspected that the abnormal swelling of the agglomerates may aggravate the problem. Hence, the understanding of the conditions under which the cold-bonded briquettes swell is essential.

2. MATERIALS AND METHODS

2.1. Raw Materials

Nine raw materials received from SSAB Merox AB were used for the study. One of the materials, pellet-fines, was a mixture of fines of Pellet A and Pellet B, two commercially available pellets. During the transportation and handling the weaker pellets break, these broken pellet segments are removed as pellet-fines by sieving before the pellets are charged into blast furnace. The remaining materials were different iron rich slags, sludges and dusts generated at SSAB Oxelösund AB. Even though Manganese slag is not a by-product it has also been included in the composition. This is because SSAB Merox also adds it during the production of its briquettes, since manganese in hot metal is required during the steelmaking process. Ordinary Portland cement (Standard Portland Cement, Type P, Cementa) was used as a binder. Using these raw materials, two types of briquettes were made. Table 1 gives the chemical analysis of various raw materials, and Table 2 gives the composition of the briquettes.

The particle size analysis, showed a wide range of distribution for all the by-products. While most of the materials ranged from very fine (-200 mesh, 75 μm) to quite coarse (+9.5 mm), blasting dust and LD dust had only fine fractions.
### Table 1. Chemical analysis of various raw materials.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.92</td>
<td>58.77</td>
<td>66.63</td>
<td>64.49</td>
<td>86.29</td>
<td>76.86</td>
<td>72.25</td>
<td>85.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe (met)</td>
<td>-</td>
<td>31.91</td>
<td>-</td>
<td>48.50</td>
<td>55.53</td>
<td>23.20</td>
<td>0.47</td>
<td>53.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.86</td>
<td>14.59</td>
<td>2.14</td>
<td>8.83</td>
<td>22.68</td>
<td>34.83</td>
<td>57.90</td>
<td>25.90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>2.06</td>
<td>12.27</td>
<td>64.50</td>
<td>7.16</td>
<td>8.08</td>
<td>18.83</td>
<td>13.88</td>
<td>6.71</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.67</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>49.25</td>
<td>1.57</td>
<td>0.07</td>
<td>1.14</td>
<td>0.75</td>
<td>1.22</td>
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<td>1.14</td>
<td>0.04</td>
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<td>CaO</td>
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<td>14.90</td>
<td>0.39</td>
<td>15.66</td>
<td>0.30</td>
<td>0.16</td>
<td>0.22</td>
<td>0.04</td>
<td>64.04</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>4.07</td>
<td>3.35</td>
<td>1.45</td>
<td>2.42</td>
<td>0.05</td>
<td>0.10</td>
<td>0.04</td>
<td>0.04</td>
<td>3.34</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
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<td>1.17</td>
<td>0.39</td>
<td>0.27</td>
<td>0.12</td>
<td>0.06</td>
<td>0.16</td>
<td>0.08</td>
<td>4.36</td>
<td>-</td>
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<tr>
<td>SiO$_2$</td>
<td>22.43</td>
<td>7.98</td>
<td>2.21</td>
<td>4.65</td>
<td>0.72</td>
<td>0.75</td>
<td>0.86</td>
<td>1.35</td>
<td>25.45</td>
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<tr>
<td>P$_2$O$_5$</td>
<td>0.05</td>
<td>0.21</td>
<td>0.03</td>
<td>0.11</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.93</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.10</td>
<td>1.09</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.36</td>
<td>0.06</td>
<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.003</td>
<td>0.26</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>0.41</td>
<td>0.68</td>
<td>0.004</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>2.03</td>
<td>-</td>
<td>0.82</td>
<td>0.10</td>
<td>0.12</td>
<td>0.06</td>
<td>0.58</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Sum (Total)</td>
<td>102.83</td>
<td>102.47</td>
<td>100.09</td>
<td>96.68</td>
<td>98.49</td>
<td>97.58</td>
<td>97.63</td>
<td>99.36</td>
<td>101.66</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2. Composition of briquettes.

<table>
<thead>
<tr>
<th>Briquette</th>
<th>Pellet-fines</th>
<th>Cutting slag (steel-work)</th>
<th>Cutting slag (rolling)</th>
<th>Grinding fines</th>
<th>Blasting dust</th>
<th>LD converter dust</th>
<th>Mill scale</th>
<th>Slag handling scrap</th>
<th>Manganese slag</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>93.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
<td>3.5</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>Mix B</td>
<td>62.7</td>
<td>1.5</td>
<td>1.5</td>
<td>0.9</td>
<td>2.0</td>
<td>1.3</td>
<td>3.5</td>
<td>15.5</td>
<td>4.6</td>
<td>6.5</td>
</tr>
</tbody>
</table>
2.2. Preparation of Briquettes

900 g of Mix A or Mix B was ground in a steel ball mill. 150 g (for Mix A & Mix B) or 100 g (for Mix C) of this mixture and optimum quantity of water (7.5 ml for Mix C and 10-15 ml for Mix A and Mix B, depending upon the composition and particle size distribution of the raw mixture) were then put in a steel trough and mixed for about a minute, so as to obtain a mouldable paste.

The plastic paste was put in a cylindrical steel mould of 4.2 cm diameter and compacted first by vibration for fixed period of time (1.0 min.) (using a vibrating machine, Retsch Vibro) and subsequently by compression under fixed load (1.5 tons) for fixed time (1.0 min.) (using a laboratory scale press, Carver Laboratory Press, Model C). The green briquette thus obtained was cured for 28 days in a high humidity chamber. The cured briquettes were dried overnight in an oven maintained at 105°C.

2.3. Reduction of Briquettes

The schematic diagram of the reduction set-up is shown in the Figure 1. The reduction set-up consisted of two parts: the gas supply and the heating furnace. The gases were supplied from cylinders. The supply of these two gases was controlled using needle valves and flow meters. The gases in the required proportions were mixed in a gas mixer consisting of a tube containing glass beads.

The heating furnace consisted of a Kanthal wire wound tube furnace (length: 100 cm, diameter: 12.5 cm). A stainless steel tube (length: 135 cm, outer diameter: 6.5 cm) closed at the bottom end was placed inside this furnace. A K-type thermocouple placed inside the furnace near the briquette monitored the furnace temperature. The gas mixture, either only nitrogen or a mixture of nitrogen and carbon monoxide (N₂:CO = 60:40) at a flow rate of 10 l/min. entered from the bottom and was burnt at the top by means of an off-gas burner.

For isothermal reduction, the furnace was heated until the desired temperature was reached and then the flow of reducing gas mixture was introduced. A briquette, placed in a high-temperature steel basket, was then lowered into the furnace and suspended from a balance placed above. The briquette was suspended in the region where the error was within ±5°C of the desired temperature. As an example, when a briquette was considered reduced at 950°C, the temperature in the space between the briquette and the steel wall was 955°C. A thermocouple implanted inside the briquette, axially midway and radially 7 mm from the surface, registered a linear rise in temperature up to 850°C in almost 11 min. It reached 940°C in 24 min., 950°C in 35 min. and finally stabilised at 954°C in 150 min. After the desired time had elapsed, the briquette was raised to the mouth of the furnace and cooled in a flowing-nitrogen environment.
2.4. Reduction under Load

A high-temperature steel crucible with small holes at the bottom was used. A layer of alumina balls (diameter 10 mm) was laid at the bottom of this crucible. A briquette was then placed over the layer of alumina balls and in the centre of the crucible. The space between the briquette and the wall was then filled with alumina balls and a layer of alumina balls was placed over the briquette. 650 g (arbitrarily decided) of stainless steel balls (diameter 10 mm) was then put over the briquette to apply a constant load (Figure 2). The crucible containing the briquette was placed inside the hot furnace and reducing gas was blown from the bottom.

2.5. Pilot Blast Furnace Tests

Some briquettes were also tested in a pilot blast furnace owned by LKAB and located in the premises of MEFOS, Luleå. The pilot plant has the following specifications: hearth diameter = 1.2 m, height = 14 m, volume = 8.2 m³, production = 36 tons/24 h, blast temperature = 1200°C, coke / coal consumption = 510 kg/ton hot metal.

The briquette to be tested was put in a steel basket and surrounded by commercially available Pellet A (Figure 3). Just prior to the quenching of the furnace the baskets were introduced into the furnace from the top at regular intervals. The furnace was then quenched by flushing nitrogen from the top. Within minutes the reducing gases were removed and the reduction stopped. After cooling the furnace for ten days the baskets were excavated from the quenched furnace.

2.6. Degree of Reduction

The degree of reduction was calculated according to the formula:

\[
\text{Degree of reduction} = \frac{\text{Total loss in weight} - \text{Loss in weight due to the removal of moisture}}{\text{Total possible loss in weight due to oxygen removal}}
\]

Total loss in weight was obtained by recording the change of weight of briquettes during reduction. Loss in weight due to the removal of moisture was obtained by recording the weight of similar briquettes heated in a nitrogen environment. Total possible loss in weight due to oxygen removal was obtained from TGA and cross-checked using the chemical analysis of individual components. An average value of three briquettes per test was accepted. A variation within ±10% of the mean value was accepted.
2.7. Chemical Analysis

Chemical analysis was carried out at LKAB’s laboratory using an Inductively Coupled Plasma (ICP) Spectrometer.

2.8. Optical Microscopic Examination

A test piece of the sample to be observed was cast in a cold-mounting epoxy resin mould under vacuum. The moulded sample was then ground and polished using standard techniques. The polished sample was then observed using a Nikon Eclipse E600 Pol optical microscope.

2.9. Particle Size Analysis

Approximately 100 g of dried material was dry-sieved to various size fractions using a set of U.S. Standard Sieves conforming to ASTM. In this paper the particle size has been reported as $d_{50}$, which is the cumulative fifty percent finer than the value.

2.10. Volume Measurements

The bulk volume of briquettes and pellets was calculated under the assumption that they were perfectly cylindrical and spherical, respectively. The diameter and the length were measured using callipers. After reduction, the briquettes and pellets often distorted. Even in this case the diameter and length were measured at several places and an average of the readings was taken. This method of measuring the volume gave only rough values; hence, they should be taken only qualitatively.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature

Two different types of Mix A briquettes, A1 ($d_{50} < 74 \, \mu m$) and A2 ($d_{50} = 2512 \, \mu m$) were isothermally heated or reduced at different temperatures for 5 hours.

When heated in nitrogen environment, the briquettes show almost constant volume expansion of about 10%, irrespective of the heating temperature. The expansion is accompanied by the development of many small and large cracks. The cracking is most likely due to the loss of cement bonding, which weakens the structure. At higher temperatures, the degree of sintering is higher, thereby, resulting in less cracking. This is especially true for briquettes made of finely ground materials that expand slightly less than coarsely ground materials. This difference may be due to the greater amount of sintering that takes place with finely ground material as opposed to coarsely ground materials.

Figures 4 and 5 show the effect of temperature on the swelling of briquettes A1 and A2 reduced at different temperatures. When the briquettes are reduced at low temperature (<800°C), they experience swelling leading to cracking and disintegration. For these briquettes, the measured volume expansion reduces with increase in reduction temperature. This is because at low temperatures the cracks formed are bigger, which gives bigger measured diameter and height and thereby greater volume expansion. If the volume of briquettes were measured by immersion method, perhaps the results would be otherwise. In the temperature range 800-900°C, the swelling is rather low and within the acceptable limit. In the temperature range 850-1000°C, the briquettes show catastrophic swelling wherein the coarse pellet-fines particles present in the briquettes start popping up like “pop-corn”. The overall swelling of the briquettes may be due to the combined effect of loss of strength of the cement matrix and expansion due to the hematite $\rightarrow$ magnetite $\rightarrow$ wustite $\rightarrow$ iron transformations. The popped-up particles are very soft and spongy. XRD analysis of the spongy mass and of material collected from the surroundings shows that the material in the spongy mass is mostly iron, while in the surroundings the material is mostly wustite.
Figure 4. Effect of reduction temperature on Mix A briquettes reduced in N2:CO=60:40 environment for 5 h, (a) A1 ($d_{50} < 74 \mu m$); and (b) A2 ($d_{50} = 2512 \mu m$).

Figure 5. Effect of temperature on the volume of briquettes made of Mix A (A1 and A2) reduced for 5 h and Pellet A reduced for 3 h in N2+CO (3:2) environment.

The effect of temperature on swelling may be summarised as:

- 750-850°C: The swelling is rather low and within the acceptable limit. It is due to the formation of large cracks.
- 900-1000°C: The swelling increases and then falls with temperature so that the swelling reaches a maximum at 950-1000°C. The swelling is due to the formation of a soft spongy mass of iron.
- At 1050°C: The swelling is within the permissible limits.

While the above description is true, the figure should not be interpreted quantitatively. This is because the samples were reduced for fixed time, 5 hour. However, the rate of reduction is dependent upon the temperature. The rate of reduction increases with temperature up to 900°C and thereafter it does not increase. Hence, while the briquettes reduced at 750-850°C reduced to 67-77%, those reduced at 900-1050°C had reduced to 81-85%. Since, the swelling increases with the degree of reduction the briquettes reduced at 750-850°C would have shown further swelling had they been reduced to over 80%.
Figure 6. Optical micrographs of briquettes of A2 ($d_{50} = 2512$ µm) reduced at different temperatures in $N_2$:CO = 60:40 for 5 h, (a) 750°C (grey particles are iron carbide, White particles are iron); (b) 950°C (white particles are iron); and (c) 1050°C (white particles are iron).

For the sake of comparison, Figure 5 also shows the effect of temperature on the swelling of Pellet A. It can be seen that under the same conditions the Pellet A does not have the tendency to swell abnormally.

Figure 6 shows the optical micrographs of briquettes of A2 ($d_{50} = 2512$ µm) reduced at different temperatures. At 750°C and 800°C, iron carbide (Fe₃C) is the main component and iron is the minor component. The grains are laminar and well connected. At 850°C, even though the iron is the main phase, the grains are large and well compacted. At 950°C, the iron grains are rather small, spherical and scattered. At 1000°C, even though the iron particles are small and spherical, they are not dispersed as in the previous case. At 1050°C the iron grains are large and well sintered.

3.2. Effect of Degree of Reduction

Two different types of Mix A briquettes, B1 ($d_{50} < 74$ µm) and B2 ($d_{50} = 2465$ µm), were isothermally reduced at 950°C for varying periods of time.

The briquettes, B1, were reduced using $N_2$:CO (60:40). Figure 7 shows the effect of reduction time on the volume of briquettes. As can be seen, the reduction time (also reduction degree) has tolerable effect on the briquettes made of finely ground material B1. On the other hand, briquettes made of coarse material, B2, show catastrophic swelling. Visual observations show that in the briquettes, B2, the larger particles of pellets-fines blow up like “pop-corns”. Large-scale formation of a soft spongy iron mass could be seen with the naked eye.
Figure 7. Effect of degree of reduction on the volume of briquettes B1 and B2. (Reduction temperature = 950°C, N$_2$:CO=60:40)

Figure 8. Effect of reduction potential on a particle in briquette B2 reduced at 950°C for 5 h, (a) cured (grey particles are pellet-fines particles), (b) CO/CO$_2$=12.5% (grey particles are fragmented magnetite formed from a pellet-fines particle); (c) CO/CO$_2$=50% (grey particles are wustite formed from a fragmented pellet-fines particle); and (d) CO/CO$_2$=100% (white particles are iron).
The briquettes, B2, were reduced using gas mixtures having three different reduction potentials ($\text{CO}/(\text{CO} + \text{CO}_2 = 12.5, 50, 100 \text{ volume }\%$) at 950°C for 5 h. This was done to reduce the briquettes to magnetite, wustite and iron stages respectively. Briquettes reduced in an environment having low reduction potentials ($\text{CO}/(\text{CO} + \text{CO}_2 = 12.5 & 50$) show swelling of only 10 and 14 percent, respectively. On the other hand, similar briquettes reduced in an environment with a high reduction potential ($\text{CO}/(\text{CO} + \text{CO}_2 = 100$) show catastrophic swelling (232 volume %). This clearly shows that the catastrophic swelling takes place during the reduction from wustite to iron. Figure 8 shows the optical micrographs of the samples. It shows that on reduction from hematite $\rightarrow$ magnetite the large pellet-fines particles develop cracks and disintegrate to smaller and detached grains. On further reduction to wustite, the grains disintegrate even further, as a result of which the wustite grains are much smaller and fragmented. At this stage, the wustite grains are still close to each other and a rough outline of the original particle may still be there. During reduction to iron, the wustite grains disintegrate and disperse even further. The iron is formed as small spheres and appears in well-dispersed patches. At this stage the boundaries of the original particles totally disappear. It seems that the reduction of wustite to iron takes place in a pool of molten slag (comprised of CaO, SiO$_2$, FeO, MgO, Al$_2$O$_3$). As a result, the reduced iron is able to move away from the wustite structure and, due to the surface tension, takes a spheroid shape.

### 3.3. Effect of Particle Size ($d_{50}$)

900 g of Mix A or Mix B was ground in a steel ball mill for varying period of time (1.0, 2.5, 5.0, 7.5, 10.0, 15.0, 120 min.). One set of material was also mixed for 30 min. in a small porcelain jar by rotating the material (without balls). Thus, two sets of briquettes CA1-CA8 and CB1-CB8, comprising Mix A and Mix B, respectively, were prepared. Table 3 gives the average particle size ($d_{50}$) of the raw materials used for making the briquettes.

Figure 9 shows the effect of particle size ($d_{50}$) on the swelling of briquettes. Briquette CA1 does not show any catastrophic degradation. 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.

### Table 3. Average particle size of raw materials of briquettes CA1-CA8 and CB1-CB8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CA1</th>
<th>CA2</th>
<th>CA3</th>
<th>CA4</th>
<th>CA5</th>
<th>CA6</th>
<th>CA7</th>
<th>CA8</th>
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<tbody>
<tr>
<td>Grinding Time (min.)</td>
<td>120</td>
<td>15</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$d_{50}$ ($\mu$m)</td>
<td>30</td>
<td>70</td>
<td>149</td>
<td>253</td>
<td>1058</td>
<td>1595</td>
<td>2465</td>
<td>2512</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>CB1</th>
<th>CB2</th>
<th>CB3</th>
<th>CB4</th>
<th>CB5</th>
<th>CB6</th>
<th>CB7</th>
<th>CB8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding Time (min.)</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$d_{50}$ ($\mu$m)</td>
<td>-</td>
<td>-</td>
<td>274</td>
<td>323</td>
<td>595</td>
<td>986</td>
<td>1337</td>
<td>2194</td>
</tr>
</tbody>
</table>
Figure 9. Effect of average particle size on the volume of briquettes. (Reduction temperature = 950°C, time = 3 h, N₂:CO = 60:40)

Figure 10 shows the optical micrographs of the reduced samples. From the figure, it is seen that in the briquette CA1, the fine pellet-fines particles are surrounded by matrix. On heating, the matrix breaks and becomes porous. When the small pellet-fines particles reduce, disintegrate and scatter they occupy the space originally occupied by the matrix. There is some dispersion of grains on the transformation of wustite to iron but not much, hence, there is not much swelling. In the case of briquette CA8, as the reduction of hematite $\rightarrow$ magnetite $\rightarrow$ wustite $\rightarrow$ iron proceeds, the dispersion of grains increases and the size of grains decreases. During wustite $\rightarrow$ iron reduction, the scattering reaches a maximum. This disintegration and “explosion” of the original large particles leads to the popping-up of large grains. When there are many large grains in one area and there is not enough space to scatter, they push against each other, resulting in an overall swelling of the briquettes.

When the Pellet A is reduced in an N₂+CO (60:40) environment at 950°C the reduction of hematite $\rightarrow$ magnetite $\rightarrow$ wustite $\rightarrow$ iron proceeds without catastrophic swelling of the pellets. Under such conditions, the hematite / magnetite / wustite grains are of laminar shape and rather large. In the case of pellets, the reduction of wustite to iron is completely caused by solid-gas reaction. The reduced iron remains bound to the wustite and cannot move freely; hence, it forms relatively large, laminar and interconnected iron grains.

3.4. Effect of Cement Content

Two sets of briquettes containing 0, 2, 4, 6, 8, 10, 15, 20 and 25 weight % cement and the rest pellet-fines were prepared in the normal way. The briquettes without any binder obviously did not have any strength but retained its shape during handling, due to the presence of moisture. One of the sets of briquettes, DF1-DF9, was prepared using finely ground pellet-fines and the other, DC1-DC9, using coarse pellet-fines.

In the first set of experiments the briquettes were reduced for 5 h at 950°C in N₂+CO (60:40) environment. In the second set of experiments the briquettes were first reduced for 3 h in N₂+CO+CO₂ (60:4:36), then for 3 h in N₂+CO+CO₂ (60:20:20) and finally for 4 h in N₂+CO+CO₂ (60:40:0). In this way the iron oxides in the briquettes first remained as magnetite for some time, then as wustite and finally as iron. This stepwise reduction allowed the system to homogenise more.
Figure 10. Optical micrographs of briquettes CA1 ($d_{50} < 74 \mu m$) and CA8 ($d_{50} = 2465 \mu m$) after reduction in $N_2+CO$ for 3 h at 950°C. (a) CA1 ($d_{50} < 74 \mu m$) centre (light grey particles are wustite, dark grey particles are dehydrated cement). (b) CA1 ($d_{50} < 74 \mu m$) periphery (white particles are iron, dark grey particles are dehydrated cement). (c) CA8 ($d_{50} = 2465 \mu m$) centre (light grey particles are wustite, dark grey particles are dehydrated cement). (d) CA8 ($d_{50} = 2465 \mu m$) periphery (white particles are iron, dark grey particles are dehydrated cement).
Figure 11 shows the effect of cement as binder on the swelling of briquettes reduced in one step. Figure 12 shows that the briquettes reduced in one step exhibits 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.

The decrease in swelling with increase in cement content for the briquettes made of coarse raw mix, DC1-DC9, may be due to the following:

- decrease in d50 of raw mixture due to increase in finely ground cement content;
- decrease in the amount of pellet-fines;
- changes in the reaction mechanism.

Previous studies have shown a rather modest swelling when the briquettes made of finely ground material containing 6.5% cement are reduced. Figure 12 shows that even the briquettes made of finely ground raw material containing 4% cement can show catastrophic swelling. Hence, in order to control abnormal swelling, not only should the raw material be ground finely, but the amount of cement should also be controlled.

Figure 13 shows the effect of cement on the swelling of briquettes that have been reduced in steps. The figure shows a shift in the maximum point. Here, the maximum swelling takes place for the briquettes made using 6-8% cement.

Figure 14 shows the optical micrographs of briquettes, DC1, DC2 and DC9, made of coarse material. In the case of the briquette containing no cement, the reduced iron particles are laminar in structure and compactly bound. In the case of the briquette containing 2% cement, on reduction, a pellet-fines particle initially severs to pieces and then spreads out. On the other hand, even though the pellet-fine particles in the briquette containing 25% cement break to pieces, the pieces are not so free to disseminate. This, along with presence of non-swelling dicalcium silicate particles (from dehydration of cement gel), prevents abnormal swelling of the briquettes. Hence, the strength is higher in the case of briquettes having more cement.

When the reduced briquette made of finely ground raw mixture is observed under a microscope it is apparent that, at low reduction levels the FeO reacts with CaO, SiO2, MgO and Al2O3 to form slag. The slag is well distributed in the case of briquettes having low cement content. In the case of briquettes with a high level (20% and above) of cement, the slag almost envelops all the wustite particles. On reduction to iron, the briquette with 2% cement shows catastrophic swelling due to the large-scale dispersion of the iron particles. In the briquette with 8% cement the iron particles formed are larger and less dispersed. In the briquette containing 25% cement the iron particles are restricted from dispersing by the slag particles, which are present in substantial amount all around.
**Figure 11.** Effect of cement content on the briquettes heated in nitrogen environment and reduced in N$_2$+CO (60:40) environment at 950°C.

**Figure 12.** Effect of cement content on the swelling of briquettes on reduction. (Reduction time = 5 h, reduction temperature = 950°C, N$_2$:CO = 60:40)

**Figure 13.** Effect of cement content on the swelling of briquettes reduced in steps. (Reduction time 3 h for CO/CO+CO$_2$ = 0.1, 3 h for CO/CO+CO$_2$ = 0.5, 4 h for CO/CO+CO$_2$ = 1)
Figure 14. Optical micrographs of briquettes DC1 (pellet-fines + 0% cement), DC2 (pellet-fines + 2% cement); and DC9 (pellet-fines + 25% cement) reduced in N₂+CO for 5 h at 950°C, (a) DC1 (0% cement) centre (grey particles are wustite); (b) DC1 (0% cement) periphery (white particles are iron); (c) DC2 (2% cement) centre (grey particles are wustite), (d) DC2 (2% cement) periphery (white particles are iron), (e) DC9 (25% cement) centre (grey particles are wustite, dark grey particles are dehydrated cement), (f) DC9 (25% cement) periphery (white particles are iron, dark grey particles are dehydrated cement).
3.5. Effect of Reduction under Load

One set of briquettes of Mix A ($d_{50} = 359 \, \mu m$), E1, was prepared in the normal fashion. Some of these briquettes were reduced allowing free swelling and others were reduced under load.

**Figure 15** is the photograph of a briquette reduced under load. The briquette reduced under load shows, overall, less degree of swelling when compared to a similar briquette reduced without any physical constraints.

**Figure 15** also shows the optical micrographs of briquette E1 reduced under load. It can be seen that in the centre of the briquette the individual grains of wustite are more densely packed than in the case where the briquettes were reduced allowing free swelling. In an optical micrograph of a sample from peripheral Position 1, the region between two alumina balls, which did not experience much load, shows normal swelling tendencies. On the other hand, in the optical micrograph of sample from peripheral Position 2, the region that was under the direct influence of load, shows denser and bigger iron grains. This shows that the reduction in the degree of swelling is not due to the fact that the briquette has less tendency to swell, rather it is because the applied load has restricted its swelling. On application of load the iron grains tend to sinter into larger grains and do not disperse significantly.

**Figure 15.** Photograph and optical micrographs of briquette E1 after reduction under load. (a) photograph of a briquette, E1, reduced under load; (b) centre (grey particles are wustite); (c) periphery (Position 1 – away from alumina balls) (white particles are iron); and (d) periphery (Position 2 – adjoining the alumina balls) (white particles are iron).
3.6. Testing of Briquettes in a Pilot Plant

Four different types of briquettes were prepared in the normal way. Four briquettes of each kind were then introduced at different times into LKAB’s pilot blast furnace prior to quenching of the furnace. These briquettes were:
1. F1: Pellets fines + 6.5% cement – Coarsely ground (d$_{50}$ = 2512µm).
2. F2: Pellets fines + 6.5% cement – Coarsely ground (d$_{50}$ = 2512µm) put into basket without any pellets to surround them. This was done to allow free swelling of briquettes.
3. F3: Pellets fines + 6.5% cement – Finely ground (d$_{50}$ < 74µm).
4. F4A: Pellets fines + 2% cement – Coarsely ground.
5. F4B: Pellets fines + 8% cement – Coarsely ground.
6. F4C: Pellets fines + 15% cement – Coarsely ground.
7. F4D: Pellets fines + 25% cement – Coarsely ground.

Examination of the reduced briquettes obtained by excavating the quenched pilot blast furnace reveals that the briquettes do not swell inside the furnace. The difference in the behaviour of the briquettes when tested in the laboratory and when tested in the pilot plant maybe because the laboratory tests do not replicate the actual conditions inside a blast furnace. In the laboratory, all the experiments are carried out in the isothermal condition (950 oC) using a fixed environment (N$_2$:CO=60:40) as stipulated by the reduction test ISO 4695. This test intends to simulate the reserve zone of a typical blast furnace. On the other hand the conditions inside the pilot blast furnace are different in many ways. Two important differences are:

- In the pilot plant the reduction takes place in non-isothermal condition. Basically there are four zones inside the furnace – drying, reserve, cohesive and dripping zones. The reserve zone has a temperature range of 800-1100 oC, retention time of approximately 2 h 30 min and the temperature gradient of 2 oC/min. The earlier experiments have shown that the swelling takes place only in the range of 900-1000 oC and since in the pilot plant the briquettes stay in this temperature range only for a short time they may not swell.
- In the pilot plant there is a presence of hydrogen inside the furnace. Experiments have shown that the briquettes have lesser tendency to swell in the presence of hydrogen.

Even though the briquettes excavated from the pilot blast furnace do not swell, the optical microscopic examination of the briquettes shows some similarity to the briquettes reduced in the laboratory. At the hematite stage the structure of pellet-fines particles is well bound. On reduction to magnetite, the pellet-fines structure breaks into small fractions. On further reduction to wustite, the structure completely falls apart. This behaviour matches quite closely to the behaviour of briquettes tested in the laboratory furnace (Figure 8). In spite of the similarity there are certain differences. Firstly, while in the laboratory-tested briquettes almost all the particles disintegrate, in the pilot plant tested briquettes substantial amount of particles do not disintegrate. Secondly, on reduction to iron, while the briquettes tested in laboratory swell due to moving asunder of the individual spherical iron particles, in the case of briquettes tested in pilot plant this does not happen. Figure 16 shows the optical micrograph of reduced briquette F1. The figure shows two distinct regions. On the left, the iron particles are compactly packed and are probably remnants of a large pellet-fine particle. On the right the iron particles are sparsely packed and are probably from the fine particles that were distributed between the cement matrix.

The briquettes F1 were enclosed in steel basket and surrounded by Pellet A which could have restricted the swelling of the briquettes, but the examination of briquettes F2, which were not surrounded by the pellets, again do not show any swelling tendencies. The optical microscopic examination of the briquettes shows similarity in microstructures of F1 and F2.
In spite of the fact that the reduced F1 briquettes do not have tendency to swell they have rather low strength and tend to fall apart. This may be because the bond between the pellet-fines particles are not strong. This is due to the large distance that exist between them.

**Figure 17** shows the optical micrograph of the briquette F3. Like the previous case the relatively large pellet-fines particles dissociate and fall apart, so that at the magnetite and wustite stage the iron oxide particles are quite evenly distributed in the briquettes. On reduction to iron, again the iron particles are rather well distributed throughout the briquette. This even distribution of particles could be the cause of better strength characteristics of the briquettes F3.

In the case of F4A-F4D only a few briquettes could be recovered from the pilot plant. These briquettes were from the upper half of the shaft. Among these briquettes, it is observed that the strength of briquettes increases with an increase in the cement content. Also, none of the briquettes show any swelling tendency.

**Figure 18** shows the optical micrograph of a reduced Pellet A. When Pellet A is reduced in pilot plant the structure of the pellet does not crumble on conversion to magnetite and wustite. Hence, the final iron grains are compact and well bound. This results in strong structure.

From the pilot plant experiments it seems that the quality of briquettes may be improved by grinding the raw material fine or by using only the fine fractions. The strength may also be improved by increasing the cement content in the briquettes.
The conditions inside the pilot plant are very close to those of an actual blast furnace. Still the conditions inside vary from blast furnace to blast furnace depending upon the design and operation. Larger blast furnaces normally have larger isothermal reserve zone having a temperature of about 950°C. Under such condition there may be a possibility for the briquettes to swell. Hence, steps should be taken to reduce this possibility.

4. CONCLUSIONS

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

1. The swelling of briquettes reaches a maximum when reduced at 950°C.
2. The swelling takes place during the transformation of wustite to iron. This swelling is not due to the formation of iron whiskers, but rather due to the movement of iron particles away from each other in a bath of molten slag.
3. The swelling of briquettes increases with the increase in average particle size of the raw material. The swelling is almost proportional to the log of d50 of the raw mix.
4. The swelling does not take place in the absence of cement. It reaches a maximum when the briquette contains about 4-6 weight percent cement. It falls with a further increase in cement content.
5. During the reduction under load, the briquettes still have the tendency to swell, but applied load prevents the swelling from taking place.
6. The briquettes do not swell during reduction inside the pilot plant. Like the briquettes tested in the laboratory, the pellet-fines present in the briquettes tend to disintegrate resulting in the loss of strength. The performance of briquettes inside the furnace improves by increasing the fineness of the raw material or by increasing the cement content.

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REFERENCES


PAPER IV

Maneesh Singh and Bo Björkman, Swelling behaviour of cement-bonded briquettes – Part 2, ISIJ International (In press).
SWELLING BEHAVIOUR OF CEMENT-BONDED BRIQUETTES – PART 2

Maneesh Singh and Bo Björkman
Division of Process Metallurgy
Luleå University of Technology
SE-971 87, Luleå, Sweden
{Maneesh.Singh, Bo.Bjorkman}@km.luth.se

Abstract
The use of cement-bonded agglomerates of iron-rich by-products generated in iron and steel plants as burden material for blast furnaces is becoming quite common. It has been observed that under certain conditions the briquettes containing pellet-fines show a tendency to swell catastrophically when reduced at 900-1000°C using carbon monoxide as a reducing agent. This swelling is dependent upon a number of factors, such as: reducing conditions, type of raw material, composition of cement, and coke content. It is not dependent upon the size of agglomerate or hydration period. From the optical micrographs, it is apparent that the swelling may be attributed to the formation of small spheroidal iron particles that move apart, thereby causing swelling. This paper describes the effect of various parameters that cause the abnormal swelling in cement-bonded briquettes made of pellet-fines.

Key words: Cement-bonded agglomerates, blast furnace, swelling, reduction, pilot plant.

1. INTRODUCTION

During the course of steel production a wide variety of iron-rich by-products are generated. Most of the time, these by-products are sintered and recycled back to the blast furnace. In recent years, the cold-bond agglomeration process has emerged as an alternative to the sintering process. In this process, various iron-rich steel-plant by-products are mixed together with a binder and agglomerated. Such cement-bonded briquettes have been in regular use as a burden material in a number of plants including SSAB Tunnplåt AB, Luleå and SSAB, Oxelösund AB (Sweden) 1,2. A common observation among the plant operators has been that addition of cold-bonded briquettes comprising up to 5% of the burden material does not pose any major problem; but at higher percentages, the blast furnace starts operating in an erratic manner 3. This is often attributed to the disintegration of briquettes inside the blast furnace. The destruction of cementitious phase is the major cause for the disintegration of cement-bonded agglomerates; but it is suspected that the abnormal swelling of the agglomerates may be aggravating the problem. Hence, an understanding of the conditions under which the cold-bonded briquettes swell is essential.

The swelling of burden material is a characteristic only of indurated pellets. It does not take place in the case of lump ore or sinters. The swelling is a complex phenomenon in which a number of parameters play an important role. This has made it difficult to develop a generalised swelling model. It is now generally accepted that the swelling in pellets is due to selective nucleation and growth of iron whiskers. When these iron whiskers grow, they push the adjoining grains, resulting in swelling.

Swelling has also been observed in the cement-bonded agglomerates, although not much work has been done on the swelling of cold-bonded agglomerates. In the case of cold-bonded agglomerates, the swelling has been observed in conjunction both with and without the formation of iron whiskers. The conditions for swelling of indurated pellets differ from the conditions for the swelling of cement-bonded agglomerates.
The swelling of indurated pellets has been studied extensively. It has been found that the swelling depends upon a number of factors. Some of these factors are:

Reduction Conditions: The indurated pellets swell more when reduced under isothermal conditions and swelling reaches a maximum at 950°C. The lower degree of swelling in the case of non-isothermal conditions is due to the significant degree of reduction that takes place below 850°C. Abnormal swelling does not take place when reduced in hydrogen; it only takes place when the reduction takes place in the presence of carbon monoxide. It has also been observed that the swelling problem is aggravated by the increase in the reduction rate, which can be done by increasing the reduction potential or gas flow rate. It has also been noted that the swelling can be reduced by keeping the pellets in CO/CO₂ 10:90 (magnetite state) or 50:50 (wustite state) for a long time.

Pellet Characteristics: The amount of gangue present in the pellets is an important parameter affecting swelling. It has been shown that in pellets the tendency to swell decreases with an increase in gangue content due to the increased formation of minor slag bonding. It has also been observed that the swelling problem is aggravated by the increase in the reduction rate, which can be done by increasing the reduction potential or gas flow rate. It has also been noted that the swelling can be reduced by keeping the pellets in CO/CO₂ 10:90 (magnetite state) or 50:50 (wustite state) for a long time.

Free Lime: The presence of free lime leads to catastrophic swelling in pellets due to the dissolution of CaO on the surface of FeO, leaving only a few nucleation sites. From these few nucleation sites the whiskers can grow, leading to the excessive swelling.

Size of Pellets: The swelling decreases with the increase in the size of the pellets. This is probably due to the decline in the rate of reduction as the pellet size increases.

Carbon Content: It has been observed that the catastrophic swelling of cement-bonded agglomerates containing carbon can take place under certain reducing conditions.

In a previously published paper the effect of temperature, degree of reduction, particle size of the raw material, cement content and reduction under load on the swelling of cement bonded briquettes has been discussed. In this paper the effect of effect of (a) non-isothermal reduction and presence of hydrogen, (b) pellet type, (c) pre-firing, (d) hydration time, (e) cement composition, (f) artificial cement, (g) binder type, (h) alkalis, (i) briquette size, and (j), coke content have been discussed.

2. MATERIALS AND METHODS

The experiments were conducted on cement-bonded briquettes made using pellet-fines (93.5 weight%) with ordinary Portland cement (6.5 weight%) (Standard Portland Cement, Type P, Cementa) 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 generation of fines took place due to 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.

In one of the experiments eight different types of pellets (Pellets A-H) were also used for the experiments. Pellets A and B are commercially available and the rest are experimental pellets produced in a small batch. Table 1 gives the chemical composition of the pellets and pellet-fines. It can be seen that the pellet-fines contains relatively higher percentage of FeO compared to the rest showing that the pellet-fines are not properly oxidised.

Details about the experimental procedure followed are given in previously published papers.
Table 1. Chemical composition of pellets used for the experiments.

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<th>F</th>
<th>G</th>
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3. RESULTS AND DISCUSSION

3.1. Effect of Non-isothermal Reduction and Presence of Hydrogen

One set of briquettes A1-A7 (d₅₀ = 1595 µm) was prepared according to the standard procedure using 93.5 weight% of pellet-fines and 6.5 weight% of cement. These briquettes were reduced under isothermal / non-isothermal conditions. The reducing gas contained different amounts of CO and H₂.

Briquettes A1, A2 and A3 were heated under isothermal conditions by introducing the briquettes into the furnace maintained at 950°C. Figures 1 and 2 show the effect of reduction on the volume expansion. Since the volume expansion depends upon the degree of reduction and particle size, the data for briquettes (d₅₀ = 2465 µm) reduced under isothermal conditions (N₂:CO=60:40, 950°C) has also been included as a comparison in Figure 2 [17]. As can be seen from the figure, the degree of expansion increases with the degree of reduction. Irrespective of the experimental condition, the points follow almost the same trend (except for sample A2). The consistently lower degree of swelling may be explained by the lower average particle size (d₅₀) of samples A1-A7. Taking into account the degree of reduction, briquette A2 showed a lower degree of expansion compared to briquette A1. The reason may be the presence of 5% hydrogen in the reducing gas for briquette A2. Briquette A3 did not show any tendency to swell with the formation of spongy mass, but large cracks appeared in the briquette.

Figure 2 shows that the briquettes reduced under isothermal conditions are less prone to swelling than the briquettes reduced under non-isothermal conditions. This observation is contrary to the ones made when pellets were used.

Figure 3 shows the optical micrographs of briquette A3 reduced in N₂:H₂ (75:25). It can be seen that the briquette has no tendency to swell, because the iron grains formed are more compact and laminar. This clearly shows that the presence of carbon monoxide is an essential condition for swelling.
Table 2. Summary of tests carried out to study the influence of reduction conditions on the swelling of briquettes (RT = Room Temperature)

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<th>Type</th>
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<th>Gas Composition (N₂:CO:H₂)</th>
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<th>Reduction Time</th>
<th>Degree of Reduction</th>
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<td>7</td>
<td>80.85</td>
<td>123</td>
</tr>
<tr>
<td>A5</td>
<td>Non-isothermal</td>
<td>RT-950</td>
<td>60:35:5</td>
<td>7</td>
<td>2</td>
<td>69.07</td>
<td>102</td>
</tr>
<tr>
<td>A6</td>
<td>Non-isothermal</td>
<td>RT-950</td>
<td>60:40:0</td>
<td>5.4</td>
<td>1.25</td>
<td>58.31</td>
<td>56</td>
</tr>
<tr>
<td>A7</td>
<td>Non-isothermal</td>
<td>RT-950</td>
<td>60:35:5</td>
<td>4.65</td>
<td>2</td>
<td>67.75</td>
<td>70</td>
</tr>
</tbody>
</table>

Figure 1. Photograph of briquettes A1-A7 showing the effect of test conditions.
Figure 2. Effect of degree of reduction on the swelling of briquettes (d50 = 1595 µm) when tested under different reducing conditions. As a comparison, the swelling behaviour of briquettes (d50 = 2465 µm) with respect to the calculated degree of reduction is also included.

Figure 3. Optical micrograph of a briquette A3 reduced in N2:H2 (75:25) environment, (a) centre (grey particles are wustite), and (b) periphery (white particles are iron).

3.2. Effect of Pellet Type

Eight different types of pellets (A-H) were crushed and made into cement-bonded briquettes, BA-BH, respectively in the normal way. One set of briquettes (BPF) was also made using pellet-fines. In each case, 1870 g of pellets were crushed and ground with 130 g of cement (6.5% cement) for 3 minutes in a rod mill. The raw materials were then briquetted in the normal way.

In the first set of experiments the briquettes were reduced for 5 h at 950°C in N2:CO (60:40) environment. In the second set of experiments the briquettes were first reduced for 3 h in N2:CO:CO2 (60:4:36), then for 3 h in N2:CO:CO2 (60:20:20) and finally for 4 h in N2:CO:CO2 (60:40:0). In this way, the iron oxides in the briquettes first remained as magnetite for some time, then as wustite and finally as iron. This stepwise reduction allowed the system to homogenise to a greater degree. As a reference, uncrushed pellets were also reduced under similar conditions.
Figure 4. Effect of pellet-type on the swelling of briquette and pellets after reduction in one step and of briquette after reduction in three steps at 950°C.

Figure 5. Effect of temperature on the swelling of briquettes made of different types of pellets reduced for 5 h at 950°C in N₂+CO (60:40).

Figure 6. Effect of temperature on the swelling of briquettes made of different types of pellets reduced for 5 h at 950°C in N₂+CO (60:40).

Figure 4 shows that, except for Pellet E, none of the pellets have any tendency to swell catastrophically. Even Pellet E does not show swelling due to formation of spongy mass, as is the case for the briquettes, or formation of iron whiskers; instead, the large-scale swelling is due to formation of a “mouth”, i.e., a big crack running along its equator. This clearly shows that pellets themselves do not have any swelling tendencies. When the pellets are crushed and made into cement-bonded briquettes, some briquettes, notably BB, BC, BD, BG and BH, develop a tendency to swell catastrophically. It also shows that, in almost all cases, the briquettes reduced in one step swell more than the briquettes reduced in three steps.

Figures 5 and 6 show the effect of temperature on the swelling of briquettes made of different types of crushed pellets. All the types of briquettes swell the most at 950°C. The figures show that briquettes BA, BE & BF swell relatively less than the briquettes made of other types of pellets.
**Figure 7** shows the optical micrographs of reduced cement-bonded briquettes BA and BB. It can be seen that in the centre of briquette BA the individual grains of wustite are more densely packed than the grains of wustite in the centre of briquette BB. The micrographs also show that at the peripheral position of briquette BA, the iron particles are larger and more compact than those at the corresponding position of the briquette BB. Microscopic observations of reduced briquettes made using other types of crushed pellets show that the briquettes that have a tendency to swell (BB, BC, BG and BH) disintegrate at the wustite stage and scatter on reduction to iron.

**Figures 8 and 9** show the relationship between the volume expansion and the presence of slag-forming oxides, CaO, SiO₂, MgO and Al₂O₃ in the pellets. The figures show that the swelling increases with increasing oxide content. The figure also shows that for the swelling to take place the ratio of basic oxides to acidic oxides (CaO+MgO/SiO₂+Al₂O₃) should be about one.

**Figures 8 and 9** also show that the briquettes made of pellet-fines swell much more than the briquettes made of crushed Pellet A, even though the pellet-fines consists of fines of approximately 75% Pellet A and 25% Pellet B by weight. One of the reasons may be the presence of Pellet B, which swells much more than Pellet A.

![Figure 7. Optical micrographs of briquettes A and B reduced in N₂:CO for 5 h at 950°C, (a) Pellet A centre (grey particles are wustite), (b) Pellet A periphery (white particles are iron), (c) Pellet B centre (grey particles are wustite), and (d) Pellet B periphery (white particles are iron).](image-url)
Figure 8. Effect of amount of oxides on the swelling of briquettes made of various pellet types reduced for 5 h at 950°C in N₂+CO(60:40).

Figure 9. Effect of basicity on the swelling of briquettes made of various pellet types reduced for 5 h at 950°C in N₂+CO(60:40).

Figure 10. Optical micrographs of Pellet A and pellet-fines particles, (a) Pellet A (grey areas are hematite), (b) Pellet-fines particles (light grey regions are hematite and the dark grey are magnetite), and (c) Pellet-fines particles (light grey regions are hematite and the dark grey are slag).
Figure 10 shows the optical micrographs of Pellet A and pellet-fines particles. While Pellet A is properly sintered (Figure 10A), the substantial numbers of the pellet-fines particles are under-fired and hence weak. This is explained by the fact that pellet-fines particles either contain a large portion of magnetite (Figure 10B) or the hematite grains are not sintered properly, leading to a much more porous and weaker structure (Figure 10C). The difference between the two is explained by the fact that it is mostly the weaker pellets that break during transportation and handling and finally end up as pellet-fines. During the reduction process, due to the weaker bonding, the pellet-fines particles swell much more than the crushed Pellet A particles.

3.3. Effect of Pre-firing

Two sets of briquettes (C1 and C2) were prepared in the normal manner using coarsely ground pellet-fines and 6.5% cement. Both these sets of briquettes were cured for 28 days. After curing, the second set, C2, was heated in a muffle furnace at 1275°C for 0.5 h. The cooled briquettes C2 had glassy coating over all the pellet-fines particles. The briquettes were then reduced at 950°C using N₂+CO (60:40) for 5 h.

The briquettes C1 show catastrophic swelling; on the other hand, the briquettes C2 do not show swelling. Figure 11 shows the optical micrographs of the fired and reduced briquettes. It can be seen that due to the reaction between cement and hematite, additional slag is generated. This slag diffuses into the pellet-fines particles and forms additional bonding. This slag bonding prevents the disintegration of pellet-fines on reduction to wustite. On further reduction, first the wustite is reduced and then the iron oxide component of the slag. As a result, the slag bonding is not destroyed till the late stage. The iron grains produced after reduction are large, laminar and interconnected. Hence, there is no swelling of the briquette.

The other reason for the low degree of swelling of briquettes C2 may be the stronger structure of pellet-fines particles. In a comparison of the structure of pellet-fines in Figure 11a and Figure 10, it can be seen that the grains of hematite become more sintered and crystalline upon heating. This improves the strength of the pellet-fines particles. On reduction, the stronger structure of pellet-fines would prevent the grains from disintegrating.

3.4. Effect of Hydration Time

Two sets of briquettes (D1 and D2) were made according to the procedure given below. These briquettes were then reduced at 950°C in N₂+CO (60:40) for 5 h.

- **D1:** The green briquettes were made using coarse pellet-fines (93.5%) and cement (6.5%) and cured for 30 days.
- **D2:** The green briquettes were made and immediately tested for swelling on reduction. In the second experiment, the cement did not get sufficient time to hydrate and release hydrated lime (portlandite).

On reduction, it is observed that the briquettes swell catastrophically in both cases, indicating that the hydration of cement and release of free lime are not necessary conditions for swelling to take place.

The most important phases in ordinary Portland cement (OPC) are the calcium silicates (C₃S and β-C₂S). These calcium silicates react with water to form calcium silicate hydrates of variable composition and structure (classified under a general term C-S-H gel). The structure of C-S-H gel depends on, among other factors, C/S, S/H, time of hydration, pH of slurry and presence of other compounds / impurities. The composition of the gel can be expressed by a very rough approximation as $C₃S·₂H₃(Ca₃Si₂O₇·3H₂O)$ and the reactions involved as:

\[
C₃S \cdot xH \rightarrow C₃S·ₙHₙ(ₙ₋₃) \cdot (ₙ₋₃)CH \\
C₂S \cdot xH \rightarrow C₂S·ₙHₙ(ₙ₋₂) \cdot (ₙ₋₂)CH
\]

In this experiment, the role of calcium silicate, calcium silicate hydrate and hydrated lime in the swelling two sets of briquettes has been investigated. The results of the experiment show that the presence of free lime is not necessary for swelling to take place; instead, it is the presence of all the oxides together in the briquettes that is the cause of swelling.
3.5. Effect of Cement Composition

Eight types of briquettes were made using pellet-fines and different types of binders. These binders were made by mixing laboratory grade chemicals in a porcelain ball mill. The oxides were taken in the proportions in which they are present in ordinary Portland cement. The green briquettes were then cured for 30 days and then reduced for 3 h at 950°C in N₂+CO (60:40) environment. The composition of the binders is given in the Table 3. Results of the experiment are also given in Table 3.

It has been observed that the maximum swelling takes place in the presence of all the four oxides. To a lesser degree, the swelling takes place in the presence of CaO, SiO₂ and MgO / Al₂O₃. In the absence of MgO or Al₂O₃, swelling does not take place. This experiment clearly proves the necessity of the slag-forming oxides for swelling to take place.

In any case, the swelling is considerably less than the swelling that takes place in the cement-bonded briquettes. This is probably due to the inhomogeneous nature of mixture of these oxides.

This experiment also shows that free lime, alkalis and sulphur present in commercial cement are not the cause of swelling; instead, the combined presence of all the slag-forming oxides is the cause.
Table 3. Summary of tests carried out to study the influence of various oxides on the swelling of briquettes

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Ca(OH)$_2$ (71.80%)</th>
<th>SiO$_2$ (21.58%)</th>
<th>MgO (2.87%)</th>
<th>Al$_2$O$_3$ (3.74%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>Swelling</td>
</tr>
<tr>
<td>E2</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>Slight Swelling</td>
</tr>
<tr>
<td>E3</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>Slight Swelling</td>
</tr>
<tr>
<td>E4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>No swelling</td>
</tr>
<tr>
<td>E5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>No swelling</td>
</tr>
<tr>
<td>E6</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>No swelling</td>
</tr>
<tr>
<td>E7</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>No swelling</td>
</tr>
<tr>
<td>E8</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>No swelling</td>
</tr>
</tbody>
</table>

3.6. Effect of Artificial Cement

The previous set of experiments showed that the presence of slag-forming oxides is essential for swelling to take place; but the swelling did not take place to the same extent as in cement-bonded briquettes, probably due to the inhomogeneous nature of the oxide mixtures. Hence, three types of artificial binders were used for making briquettes. The first one, F1, was pure laboratory-grade hydrated lime and the other two types were the artificial cements made by firing a mixture of pure laboratory-grade CaO, SiO$_2$ (quartz), MgO, Al$_2$O$_3$ and Fe$_2$O$_3$ in the same proportion as in ordinary cement at 1300°C for 3 h.

- F1: Ca(OH)$_2$
- F2: Ca(OH)$_2$ (76.88%) + SiO$_2$ (23.12%)
- F3: Ca(OH)$_2$ (70.26%) + SiO$_2$ (21.13%) + MgO (2.77%) + Al$_2$O$_3$ (3.62%) + Fe$_2$O$_3$ (2.22%)

The artificial cement so formed did not contain $\beta$-C$_2$S; instead, it contained $\gamma$-C$_2$S. This is because in the absence of impurities, $\beta$-C$_2$S is not a stable phase at room temperature. During cooling from 1300°C to room temperature, it transforms to $\gamma$-C$_2$S. Even in F3, only $\gamma$-C$_2$S was observed. Some C$_3$S was formed and some lime remained unreacted. The artificial cements were used for making briquettes in the ordinary way. The briquettes did not attain any strength, since $\gamma$-C$_2$S did not hydrate, so the briquettes were carefully placed inside the furnace and reduced in the previously described way.

It is observed that briquettes F1 and F2 do not swell appreciably. The only swelling is due to cracking. On the other hand, the F3 briquettes swell catastrophically. This experiment clearly shows that the presence of free lime, or only lime and silica, is not a sufficient condition for swelling to take place; instead, the swelling is dependent on the presence of slag-forming oxides.
3.7. Effect of Binder Type

Five sets of briquettes were prepared using five different types of binders. The briquettes were prepared in the normal way using 6.5% binder. The binders were prepared by mixing cement with 25 weight percent of different oxides, taken in powdered form of laboratory-grade reagents, in a small table porcelain ball mill for half an hour. The briquettes contained:

1. G1: Cement
2. G2: 75% cement + 25% CaO (as Ca(OH)$_2$) Calcium hydroxide was taken instead of calcium oxide to prevent generation of heat on hydration.
3. G3: 75% cement + 25% SiO$_2$ (as quartz)
4. G4: 75% cement + 25% MgO
5. G5: 75% cement + 25% Al$_2$O$_3$

In the first set of experiments, the briquettes were reduced for 5 h at 950°C in N$_2$:CO (60:40) environment. In the second set of experiments, the briquettes were first reduced for 3 h in N$_2$:CO:CO$_2$ (60:4:36), then for 3 h in N$_2$:CO:CO$_2$ (60:20:20) and finally for 4 h in N$_2$:CO:CO$_2$ (60:40:0).

Figure 12 shows the effect of various binders on the swelling of briquettes when reduced for 5 h in N$_2$:CO (60:40) and when reduced in three steps using 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. The figure shows that when a part of cement is replaced by the oxides the briquettes tend to swell less. This suggests the possibility of lowering the swelling tendency by incorporating hydrated lime, silica fumes or crushed magnesia / alumina bricks in the cement. It may also be possible to lower the swelling by using high-strength cement, which has relatively higher CaO/SiO$_2$ ratio as compared to ordinary Portland cement.

3.8. Effect of Alkalis

Two sets of samples (H1 and H2) were prepared using finely ground pellet-fines (93.5%) and cement (6.5%). In set H2 1% sodium silicate was also added and mixed. The two sets of briquettes were reduced at 950°C in N$_2$:CO (60:40) for 5 h.

On reduction, it has been observed that H1 does not swell; on the other hand, H2 shows catastrophic swelling. The earlier experiments have shown that the presence alkali is not essential for swelling to take place. This experiment shows that in the presence of alkali the swelling drastically increases. The presence of alkali can even cause the briquettes made of finely ground raw material to swell. This is something that does not take place in the absence of alkali.
3.9. Effect of Briquette Size

In order to study the effect of briquette size on swelling, one briquette was cut into smaller pieces of different sizes. All these samples were reduced in the normal way at 950°C for 1.5 h in N₂:CO (60:40) environment.

- I1-I5: 5 pieces measuring 2 cm × 1.5 cm × (1.2-1.6) cm
- I6: 1-mm thin section of briquette (4.2 cm diameter)
- I7: Some big particles of pellet-fines coated with cement

All these briquette pieces show abnormal swelling of 200-400 volume %. Even the big cement-coated pellet-fines particles swell. The optical micrograph of a reduced piece shows a structure that is similar to that of the reduced complete briquette. This shows that the swelling behaviour is independent of the size of sample.

Close examination of reduced sample I6 shows swelling tendencies along the rim of the pellet-fines particles. The inner portions of the large particles do not show such swelling. Figure 13 shows the optical micrographs of the thin section from region (a), a small particle between two large particles, and (b), adjoining a large pellet-fines particle. The micrographs clearly show that small particles influenced by cement from all sides show considerable swelling. On the other hand, in the case of the large particle, the outer portions, where cement may have been present, show swelling, but the region away from the surface, which may not have been influenced by cement, does not show swelling. This clearly shows the importance of cement in causing swelling.

3.10. Effect of Coke Content

Eight types of briquettes were made according to the normal procedure. These briquettes contained varying amounts of coke fines. Table 4 gives the composition and average particle size of the raw mix used. The cured briquettes were then reduced at 950°C either using only N₂ for 3 h or using N₂+CO (60:40) for 3 h.

Figure 14 shows the effect of coke content on the swelling of briquettes made using finely ground raw material (briquettes JF1-JF5). The graph shows that in case of heating in nitrogen environment swelling does not take place. On the other hand, when the briquettes are reduced in N₂+CO (60:40) environment the swelling increases with increase in coke content. The main reason may be the low degree of reduction that takes place in the case of briquettes heated in N₂. This experiment shows that sudden volatilisation of coke does not cause rupture and disintegration.
Table 4. Summary of tests carried out to study the influence of coke on the swelling of briquettes

<table>
<thead>
<tr>
<th></th>
<th>Pellet-fines (%)</th>
<th>Cement (%)</th>
<th>Coke (%)</th>
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<tbody>
<tr>
<td>JF1</td>
<td>93.5</td>
<td>6.5</td>
<td>0</td>
<td>&lt; 74</td>
</tr>
<tr>
<td>JF2</td>
<td>91.5</td>
<td>6.5</td>
<td>2</td>
<td>&lt; 74</td>
</tr>
<tr>
<td>JF3</td>
<td>89.5</td>
<td>6.5</td>
<td>4</td>
<td>&lt; 74</td>
</tr>
<tr>
<td>JF4</td>
<td>87.5</td>
<td>6.5</td>
<td>6</td>
<td>&lt; 74</td>
</tr>
<tr>
<td>JF5</td>
<td>85.5</td>
<td>6.5</td>
<td>8</td>
<td>&lt; 74</td>
</tr>
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<td>JC1</td>
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<td>JC2</td>
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<td>6.5</td>
<td>2</td>
<td>2120</td>
</tr>
<tr>
<td>JC3</td>
<td>89.5</td>
<td>6.5</td>
<td>4</td>
<td>1980</td>
</tr>
</tbody>
</table>

Figure 14. Effect of coke content on the swelling of briquettes made of finely ground raw material

Figure 15. Effect of coke content on the swelling of briquettes

Figure 15 shows the effect of coke content on the briquettes made of finely and coarsely ground raw materials (JF1-JF3 and JC1-JC3). The figure shows that swelling takes place more in the case of JC1-JC3 than in the case of JF1-JF3. It also shows that up to 4% coke content, coke content has no effect on the swelling of briquettes.

3.11. Pilot Plant Tests

Four different types of briquettes were prepared in the normal way. Four briquettes of each kind were then introduced at different times into LKAB’s pilot blast furnace prior to quenching of the furnace. These briquettes were:

1. K1: Pellets fines + 6.5% cement – Coarsely ground (d₅₀ = 2512 µm).
2. K2: Pellets fines + 6.5% cement – Finely ground (d₅₀ < 74 µm).
3. K3: Pellet-fines (91.6%) + cement (6.5%) + coke (2%) ground very fine (d₅₀ < 74 µm)
4. K4: Pellet-fines (91.6%) + cement (6.5%) + coke (2%) ground coarse (d₅₀ = 2120 µm)
5. K5: Pellet-fines (89.6%) + cement (6.5%) + coke (4%) ground very fine (d₅₀ < 74 µm)
6. K6: Pellet-fines (89.6%) + cement (6.5%) + coke (4%) ground coarse (d₅₀ = 1980 µm)
When the reduced briquettes obtained by excavating the quenched pilot blast furnace are examined, it is observed that the briquettes do not swell inside the furnace. That no swelling occurs in briquettes inside the pilot blast furnace may be explained by the following:

- In the pilot plant, the reduction takes place in non-isothermal condition and the reserve zone has a temperature range of 815-1100°C. The earlier experiments have shown that the swelling takes place only in the range of 900-1000°C, and since in the pilot plant the briquettes stay in this temperature range only for a short time, they may not swell.
- In the pilot plant, hydrogen is present inside the furnace. Experiments have shown that the briquettes have less of a tendency to swell in the presence of hydrogen.

Even though the briquettes excavated from the pilot blast furnace do not swell, the optical microscopic examination of the briquettes shows some similarity to the briquettes reduced in the laboratory. **Figure 16** shows the optical micrographs of briquettes J1 at different degrees of reduction. The figure shows that at the hematite, magnetite and wustite stages the structure of pellet-fines particles is well bound. Unlike the case of laboratory reduced briquettes, in the briquettes reduced in pilot plant the pellet-fines particles do not always disintegrate. In fact, the disintegration takes place only in approximately 50% of the particles. On reduction to iron, a dense structure is formed, which prevents any swelling from taking place.

In cases where the pellet-fines particles disintegrate, the disintegration process starts right at the hematite stage and continues until the wustite stage. This behaviour matches the behaviour of briquettes tested in the laboratory furnace quite closely.
4. CONCLUSIONS

From the work carried out it may be concluded that:

1. The swelling of briquettes is suppressed in the presence of hydrogen.

2. The swelling depends upon the type of pellets used for making briquettes. Briquettes made using pellets containing a larger amount of slag-forming oxides, CaO, SiO₂, MgO and Al₂O₃ have been observed to swell more.

3. Even though the 75% of pellet-fines particles are broken Pellet A, the briquettes made of pellet-fines particles swell much more than those made of Pellet A. This is because it is mostly the under-fired and weaker Pellet A that breaks and ends up as pellet-fines particles.

4. The swelling of briquettes can be prevented if the briquettes are heated at high temperature (about 1275°C) in non-reducing environment prior to reduction. The heating causes cement to react with hematite and form slag. On cooling, the slag forms additional bonding. Due to high-temperature heating, the structure of pellet-fines particles also improves.

5. Swelling is not caused by the presence of free lime only; it is caused by the presence of all slag-forming oxides.

6. Replacing a part of the cement with lime, silica, magnesia or alumina may decrease the swelling.

7. Swelling is not caused by the presence of alkalis in the cement, but the swelling behaviour of the briquettes can be enhanced by the addition of alkalis.

8. The size of the briquette has no influence on swelling characteristics.

9. The presence of up to 4% coke in the briquette does not affect the swelling of briquettes, but beyond 4% it increases the swelling.

10. The briquettes do not swell during reduction inside the pilot plant. Like the briquettes tested in the laboratory, the pellet-fines particles present in the briquettes tend to disintegrate, resulting in the loss of strength.

ACKNOWLEDGEMENTS

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Maneesh Singh and Bo Björkman, Swelling behaviour of cement-bonded briquettes – Proposed model, ISIJ International (In press).
SWELLING BEHAVIOUR OF CEMENT-BONDED
BRIQUETTES – PROPOSED MODEL

Maneesh Singh and Bo Björkman
Division of Process Metallurgy
Luleå University of Technology
SE-971 87, Luleå, Sweden
{Maneesh.Singh, Bo.Bjorkman}@km.luth.se

Abstract

The cement-bonded agglomeration process is an alternative to the traditional balling-sintering process for recycling iron-rich by-products generated in iron and steel plants back to the blast furnaces. It has been observed that, under certain conditions, the briquettes containing pellet-fines show a tendency to swell catastrophically when reduced. This swelling is dependent upon a number of factors like: reducing temperature, composition of briquettes, particle size of raw material, amount of cement and composition of reducing gas. The SEM and optical micrographs do not show the formation of iron whiskers as the cause of swelling; instead, the swelling is due to the movement of reduced iron particles away from each other. It has been proposed that the swelling takes place in three steps: (a) fragmentation of weak pellet-fines particles during reduction to wustite; (b) formation of liquid slag due to reaction between CaO, MgO, FeO, SiO2 and Al2O3; (c) generation of high gas pressure due to formation and subsequent oxidation of metastable iron carbide.

Key Words:
Cement-bonded agglomerates, blast furnace, mechanism, swelling, reduction.

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 900-1000°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 950-1000°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 weight.

4. **Effect of Particle Size**: As the particle size (d₅₀) 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 d₅₀ of the raw mix.

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.

6. **Effect of Reduction in Steps**: The swelling in the case of three-step reduction using reducing gas having different compositions (N₂:CO:CO₂ = 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 (N₂:CO:CO₂ = 60:40:0 for 5 h) at 950°C for the same type of briquettes.

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.

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. **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.

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.

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 (N₂:CO:CO₂ = 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.
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 N₂+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 \(^8\).

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 \(^{14-16}\). 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 µm 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**

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 mm X 7 mm X 0.7 mm), were heated in a flowing nitrogen environment. The temperature was ramped at a rate of 8.3°C/min. Cu Kα (50kV, 30mA) 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 1a 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 (Figure 1b).

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 silicoferite (C$_3$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 (Figure 1c). When the magnetite is reduced to wustite, the cracks become wider (Figure 1d) due to the shrinking of structure during magnetite to wustite transformation.

![Figure 1a](image1a.png) ![Figure 1b](image1b.png) ![Figure 1c](image1c.png) ![Figure 1d](image1d.png)

Figure 1. Optical micrograph of pellet-fines particles showing the different stages in cracking of hematite grains during reduction at 950°C in N$_2$+CO (60:40) environment, (a) cured (grey particles are pellet-fines particles), (b) conversion to magnetite, (c) magnetite, and (d) wustite
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 C₂S and CaO. The portlandite (Ca(OH)₂) crystals start losing water at about 500°C and convert to CaO.

When the pellet-fines (75%) – cement (25%) briquette is heated in the nitrogen environment, the hydrated cement dissociates to C₂S and CaO. A part of C₂S reacts with CaO and Fe₂O₃ to form calcium silicoferite (C₃SF₃) and the rest of the C₂S remains unreacted. CaO also reacts with Fe₂O₃ to form CaO·Fe₂O₃ (Figure 3). Figure 4 is a SEM micrograph of a heated briquette sample showing very limited reaction between C₃S, olivine and hematite.

In the magnetite stage, there is almost no reaction between Fe₃O₄ and other oxides (Figure 5).
Figure 4. SEM of centre of a briquette after 0.5 h reduction showing the presence of unreacted dehydrated cement (C2S) and olivine along with hematite.

Figure 5. SEM of a portion inside a briquette after 0.5 h reduction showing the presence of unreacted dehydrated cement (C2S) and olivine along with magnetite.

Figure 6. High-temperature XRD of cured pellet-fines (75%) – cement (25%) briquette sample showing the phase transformations during reduction at 950°C in the N2+CO (60:40) environment.

Figure 6 shows the effect of reduction on the formation of various phases. When the magnetite converts to wustite, the reaction between the wustite, CaO, C2S and olivine takes place. The reaction between these leads to the formation of (Ca,Fe,Mg)2SiO4. 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, SiO2, FeO, MgO and Al2O3, 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 (Figure 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 minimal.
Figure 7. Effect of cement content on the softening and melting points of briquettes reduced at 950°C.

Figure 8. Secondary Electron image of reduced briquette showing reduced iron in a liquid slag.

Figure 9. Back Scatter Electron image showing the separation of CaO-SiO\textsubscript{2} and FeO phases. (Medium grey: calcium silicate, light grey: wustite)

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 Figure 7 shows, the minimum melting point for the CaO-MgO-FeO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{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\textsubscript{2} and FeO. In this particle, the CaO-SiO\textsubscript{2} and FeO rich regions also separate very distinctly. It is quite possible that the region contained only the CaO-SiO\textsubscript{2}-FeO phase in a molten state. On cooling, the FeO phase separated from the CaO-SiO\textsubscript{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-SiO₂ rich core, (b) CaO-SiO₂ 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. Optical micrograph of a reduced briquette showing wide-spread formation of CaO-MgO-FeO-SiO$_2$-Al$_2$O$_3$ phases.

Figure 13. Optical micrograph of a reduced briquette showing the formation of liquid slag over a large region.

Figure 14. Secondary Electron micrograph of reduced briquette showing spherical iron particles surrounding the CaO-MgO-SiO$_2$ phase.

Figure 12 shows the optical micrographs of the pellet-fines and cement interface. It shows that the formation of such CaO-SiO$_2$-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 (Figure 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 N₂+CO (60:40). The XRD shows the formation and subsequent disappearance of Fe₃C. It can be seen that as the reduction proceeds, the hematite reduces to magnetite and then to wustite. On further reduction Fe₃C is formed. With the passage of time, Fe₃C again oxidises forming Fe. The steps may be written as:

\[
\begin{align*}
3\text{FeO} + 5\text{CO} &= \text{Fe}_3\text{C} + 4\text{CO}_2 \\
\text{Fe}_3\text{C} + \text{FeO} &= 4\text{Fe} + \text{CO} \\
\text{Fe}_3\text{C} + \text{CO}_2 &= 3\text{Fe} + 2\text{CO}
\end{align*}
\]

Figure 16 is the room-temperature XRD of pellet-fines (75%) – cement (25%) briquette reduced at different temperatures, using N₂+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 Fe₃C.
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 Fe$_3$C 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 Fe$_3$C.

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 Fe$_3$C to Fe with the release of CO / CO$_2$. The CO / CO$_2$ may have exerted a pressure resulting in the formation of iron bubbles. In the same way, a reduction-oxidation reaction between Fe$_3$C 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, C$_2$H$_2$ gas was generated. This was probably due to the reaction between Fe$_3$C and H$_2$O. This experiment also shows the formation of Fe$_3$C.

### 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:

1. **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.

2. **Formation of liquid slag.** 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. This liquid slag acts as a lubricant.

3. **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, Fe$_3$C. In the first stage the iron carbide is formed and later this iron carbide oxidises back to iron and CO / CO$_2$ 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 take place till the formation of wustite; it takes place only during the formation of iron. As the amount of iron formed increases, more iron particles are pushed away from each other and from the core. Hence, swelling increases with an increase in degree of reduction.

3. **Effect of Raw Material Composition**: Cement-bonded briquettes made of crushed Pellet A do not swell while the cement-bonded briquettes of pellet-fines swell, even though the pellet-fines essentially contain 75% broken Pellet A. This is because the pellet-fines particles have a weaker structure and have a greater number of defects along which the transformation can preferentially take place. This leads to disintegration of pellet-fines particles but not of crushed Pellet A particles on reduction to magnetite.

4. **Effect of Particle Size**: Grinding of raw materials too finely spreads the cement throughout the briquette; hence, there is no region where a sufficient amount of slag can form. On the other hand, in the case of briquettes having larger particles, the cement is concentrated around large particles; hence, a sufficient amount of liquid slag can form around the large pellet-fines particles. As the reduction proceeds from the outer surface inwards, the slag also moves from outside to inside by the capillary motion through the cracks in the wustite particle.

5. **Effect of Reduction Conditions**: The lesser degree of swelling for isothermal reduction may be due to the introduction of the samples into a hot furnace resulting to some extent in simultaneous reduction and sintering before the complete breakdown of the cement bonding. This helps retain the shape of the briquette. On the other hand, in the case of non-isothermal reduction, the cement bonding breaks at low temperatures. The loss of cement bonding coupled with expansion due to reduction results in large-scale expansion.

6. **Effect of Reduction in Steps**: The swelling in three-step reduction (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 at 950°C for 5 h) for the same type of briquettes because in the three-step reduction the slag has sufficient time to diffuse away. In the absence of sufficient slag around the reduced iron particles, the particles do not have a chance to spread out much.

7. **Effect of Cement Content**: The decrease in swelling on increase in the cement content may be due to imbalance caused by increase in CaO and SiO\(_2\) over available FeO, so that the liquid slag is not formed. It is quite possible that the swelling would increase with increase in cement content given the sufficient time for FeO to react with CaO and SiO\(_2\) to form slag. This is partly proven by the fact that when the briquettes are reduced in a single stage using nitrogen + carbon monoxide (60:40), the maximum swelling takes place when the cement content is 4 weight percent; but when the briquettes are reduced in three stages the maximum swelling takes place when the cement content is 6-8 weight percent. This may be due to the fact that when the reduction takes place in one step FeO does not have sufficient time to react with CaO and SiO\(_2\); hence, only a small amount of dehydrated cement can turn to molten slag. On the other hand, when the reduction takes place in steps FeO has sufficient time to react with relatively more dehydrated cement to form molten slag. Hence, there is a larger requirement of cement for swelling.
8. **Effect of Hydration Time:** There is no effect of hydration time, since it is not the availability of free lime that causes swelling. Instead, it is the correct proportion of the oxides CaO, SiO₂, FeO, MgO and Al₂O₃ that causes the formation of liquid slag. For the formation of slag, it does not matter whether it is available as individual oxides or as combined phases.

9. **Effect of Cement Composition:** For slag having a low melting point to form, the oxides should be present in the correct proportions.

10. **Effect of Alkalis:** While the presence of alkali is not essential, since the slag formed already has a low melting point, its presence increases the swelling because it tends to lower the melting point even further.

11. **Effect of Binder Type:** The decrease in the swelling on addition of 25% CaO, SiO₂, MgO or Al₂O₃ to cement may be due to the increase in melting point of slag.

12. **Effect of Pre-firing:** There is no swelling if the briquette is pre-fired, because the CaO, SiO₂, MgO, Al₂O₃ and Fe₂O₃ react to form 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.

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

14. **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.

### 4. 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, 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.

3. In the presence of cement, there is a formation of metastable iron carbide at 950°C. Later, a redox reaction between Fe₃C and FeO can take place resulting in the formation of Fe and CO₂/CO.

4. A model has been proposed to explain the swelling of cement-bonded briquettes.

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PAPER VI

Maneesh Singh and Bo Björkman, Testing of cement-bonded briquettes under laboratory and blast furnace conditions, (Manuscript).
TESTING OF CEMENT-BONDED BRIQUETTES UNDER LABORATORY AND BLAST FURNACE CONDITIONS

Maneesh Singh and Bo Björkman
Division of Process Metallurgy
Luleå University of Technology
SE-971 87, Luleå, Sweden
{Maneesh.Singh, Bo.Bjorkman}@km.luth.se

Abstract

Cement-bonded agglomerates made of iron-rich by-products from the iron and steel industry have been used as burden material for blast furnaces for over a decade. In spite of that, their use is restricted to less than 5% of the total burden material, because at higher percentages the blast furnace starts behaving erratically. It is suspected that this is due to the disintegration of the agglomerates under high temperature and reducing conditions. In order to improve the quality of the cement-bonded briquettes, the effects of various parameters on their behaviour have been studied. The briquettes have been tested in the laboratory under isothermal test conditions and under simulated blast furnace conditions. The briquettes have also been tested in a pilot blast furnace. This paper describes the effect of different parameters on the performance of briquettes tested under the three conditions.

Keywords:
Reduction, swelling, pilot blast furnace, cement-bonded agglomerates, iron-rich by-products.

1. INTRODUCTION

Cement-bonded agglomeration has been in use for over a decade as a means of recycling iron-rich by-products generated at iron and steel plants back to the blast furnace. In this process, the iron-rich by-products are mixed with cement and other beneficial components, like coke fines and manganese slag, and agglomerated into pellets or briquettes. These agglomerates are then cured for about a month so that the agglomerates attain the required strength. The cement-bonded agglomeration process has a number of advantages over the traditional balling and sintering process, like (a) no generation of toxic gases; (b) possibility of inclusion of carbonaceous components; and (c) better economic viability.

In spite of these benefits and the fact that it has been in use for so long, the use of these agglomerates is restricted to less than 5% of the total burden. This is because blast furnace operation becomes erratic when these agglomerates constitute more than 5% of the burden. Plant operators attribute this poor performance to the loss of strength due to dissociation of binder at high temperatures. There is no direct evidence to support this conjecture, due to the fact that it is difficult to study the performance of agglomerates inside the furnace and to procure samples from an operating plant.

The laboratory investigation has shown that the strength of briquettes falls drastically when the briquettes are subjected to high temperature under reducing conditions. This is because under such conditions, the hydrated cement dissociates and the iron oxide based aggregates undergo phase transformations. To some extent, the performance may be improved by controlling the processing parameters; but as compared to the commercially available pellets, the cement-bonded agglomerates tend to lose more strength.

No test method has been specifically designed to study the behaviour of cement-bonded agglomerates. In the absence of any specific test methods, the test methods for pellets and lump ores often are used. Two of the most common tests are:
• ISO 4695 – Iron ore: determination of reducibility, in which the pellets are reduced at 950°C in N2+CO (60:40).
• ISO 4698 – Iron ore pellets – determination of relative free-swelling index, in which the pellets are reduced at 900°C in N2+CO (70:30).

The laboratory study has shown that the commercially available pellets do not swell under these conditions; but it has been observed that the cement-bonded briquettes made of these pellets may have a tendency to swell. The swelling does not take place because of the nucleation and growth 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 \(^{2,4}\).

Another important aspect is the reducibility of the cement-bonded agglomerates. The blast furnaces are designed and operated based on the characteristics of the main burden material. In Sweden, all the blast furnaces use pellets having diameter less than 1.5 cm as the source of iron ore. On the other hand, the briquettes produced are much larger; hence, they may have a different rate of reduction. Therefore, if any corrective action is not taken, the briquettes may reach the hearth without undergoing complete reduction.

LKAB has designed, built and operates an experimental blast furnace at Luleå, Sweden. This blast furnace is a scaled down model of an actual blast furnace and performs very much like a commercial blast furnace. While the results of this experimental blast furnace and actual blast furnaces may differ due to the scale of operation, this experimental blast furnace is a very powerful tool for studying the performance of burden material under test conditions. Compared to a commercial blast furnace, the experimental blast furnace has less burden compression, shorter gas and iron ore residence time, higher heat losses (per tonne of hot metal), lower hot metal temperature and higher hot metal silicon content. In spite of these differences, the experimental blast furnace simulates the chemical and thermal treatment of the burden material quite closely to that of a commercial blast furnace \(^5\)\(^{-}\)\(^9\).

The LKAB’s experimental blast furnace was used to test the properties of the cement-bonded briquettes. The results were then compared with those from the laboratory experiments. In the laboratory, the briquettes were reduced isothermally and by means of a simulated blast furnace test program. This paper discusses the results from the various tests carried out on cement-bonded briquettes.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

The experiments were conducted on briquettes made using nine by-products received from SSAB Merox AB with ordinary Portland cement as binder. Pellet-fines was a mixture of fines of Pellets A and Pellets B, two commercially available pellets collected by sieving before the pellets were fed to a blast furnace. As a reference, Pellets A were tested under similar conditions. The details concerning the materials and the experimental procedure followed are given in previously published papers \(^1\)\(^{-}\)\(^3\). Additional details are given below.

Effects of five parameters were studied by reducing the briquettes under different conditions. **Effect of Raw Material Composition**

Briquettes were made using two different compositions, Mix A and Mix B. Table 1 gives the composition of the two mixes. Two types of briquettes of each composition were made. In the first type, the raw materials were ground for a short time (about 5 min.) and in the other for a long time (almost 3 h). Hence, the raw materials had different particle size distributions. The briquettes were then prepared in the standard way. These four different types of briquettes were reduced isothermally at 950°C using N2+CO (60:40) in the laboratory. Four briquettes of each kind were also introduced into the pilot blast furnace at different times. These briquettes were excavated from different locations in the furnace. Figure 1 shows the location from which they were excavated. Table 2 gives a summary of the briquettes (A1-A8) tested.
Effect of Particle Size ($d_{50}$)

900 g of Mix A was ground in a steel ball mill for varying periods (1.0, 2.5, 5.0, 7.5, 10.0, 15.0, 120 min.). One set of material was also mixed for 30 min. in a small porcelain jar by rotating the material (without balls). These eight different types of raw material were used to prepare briquettes B1-B8. Table 3 gives the average particle size ($d_{50}$) of the ground raw materials used for making the briquettes. All the different types of briquettes were reduced isothermally at 950°C using N$_2$+CO (60:40) in the laboratory. Briquettes B1 and B8 were tested under simulated blast furnace conditions and briquettes B1, B4 and B8 were also tested in the pilot plant. Figure 1 shows the location from which they were excavated.

Effect of Load on Swelling

Eight briquettes (C1-C8) of Mix A were tested under different conditions to understand the effect of load on swelling (Table 4). In the laboratory, isothermal reduction was carried out at 950°C using N$_2$+CO (60:40). In isothermal tests, the briquettes tested without load were reduced hanging free and the briquettes tested with load were reduced under a constant load. In pilot plant test, the briquettes tested without load were put into basket without pellets surrounding them, and the briquettes tested with load were put into basket with Pellets A surrounding them. Figure 1 shows the location from which they were excavated.

Effect of Cement Content

Two sets of briquettes D1-D9 and E1-E11 were prepared to study the effect of cement content on the behaviour of cement-bonded briquettes. In the first set, nine different compositions (D1-D9) containing 0, 2, 4, 6, 8, 10, 15, 20 and 25 weight% cement and the rest pellet-fines were prepared in the normal way (Table 5). The briquette without any binder obviously had virtually no strength but retained its shape during handling, due to the presence of moisture. The D1-D9 briquettes were prepared using raw materials ground to two different particle size distribution. One of the sets of briquettes, DF1-DF9, was prepared using finely ground pellet-fines and the other, DC1-DC9, using coarse pellet-fines. In the laboratory, isothermal reduction was carried out at 950°C using N$_2$+CO (60:40). Briquettes having compositions D2 (2%), D5 (8%), D7 (15%) and D9 (25%) were also tested in the pilot plant. Figure 1 shows the location from which they were excavated.

In the second set, eleven different compositions (E1-E11) were prepared by inter-grinding pellet-fines (100-0 weight %) + cement (0-100 weight %) for 2 h. The briquettes were made in the normal fashion. These briquettes were then reduced isothermally at 950°C for 5 h. Behaviour of briquettes under the influence of three different environments was studied. These environments were: (a) only nitrogen, (b) N$_2$+CO+CO$_2$ (60:20:20), and (c) N$_2$+CO (60:40).

Effect of Coke Content

In the first set, 5 different briquettes (F1-F5) were prepared by grinding pellet-fines + cement (100, 98, 96, 94 and 92 weight %) with coke (0, 2, 4, 6 and 8 weight %) for 2 h. The briquettes were then made in the normal fashion. These briquettes were then reduced isothermally at 950°C for 3 h. The briquettes were then made in the normal fashion. These briquettes were isothermally reduced at 950°C using N$_2$+CO (60:40) for 3 h.

In the second set of experiments, four different types briquettes were tested to study the effect of coke content (Table 7). One set of these briquettes (G1, G2, G5 and G6) was reduced isothermally at 950°C for 3 h using N$_2$+CO (60:40) in the laboratory and the other set (G3, G4, G7 and G8) were tested in the pilot blast furnace. Figure 1 shows the location from which they were excavated in the pilot blast furnace.
### Table 1. Composition of briquettes to study the effect of raw material composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pellet-fines</th>
<th>Cutting slag (steel-work)</th>
<th>Cutting slag (rolling)</th>
<th>Grinding fines</th>
<th>Blasting dust</th>
<th>LD converter dust</th>
<th>Mill scale</th>
<th>Slag handling scrap</th>
<th>Manganese slag</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>93.5 Wt.%</td>
<td>1.5 Wt.%</td>
<td>1.5 Wt.%</td>
<td>0.9 Wt.%</td>
<td>2.0 Wt.%</td>
<td>1.3 Wt.%</td>
<td>3.5 Wt.%</td>
<td>15.5 Wt.%</td>
<td>4.6 Wt.%</td>
<td>6.5 Wt.%</td>
</tr>
<tr>
<td>Mix B</td>
<td>62.7 Wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Condition of briquettes to study the effect of composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
<th>A7</th>
<th>A8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>d50 (µm)</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>1743</td>
<td>1743</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>&lt;74</td>
</tr>
<tr>
<td>Test</td>
<td>Isothermal</td>
<td>Pilot Plant</td>
<td>Isothermal</td>
<td>Pilot Plant</td>
<td>Isothermal</td>
<td>Pilot Plant</td>
<td>Isothermal</td>
<td>Pilot Plant</td>
</tr>
</tbody>
</table>

### Table 3. Average particle size of raw materials of briquettes B1-B8 used to study the effect of particle size (d50).

<table>
<thead>
<tr>
<th>Sample</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
<th>B6</th>
<th>B7</th>
<th>B8</th>
</tr>
</thead>
<tbody>
<tr>
<td>d50 (µm)</td>
<td>30</td>
<td>70</td>
<td>149</td>
<td>253</td>
<td>1058</td>
<td>1595</td>
<td>2465</td>
<td>2512</td>
</tr>
</tbody>
</table>

### Table 4. Condition of briquettes to study the effect of load.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
</tr>
</thead>
<tbody>
<tr>
<td>d50 (µm)</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>2512</td>
<td>2512</td>
<td>2512</td>
<td>2512</td>
</tr>
<tr>
<td>Test</td>
<td>Isothermal</td>
<td>No</td>
<td>Pilot Plant</td>
<td>Yes</td>
<td>Pilot Plant</td>
<td>No</td>
<td>Isothermal</td>
<td>Yes</td>
</tr>
<tr>
<td>Load</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### Table 5. Composition of briquettes to study the effect of cement content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
<th>D5</th>
<th>D6</th>
<th>D7</th>
<th>D8</th>
<th>D9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet-fines (Wt.%)</td>
<td>100</td>
<td>98</td>
<td>96</td>
<td>94</td>
<td>92</td>
<td>90</td>
<td>85</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>Cement (Wt.%)</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>

### Table 6. Condition of briquettes to study the effect of coke content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
<th>G6</th>
<th>G7</th>
<th>G8</th>
</tr>
</thead>
<tbody>
<tr>
<td>d50 (µm)</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>&lt;74</td>
<td>2120</td>
<td>1980</td>
<td>2120</td>
<td>1980</td>
</tr>
<tr>
<td>Coke (Wt.%)</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Pellet-fines (93.5%) + Cement (6.5%) (Wt.%)</td>
<td>98</td>
<td>96</td>
<td>98</td>
<td>96</td>
<td>98</td>
<td>96</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>Test</td>
<td>Isothermal</td>
<td>Isothermal</td>
<td>Pilot Plant</td>
<td>Pilot Plant</td>
<td>Isothermal</td>
<td>Pilot Plant</td>
<td>Pilot Plant</td>
<td></td>
</tr>
</tbody>
</table>

4
2.2 Methods

**Pilot Plant Tests**

The pilot blast furnace is owned by LKAB and located at the premises of MEFOS, Luleå. It has the following specifications: hearth diameter = 1.2 m, height = 14 m, volume = 8.2 m³, production = 36 tonnes/24 h, blast temperature = 1200°C, coke / coal consumption = 510 kg/tonne hot metal 5-9). The briquette to be tested was placed in a steel basket and surrounded by commercially available Pellets A. Just prior to the quenching of the furnace the baskets were introduced into the furnace from the top at regular intervals. The furnace was then quenched by flushing nitrogen from the top. Within minutes the reducing gases were removed and the reduction stopped. After cooling for about ten days, the furnace was dissected by first removing the furnace top and then removing the burden material layer-by-layer from the stockline down to the hearth. The position and nature of baskets found inside the quenched furnace was recorded 2).

**Simulated Blast Furnace Tests**

The simulated blast furnace tests were carried out at LKAB’s CK-laboratory at Malmberget, Sweden. Figure 2 shows the schematic diagram of the reduction setup. It consists of two parts – the gas supply unit and the heating furnace. The gas supply of individual gases was from the gas cylinders and was regulated by computer-controlled differential pressure transducers. The reduction equipment consisted of an electric furnace with an inner diameter of 12.5 cm in which a vertical reduction tube was suspended from a load cell placed above the furnace. The load cell was connected to a computer that continuously recorded the weight of the reduction setup. The reduction tube had a double wall for preheating of the reduction gas in the space between the walls. The reducing gas entered from above, passed between the walls of the two tubes and entered from the bottom of the inner tube. The gas reached the reducing zone through a perforated base. A test briquette was placed above alumina pellets that covered the perforated base. The spent gas left the reduction tube from the top. A thermocouple placed beside the briquette measured and monitored the temperature inside the furnace.
Figure 2. Schematic diagram of the simulated blast furnace test set-up.

Figure 3 shows the temperature and gas-flow profile of the experiment. Two sets of experiments were carried out: (a) at low gas-flow rate, 10 l/min.; and (b) at high gas-flow rate, 50 l/min. For the sake of comparison, isothermal tests were also conducted in the setup. In that case, the briquettes were heated in a nitrogen environment till the briquettes attained 950°C. Reducing gas N₂+CO (60:40) was then introduced. Two sets of experiments were carried out: (a) at low gas-flow rate, 10 l/min.; and (b) at high gas-flow rate, 50 l/min.
3. RESULTS AND DISCUSSION

3.1. Formation of Slag Phase

Isothermal Reduction Tests

Figure 4 shows the effect of reduction potential on the formation of phases in the pellet-fines (75%) + cement (25%) briquette (DF9) at 950°C. At 25% reduction potential, the magnetite converts to wustite. At 75% reduction potential, wustite reduces to iron around the same reduction potential wustite reacts with CaO, C₂S and olivine to form (Ca,Fe,Mg)₂SiO₄. (Ca,Fe,Mg)₂SiO₄ phase is stable until over 87.5% reduction potential. At 100% reduction potential, the FeO part of the (Ca,Fe,Mg)₂SiO₄ phase is reduced to Fe and the rest turns to (Ca,Mg)₂SiO₄.

Figure 5 shows the effect of temperature on the formation of phases in the pellet-fines (75%) + cement (25%) briquette (DF9) at 62.5% reduction potential. Above 800°C, (Ca,Mg)₂SiO₄ forms but (Ca,Fe,Mg)₂SiO₄ does not form until the temperature reaches 1000°C. Only the amount of (Ca,Mg)₂SiO₄ increases with increasing temperature.

Figure 6 shows the effect of cement content in the briquettes (E1-E11) reduced at 950°C for 5 h using N₂+CO+CO₂ (60:20:20). The figure shows that the formation of (Ca,Fe,Mg)₂SiO₄ begins when the cement content is 40% and continues until it is 90%. The figure also shows that with the increase in percentage of cement the peak corresponding to (Ca,Fe,Mg)₂SiO₄ shifts to the left, implying increase in substitution of FeO with CaO. Hence, the formation and the structure of (Ca,Fe,Mg)₂SiO₄ depend upon the reduction potential, reduction temperature and cement to pellet-fines ratio.

Figure 7a is a photograph of a cross section of briquette B1 reduced isothermally at 950°C in N₂+CO (60:40) for 0.5 h. The figure shows distinct zones rich in hematite, magnetite, wustite and partially reduced wustite. SEM examination of the different zones shows that in Zone A the hematite does not react with dehydrated cement (Figure 7b). Similarly, in Zone B, magnetite, C₂S and olivine remain mostly unreacted (Figure 7c). In Zone C, wustite begins to react with C₂S and olivine (Figure 7d). In Zone D, wustite begins to reduce to iron (Figure 7e) and the molten slag phase is formed. Figure 7f 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.

Figure 8a shows the photograph of a cross section of briquette B1 reduced isothermally at 950°C in N₂+CO (60:40) for 3 h. The figure shows two distinct zones, E and G, rich in partially reduced wustite and iron, respectively. SEM of the zone E shows the presence of liquid slag (Figure 8b). In the SEM of the transition zone, F, (Figure 8c) the slag appears to be solidifying. This is probably because the removal of FeO again raises the melting point of the slag and it crystallises out as (Ca,Mg)₂SiO₄. Figure 8d is 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-SiO₂ region in the middle has a homogeneous distribution. In some regions where the MgO is in excess, the MgO-SiO₂ phase forms the core and the CaO-MgO-SiO₂ phase forms the shell.

Normally, the melting point of slag is rather high (above 1300°C). With proper proportions of CaO, SiO₂, FeO, MgO and Al₂O₃, 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. It is quite possible to achieve this at the interface of cement and pellet-fines particles. Most of the reduction experiments have been carried out at 950°C and the liquid slag still seems to form. This is possibly due to the exothermic nature of the reduction reaction that raises the temperature locally leading to the melting of the (Ca,Fe,Mg)₂SiO₄ phase, resulting in the formation of liquid slag.
Figure 4. Effect of reduction potential on the pellet-fines (75%) + cement (25%) briquettes heated at 950°C for 5 h. Reduction Potential = \( \frac{\text{CO}}{\text{CO} + \text{CO}_2} \) %

Figure 5. Effect of temperature on the pellet-fines (75%) + cement (25%) briquettes heated in N₂+CO+CO₂ (60:25:15) for 5 h.

Figure 6. Effect of cement content in pellet-fines + cement briquettes reduced in N₂+CO+CO₂ (60:20:20) environment at 950°C for 5 h.

On quenching, the slag freezes into three distinct layers: (a) MgO-SiO₂ rich core, (b) FeO-CaO-SiO₂ rich middle shell and (c) FeO rich outermost shell. Figure 9 is an optical micrograph of a particle in which separation of various phases is taking place. Figure 10 shows the optical micrograph of a particle in which the separation has taken place. On the outer shell, the CaO-SiO₂ and FeO phases do not separate very well and form only dispersed phases because the viscosities of these two phases are similar.

Theoretical calculations using simple mass balance have shown that on reduction, a briquette containing 6.5 weight percent cement can form up to 26 weight percent slag at the wustite stage. Even though the amount of slag formed at an instance of time would be less than this, since not all of it would be produced at the same time, the amount may still be substantial due to the fact that its reduction takes place at much higher reduction potential and temperature. Figure 11 shows that the molten slag may coalesce to spread over a large region. This slag may even envelop small wustite particles.
Figure 7. Photograph and Secondary Electron micrographs of cross section of briquette B1 reduced for 0.5 h at 950°C in N$_2$+CO (60:40). (b) SEM from position A; (c) SEM from position B; and (d) SEM from position C; (e) and (f) SEM from position D.
Figure 8. Photograph and Secondary Electron micrographs of cross section of briquette B1 reduced for 3 h at 950°C in N₂+CO (60:40). (b) SEM from position E; (c) SEM from position F; and (d) SEM from position G.

Figure 9. Optical micrograph of a reduced particle showing the separation of FeO and (Ca,Mg)_2SiO₄.

Figure 10. Optical micrograph of a reduced particle showing the separation of (a) MgO-SiO₂ rich core, (b) FeO-CaO-SiO₂ rich middle shell, and (c) FeO rich outermost shell.
Figure 11. Optical micrograph of a reduced briquette showing the formation of liquid slag over a large region.

Figure 12. Photograph of a cross section and optical micrograph of briquette B1 recovered from Position 4 in the pilot blast furnace.

Pilot Plant Tests

Microscopic examination of the samples obtained from the pilot blast furnace shows the formation of the (Ca,Fe,Mg)$_2$SiO$_4$ phase in the briquettes. Figures 12a is a photograph of the cross section of briquette B1 obtained from Position 4. The figure shows the presence of a large unreduced core in the briquettes; on the other hand, the pellets present next to them do not have such large unreduced cores. There are probably two reasons for this. Firstly, the briquettes have lower overall rate of reduction of briquette due to their larger size. Secondly, the formation of liquid slag probably hinders the diffusion of the reducing gases through the briquettes. An optical micrograph of the core of the briquette shows that the briquette has a significant amount of slag phase enveloping the wustite grains (Figure 12b). Since the slag itself reduces at high reduction potential (above 82.7%), its presence around the wustite grains may lower the availability of the reducing gases to wustite, thereby decreasing the reduction rate of the briquette. This slag formation does not take place in the Pellets A (Figure 12c); hence, the reduction rate is not affected.

The presence of unreduced core in the briquettes may affect the operation of the pilot blast furnace, since it has been designed and operated based on the reduction kinetics of the pellets. They may reach the cohesive zone with a large percentage of wustite. This would in turn increase the coke requirement because the unreduced portion will have to be reduced by direct reduction or else the wustite would end up in slag.
3.2. Effect of Composition

Isothermal Reduction Tests

Figure 13 shows the effect of isothermal reduction on the strength of briquettes made of A1, A3, A5 and A7. The figure shows that the strength falls drastically up to 10% reduction and beyond that there is no effect of degree of reduction. The figure also shows that A1 and A5 have similar strength characteristics, but A7 has slightly better strength than A3. This is probably because the pre-reduced and flaky/angular components of the briquette act as a skeleton to hold the briquette together. This imparts additional strength. It can also be noticed that in all the cases the pellets have higher strength 1).

Figure 14 shows the effect of isothermal reduction on the swelling of briquettes. The figure shows that the swelling of A1 is more than that of A5, and the swelling of A3 is more than that of A7. This is probably again due to the fact that Mix B contains more pre-reduced components that do not swell during reduction.

Pilot Plant Tests

The compression strength tests were not carried out on the samples from the pilot plant because there were so few samples, but the physical touch and sight gave some indication of strength. The examination of excavated briquettes shows that the strength of briquettes falls initially till Position 3. The briquettes from Position 4 contain a large percentage of reduced and sintered iron; hence, they are very strong. The decrease in strength was greater in the case of briquettes made of Mix A than in the case of briquettes made of Mix B.

Examination of the reduced briquettes obtained by excavating the quenched pilot blast furnace reveals that the briquettes do not swell catastrophically inside the furnace (Figure 14).

The experiments show a distinct possibility of improving the quality of cement-bonded briquettes by replacing a part of the pellet-fines with other iron rich wastes from steel plants like mill scales, cuttings, blasting dust, etc.
3.3. Effect of Particle Size ($d_{50}$)

Isothermal Reduction Tests

*Figure 15* shows the effect of particle size on the strength of briquettes \(^1\). The figure shows that the strength of briquettes – cured or reduced – increases with the increase in fineness. This may be due to (a) the increase in compaction, (b) increase in the number of contact points, (c) there are fewer voids, and (d) elimination of larger friable pellet-fines particles that are more prone to rupturing.

*Figure 16* shows the effect of particle size ($d_{50}$) on the swelling of briquettes. As the particle size 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 material \(^2\).

*Figure 17* shows the reduction profile of the briquettes reduced isothermally in N\(_2\):CO (60:40) environment for 950°C. The figure shows that the overall rate of reduction of the briquettes is independent of the particle size of the raw material. The figure also shows that the rate of reaction is much faster for Pellets A.

*Figures 7a and 8a* show that when the briquette B1 is reduced, the reduction takes place topochemically. The boundaries between the different layers are quite sharp. On the other hand, the cross-sections of reduced Pellets A show a more diffused boundary. Mercury porosimetry showed that the B1 briquettes have an overall porosity of 33% and average pore diameter of 0.1 µm; and the Pellets A have overall porosity of 19% and average pore diameter of 6 µm. Hence, the low average pore diameter of the B1 briquettes makes the reaction predominantly diffusion-controlled, resulting in the formation of distinct layers. On the other hand, the relatively larger pore diameter of Pellets A makes the reaction mixed – pore diffusion and chemical reaction-controlled, resulting in a more diffused boundary.

The overall porosity of the briquettes has been found to be independent of the particle size ($d_{50}$). This is probably because of the two opposing phenomena:

- Increase in inter-particle voids with increase in particle size.
- Decrease in porosity due to increase in the volume percentage occupied by more dense pellet-fines.

Hence, the overall reduction rate is also independent of $d_{50}$.

Simulated Blast Furnace Test

The briquettes reduced under simulated blast furnace test showed far less tendency to swell than the briquettes reduced isothermally. *Table 7* gives the summary of experiments carried out to study the swelling of briquettes when tested by means of a simulated blast furnace program. The experiments show that under the simulated blast furnace test the swelling of briquettes is much less compared to the reduction carried out isothermally using N\(_2\)+CO (60:40). The experiments also show that the swelling increases with increase in the flow rate of the reducing gases.

Pilot Plant Tests

Examination of the briquettes recovered from the pilot blast furnace showed that the briquettes made from coarsely ground raw material are more prone to disintegration inside the furnace. The B8 briquettes have rather low strength and tend to fall apart. The B8 briquettes recovered from the upper portions of the shaft had their edges broken and those recovered from the lower portions of the shaft had been crushed (*Figure 18*). On the other hand, the B1 briquettes were recovered almost intact (*Figure 12*). This may be because the bondings between the pellet-fines particles in the B8 briquettes are not strong and the particles tend to break loose, causing the briquettes to break up. On the other hand, higher compaction in the B1 briquettes gives better strength, even after the loss of binding cementitious phase. Hence, it seems that the strength of briquettes may be improved by grinding the raw material finely or by using only the fine fractions.
Table 7. Summary of experiments conducted using LKAB’s experimental set-up at Malmberget.

<table>
<thead>
<tr>
<th></th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
<th>Experiment 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Profile</td>
<td>Isothermal (950°C)</td>
<td>Isothermal (950°C)</td>
<td>Non-isothermal (Programmed)</td>
<td>Non-isothermal (Programmed)</td>
</tr>
<tr>
<td>Reducing Gas</td>
<td>N₂+CO (60:40)</td>
<td>N₂+CO (60:40)</td>
<td>N₂+CO+CO₂+H₂</td>
<td>N₂+CO+CO₂+H₂</td>
</tr>
<tr>
<td>Gas Flow Rate (l/min)</td>
<td>10</td>
<td>50</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Reduction time (h)</td>
<td>3.5</td>
<td>3.25</td>
<td>4.5</td>
<td>4.25</td>
</tr>
<tr>
<td>Degree of Reduction (%)</td>
<td>68</td>
<td>68</td>
<td>68</td>
<td>68</td>
</tr>
<tr>
<td>Volume Expansion (%)</td>
<td>120</td>
<td>144</td>
<td>31</td>
<td>54</td>
</tr>
</tbody>
</table>

Figure 15. Effect of particle size on the strength of briquettes made of Mix A (B1-B8): (a) after curing; and (b) after reducing in N₂:CO (60:40) environment for 950°C for 1 h.

Figure 16. Effect of average particle size (d₅₀) on the volume expansion of briquettes made of Mix A (B1-B8): (a) after isothermal reduction at 950°C for 3 h in N₂:CO = 60:40; and (b) after reduction in pilot blast furnace.

Figure 16 shows the effect of particle size of raw material on swelling for briquettes reduced in the pilot plant. The figure shows that the particle size has very little effect and the briquettes have no tendency to swell catastrophically.

The work has shown that the results from the isothermal tests do not match well with the results from the pilot plant tests due to the tendency of briquettes to swell abnormally under isothermal test conditions. On the other hand, there is a close match between the results from the pilot blast furnace and those from the simulated blast furnace experiments.

The experiments clearly show that the quality of briquettes can be improved by grinding the raw material. While this would improve the performance of the briquettes, it would also increase the cost of production. One of the options may be to use only the finer fractions of the pellet-fines and find some other application of the coarser fraction.
Table 8. Effect of load on swelling and compression strength of briquettes on reduction at 950°C in N₂+CO (60:40) environment with and without load.

<table>
<thead>
<tr>
<th>d₅₀ (µm)</th>
<th>Cured Strength (kN)</th>
<th>Without Load</th>
<th>With Load</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Swelling (Volume%)</td>
<td>Strength (kN)</td>
<td>Swelling (Volume%)</td>
</tr>
<tr>
<td>&lt;74</td>
<td>28.7</td>
<td>25 (C1)</td>
<td>15 (C2)</td>
</tr>
<tr>
<td>2512</td>
<td>20.2</td>
<td>175 (C5)</td>
<td>36 (C6)</td>
</tr>
</tbody>
</table>

Figure 17. Effect of particle size on reduction of cement-bonded briquettes made of Mix A (B2-B8) when reduced isothermally in N₂:CO (60:40) environment for 950°C.

Figure 18. Photograph of a cross section of briquettes B7 recovered from Position 4 in the pilot blast furnace.

3.4. Effect of Free Swelling

Isothermal Reduction Tests

Table 8 shows the strength of briquettes after curing, after isothermal reduction without load (C1 and C5), and after isothermal reduction with load (C2 and C6). It can be seen that when the briquettes have no tendency to swell catastrophically (C1 and C2) there is no substantial difference in strength of briquettes on reduction with and without load. On the other hand, when the briquettes have a tendency to swell catastrophically on isothermal reduction (C5 and C6), then the strength of briquette reduced under load (C6) is more than the strength of briquette reduced without load (C5). This may be due to the fact that, under load, the briquettes are not free to swell, as a result of which the briquettes remain rather compact.

Pilot Plant Tests

When the briquettes recovered from the pilot blast furnace were examined, it was seen that briquette C3 suffered from some chipping of the edges; but briquette C4 did not suffer any breakage. Similarly, the C7 briquettes suffered more breakage compared to the C8 briquettes. This shows that in the presence of surrounding pellets the briquettes are able to retain more strength. Overall, the C3 and C4 briquettes suffered far less breakage than briquettes C7 and C8.
As the briquettes move down the stack in the pilot furnace, two opposing factors may affect the behaviour of the briquettes. On one hand, the load of burden material may help the briquettes to retain more strength; on the other hand, the same load may crush the briquettes. The pilot plant experiments show that the briquettes surrounded by pellets retain their shape until they have reached the lower region of the stack. At the low portions of the stack, most of the briquettes found were crushed to some extent, unlike the pellets that retain their spherical shape. The distortion took place in spite of the fact that the briquettes were kept in a steel basket that provided some protection. On the other hand, the briquettes kept in a basket without any pellets were crushed more. Figure 19 shows the baskets excavated from different positions. The figure shows increased distortion of the baskets as they move down the stack. Hence, it may be expected that in real blast furnace, where the stack is higher, the briquettes would suffer more crushing and failure.

Figure 20 shows the swelling of briquettes when reduced in the pilot plant. The figure shows that when the briquettes made of finely ground raw material (C3 and C4) are reduced in the pilot plant the degree of swelling is slightly less when the briquettes are surrounded by pellets (C4). Since the briquettes made of finely ground material themselves naturally have low swelling tendency, the difference in the swelling with and without the surrounding pellets is not significant. On the other hand, the briquettes made of coarsely ground raw material (C7 and C8) have a greater tendency to swell, so when they are surrounded by other pellets (C8), the tendency to swell falls more drastically. In all these cases the swelling does not take place due to the “popping” of large pellet-fines particles, as it does in the case of isothermal reduction. Instead of popping of the particles, the swelling takes place due to widening of cracks that form in the briquettes due to the loss of cementitious binder.
Figure 20. Swelling of briquettes (a) after reduction with free swelling for 5 h at 950°C in N₂+CO (60:40); (b) after reduction under load for 5 h at 950°C in N₂+CO (60:40); and (c) after reduction in pilot plant.

Figure 21. Effect of cement content in pellet-fines + cement briquettes heated nitrogen environment at 950°C for 5 h.

In the actual plant, pellets or other briquettes would always surround the briquettes. In that case, the briquettes would have a greater tendency to retain the shape and strength. In the lower part of the stack, the briquettes made of coarse raw material may distort and break. This may lead to generation of fines that can reduce the gas permeability and increase the amount of dust in the stack gas. On the other hand, breakage may improve reducibility.

3.5. Effect of Cement Content

Isothermal Reduction Tests

Figure 21 shows that when the pellet-fines – cement briquettes (E1-E11) are heated in a nitrogen environment, with the increase in cement content the amount of C₃S increases with a corresponding decrease in the amount of Fe₂O₃. At about 30% cement content (E4), the free lime (CaO) begins to form. The amount of CF formed reaches a maximum at about 40% cement content (E5). Beyond that, C₂F begins to form and reaches a maximum at 70% cement (E8). The structure of the cement matrix also changes with the cement / pellet-fines ratio.

The TG/DTG analysis of the pellet-fines + cement samples shows that all the water present in the micropores escapes by 400°C, and dehydration of hydrated lime takes place between 400 and 600°C, and the dehydration of CSH gel takes place above 600°C (Figure 22). Figure 23 shows that the effect of cement content on the weight loss for briquettes G1-G8 at 400°C and 600°C. The figure shows that with increase in the cement content the amount of water present in hydrated lime and in the micropores of CSH gel increases with corresponding decrease in the amount present as CSH gel. This clearly implies the presence of different structures of the CSH gel at different compositions.

A simple mass balance indicates that the dehydration reaction follows the equation:

\[
aC_nS_yH + bCH \rightarrow cC_2S + dCaO + eH_1 + fH_2
\]

H₁: Water from Ca(OH)₂ between 400-600°C
H₂: Water from CSH gel - above 600°C

For paste cement only:

\[
2C_4S_AH + 2.50CH \rightarrow 4C_2S + 2.50C + 2.50H_1 + 2H_2
\]

For Pellet-fines (75%) + Cement (25%) briquettes:

\[
C_7S_AH_5 + 3.75CH \rightarrow 4C_2S + 2.75C + 3.75H_1 + 5H_2
\]

For Pellet-fines (94%) + Cement (6%) briquettes:

\[
2C_3S_AH_7 + 4.70CH \rightarrow 4C_2S + 2.70C + 4.70H_1 + 14H_2
\]
Figure 22. TG, DTG and DTA of pellet-fines (75%) + cement (25%) (DF9) in nitrogen environment. A: Loss of free moisture, B: Dehydration of portlandite to lime, C: Dehydration of CSH gel, D: Melting of the mixture.

Figure 23. Effect of cement content on the weight loss of briquettes DF1-DF9 when heated at 400°C and 600°C in nitrogen.

Figure 24. Effect of cement content on the strength of briquettes DC1-DC9 (a) cured; and (b) reduced isothermally at 950°C in N₂+CO for 1 h.

As can be seen, with decrease in the cement content the H/C and S/C ratios increase in the CSH phase. This may be due to the fact that the decrease in cement content leads to an increase in porosity, which in turn leads to the increased access of moisture. The increase in available moisture also allows more formation of Ca(OH)₂ which results in the decrease in C in the CSH gel; hence, an increase in S/C ratio. The change in the structure of CSH with the change in cement content in the briquette explains why the increase in moisture content is not equally proportional to the increase in cement content. Hence, when the amount of cement increases from 4 to 25%, the amount of moisture increases from 2 to only 7%.

Figure 24 shows the effect of cement content on the strength of briquettes DC1-DC9 – after curing and after reduction. As is to be expected, the strength of briquettes increases with increasing cement content. This is probably due to the increase in the binding of material and decrease in particle size (d₅₀). Similarly, the strengths of briquettes DF1-DF9 – after curing and after reduction – have been found to increase almost linearly with increase in cement content ¹. 

¹: Source reference needed.
Figure 25. Effect of cement content on the swelling of briquettes.

Figure 26. Effect of cement content on the reduction of the cement-bonded briquettes.
(Reduction temperature = 950°C, N₂+CO (60:40)

Figure 25 shows the effect of cement as binder on the swelling of briquettes reduced isothermally.¹ The figure shows that 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. Some amount of cement is essential for swelling to take place, because in the absence of it liquid slag cannot form. On the other hand, the decrease in swelling with increase in cement content may be due to:

- decrease in d₅₀ of raw mixture due to increase in finely ground cement content;
- decrease in the amount of pellet-fines;
- increase in the melting point of (Ca,Fe,Mg)₂SiO₄ due to increase in the CaO. This reduces the formation of liquid slag.

Figure 26 shows the effect of cement content on the reduction profile of the briquettes. It may be seen that in the first 120 min there is almost no effect of cement content on the reduction profile. This may be due to two opposing factors:

- Increase in porosity, due to the conversion of impervious CSH gel into porous dehydrated cement, with increase in cement content.
- Decrease in porosity, due to decrease in the degree of swelling, with the increase in cement content.

After about 120 min. the rate of reduction slows down slightly with an increase in the amount of cement. This is probably because when the wustite forms it reacts with SiS and olivine to form (Ca,Fe,Mg)₂SiO₄. With the increase in cement content not only does the amount of (Ca,Fe,Mg)₂SiO₄ formed increase; the reduction potential at which (Ca,Fe,Mg)₂SiO₄ is formed also decreases. Hence, with increase in cement content, more (Ca,Fe,Mg)₂SiO₄ is formed and at earlier time. As compared to wustite, this phase reduces at higher reduction potential; hence, with an increase in the cement content there is a decrease in the reduction rate.

Pilot Plant Tests

Of all the briquettes (D2, D5, D7 and D8) put into the blast furnace, only a few briquettes could be recovered. These briquettes were from the upper half of the shaft. Among these briquettes, it is observed that the strength of briquettes increases with an increase in the cement content. Also, none of the briquettes show any abnormal swelling tendency.
With the increase in cement content, the amount of moisture – free and bound – also increases. Inside the blast furnace most of the free moisture escapes from the top part of the shaft and may not adversely affect its operation, except for increasing the fuel demand. On the other hand, the bound water present in the briquettes is released at high temperature. A substantial part of it may be released in the thermal reserve zone. This may lower the temperature of the thermal reserve zone.

The increase in cement content also increases the amount of slag formed. Normally, a blast furnace uses less than 10% cement-bonded agglomerates as burden material, and these agglomerates contain less than 10% cement as binder; this leads to an increase of less than 8% slag. When the blast furnace operates on high-quality iron ore/pellets, this additional slag formation may not be a disadvantage. On the contrary, it may improve the performance by making the movement of burden material smoother.

Another aspect of the increase in the cement content is the decrease in the overall reduction rate of the briquette because of the increased formation of relatively more stable (Ca,Fe,Mg)\(_2\)SiO\(_4\) as compared to the wustite. Hence, it is expected that the briquette would contain a large unreduced core when it reaches the cohesive zone.

Thus, with the increase in the cement content the coke requirement also increases due to:
- Increase in water to be removed.
- Increase in slag to be melted.
- Increase in wustite that needs to be reduced directly.

The increase in cement content may increase the strength of the briquettes, but it also increases the cost of production, the cost of transporting extra weight – including that due to cement, bound moisture and free moisture, and the cost of blast furnace operation.

### 3.6. Effect of Coke Content

#### Isothermal Reduction Tests

Figure 27 shows the effect of coke content on the strength of cement-bonded briquettes (F1-F5) after curing. The figure shows a near linear decrease in strength with increase in coke content. The fall in strength can be due to:
- Coke is hydrophobic in nature; as a result, the bonding between the cement matrix and coke particles is not strong.
- Coke particles are soft and friable, hence, prone to rupturing under load.

Figures 27 and 28 show the effect of coke content on the swelling of briquettes when reduced isothermally. The figures show that at up to 4% coke content the tendency of a briquette to swell increases slightly and beyond that, the swelling increases drastically with increase in coke content. The increase in swelling with increase in coke content may be due to:
- Increase in degree of reduction.
- Increase in the gas pressure inside the briquette due to the oxidation of carbon.
- Increase in the formation of liquid slag. The ash from the coke can react with C\(_2\)S\(_2\), olivine and FeO to form (Ca,Fe,Mg)\(_2\)SiO\(_4\). The oxidation of carbon can provide the additional heat to melt the (Ca,Fe,Mg)\(_2\)SiO\(_4\).

#### Pilot Plant Tests

The visual examination of the briquettes made of raw mixture containing coke that were recovered from the pilot plant showed that the addition of coke reduced the strength of the briquettes. The G4 and G8 briquettes had large cracks running along the circumference.

Figure 28 shows that the briquettes containing 4% coke have slightly more tendency to swell compared to briquettes containing 2% coke when reduced in pilot blast furnace.
Figure 27. Effect of coke content on the (a) room temperature strength of cement-bonded briquettes (F1-F5) after curing and; (b) swelling of cement-bonded briquettes (F1-F5) after isothermal reduction at 950°C using N₂+CO (60:40) for 3 h.

Figure 28. Effect of coke content on the swelling of cement-bonded briquettes (G1-G8) after curing.

Figure 29. Optical micrographs of briquette E8 recovered from Position 2 showing the formation of slag using the coke ash.

Optical microscopic examination of the samples showed the presence of partially burnt coke particles in all the samples. This shows that all the coke is consumed only towards the lower portion of the stack. Figure 29 shows the optical micrograph of briquette G8 retrieved from Position 2. The figure shows the formation of slag probably using ash from coke, since structurally the slag looks different from the slag formed from wustite+C₂S+olivine (Figure 10).

Earlier work has shown the presence of a large unreduced core in the briquettes. Addition of pulverised coke can improve the reduction kinetics (reduction rate and reducibility) owing to the presence of a larger number of reaction sites available simultaneously and due to shorter diffusion distances. It also allows recycling of cheaper carbonaceous materials present in the dust, like blast furnace flue dust, or as coke breeze to be included in the agglomerates and used in place of costlier metallurgical coke. The drawback of the addition of carbon is that it usually lowers the strength (Figure 27); hence, the amount of coke in the briquette should be kept to the minimum.
3.7. Validation of Swelling Model

The cement-bonded briquettes reduced isothermally at 950°C using N₂+CO (60:40) show a tendency to swell catastrophically. The catastrophic swelling does not take place due to the formation of iron whiskers; instead, it takes place due to popping up of individual pellet-fines particles. It has been proposed that the swelling of cement-bonded briquettes takes place in three 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.

- **Formation of liquid slag.** The CaO, SiO₂, FeO, MgO and Al₂O₃ react together to form a phase having low melting point. Due to the heat released locally 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 particle 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 this iron carbide later oxidises back to iron and CO / CO₂ by taking oxygen from wustite or carbon dioxide.

**Figure 30.** Optical micrographs of briquettes reduced isothermally at 950°C in N₂+CO (60:40) showing various stages in reduction, (a) cracking of hematite grain, (b) disintegration of hematite grain, (c) formation of slag with a low melting point, and (d) reduction to iron.
Even though the briquettes excavated from the pilot blast furnace were not swollen, optical microscopic examination of the briquettes shows some similarity to the briquettes reduced in the laboratory. Figure 30 shows the optical micrograph of briquettes reduced isothermally at 950°C in N₂+CO (60:40) and Figures 31 and 32 show optical micrographs of briquettes and Pellets A, respectively, recovered from pilot blast furnace.

Figure 30a shows the development of cracks in the grains of pellet-fines particles. These cracks progress so that the whole particle disintegrates into small particles (Figure 30b). Figure 30c shows the reaction between the olivine, wustite and calcium silicates to form slag with a low melting point. On cooling, the slag again solidifies in stages with MgO-SiO₂ phase at the centre, surrounded by a CaO-SiO₂-FeO phase and FeO forming the outermost shell. Figure 30d shows that the reduced iron particles have been pushed apart by some force. This movement of iron particles away from each other causes swelling.

Figure 31 shows the optical micrographs of briquettes recovered from pilot plant. It can be seen that Figures 31a, 31b and 31c match Figures 30a, 30b and 30c, respectively. One noticeable difference was that, while in the laboratory-tested briquettes almost all the particles disintegrate, in the pilot plant tested briquettes, substantial amount of particles do not disintegrate. Figure 31d shows that the iron particles did not move away but remained closely together; hence, there was no swelling.
Figure 32. Optical micrographs of Pellet A tested in pilot plant, (a) cracking of hematite grain, (b) wustite state, (c) olivine grain in a pellet, and (d) reduction to iron.

Figure 32 shows the optical micrographs of reduced Pellets A recovered from the pilot plant. Figure 32a shows that some of the grains in the pellets have a tendency to crack, but a majority of them do not. As a result, at the magnetite or wustite state the hematite grains are quite close to each other (Figure 32b). Figure 32c shows that the olivine in the pellets does not take part in formation of slag with a low melting point. Figure 32d shows that the reduced particles of iron stay quite close to each other and form an interlocked laminar structure. This imparts high strength to the pellets. Optical microscopic examination of pellets reduced isothermally at 950°C in N₂:CO (60:40) shows similarity with those reduced in the pilot plant.

The difference in the behaviour of the briquettes when tested in the laboratory and when tested in the pilot plant may be explained by the fact that the laboratory tests do not replicate the actual conditions inside a blast furnace. In the laboratory, all the experiments are carried out under isothermal conditions (950°C) using a fixed environment (N₂:CO=60:40) as stipulated by the reduction test ISO 4695. This test intends to simulate the reserve zone of a typical blast furnace. On the other hand, the conditions inside the pilot blast furnace are different in many ways. Two important differences are:
In the pilot plant, the reduction takes place under non-isothermal conditions. There are four general zones inside the furnace – the drying, reserve, cohesive and dripping zones. The reserve zone has a temperature range of 800-1100°C, retention time of approximately 2 h 30 min and a temperature gradient of 2°C/min. The earlier experiments have shown that swelling takes place only in the range of 900-1000°C, and since in the pilot plant the briquettes stay in this temperature range for only a short time, they may not swell.

In the pilot plant, there is hydrogen present inside the furnace. Experiments have shown that the briquettes have less tendency to swell in the presence of hydrogen.

The conditions inside the pilot plant closely approximate those of an actual blast furnace. Still, conditions vary from blast furnace to blast furnace depending upon the design and operation. Larger blast furnaces normally have larger isothermal reserve zone having a temperature of about 950°C. Under such conditions, it may be possible for the briquettes to swell.

4. CONCLUSIONS

From the work carried out it may be concluded that:

1. When the cement bonded briquettes are reduced at the wustite stage, dehydrated cement (C₂S and CaO) reacts with olivine (from pellet-fines) and wustite to form a (Ca,Fe,Mg)₂SiO₄ phase. The phase has a low melting point and melts due to the heat released by the reduction of wustite to iron in the vicinity. The molten slag reduces at high reduction potential and hence reduces the overall rate of reduction of the briquettes.

2. The briquettes containing pre-reduced and angular / flaky by-products have higher strength and are less prone to swelling.

3. The use of finely ground material for making briquettes increases the strength of the briquettes and reduces their tendency to swell catastrophically. The examination of briquettes tested in the pilot blast furnace shows that the briquettes made of finely ground material can withstand the burden load but those made of coarsely ground material deform under the load.

4. The briquettes do not have a tendency to swell when reduced under simulated blast furnace conditions.

5. Increase in cement content in the briquettes increases the strength and lowers the tendency to swell. Increase in cement content also adversely affects blast furnace operation because it increases the amount of slag formed and moisture to be removed and it decreases the rate of reduction.

6. Addition of coke fines in the cement-bonded briquettes increases the reduction rate of the briquettes but lowers the strength.

7. When the cement-bonded briquettes are reduced isothermally at 950°C using N₂+CO (60:40) the briquettes swell catastrophically, but when the briquettes are tested in pilot blast furnace the briquettes do not swell catastrophically. It has been proposed that the swelling of briquettes reduced isothermally at 950°C using N₂+CO (60:40) takes place in three steps:
   - Disintegration of pellet-fines particles.
   - Formation of slag having low melting point.
   - Generation of localised high gas pressure due to formation and oxidation of metastable iron carbide.

   Of the three steps, the first two take place in the pilot plant; but the third step does not take place in pilot plant; hence, the briquettes do not swell when tested in pilot blast furnace.
ACKNOWLEDGEMENTS

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REFERENCES

Education
Doctoral Thesis

Department
Chemical and Metallurgical Engineering

Division
Process Metallurgy

Title
Studies on the Cement-Bonded Briquettes of Iron and Steel Plant By-products as Burden Material for Blast Furnaces

Author
Maneesh Singh

Summary
During the various stages of iron and steel production a number of iron bearing by-products are generated. These by-products can be made into cement-bonded agglomerates for use as burden material for blast furnaces. In order to improve the quality of agglomerates, the effect of various processing parameters on the properties of cement-bonded briquettes has been studied.

It has been found that the room-temperature properties of briquettes depend upon various processing parameters like solid / water ratio, vibration time, briquetting force, compression time and particle size distribution of the raw material.

The study has also shown that the strength of briquettes decreases after heating in a nitrogen environment and after reduction. The strength of briquettes can be increased by increasing the amount of pre-reduced / flaky components, increasing the amount of cement and decreasing the particle size of the raw material.

Under certain reducing conditions, the cement-bonded briquettes exhibit a tendency to swell catastrophically. This happens especially during the reduction of wustite to iron at 950°C using CO as the reducing gas. The briquettes that contain coarse pellet-fines particles are specially prone to swelling since the pellet-fines contains a large percentage of under-fired and weak fraction of the pellets. This swelling can be controlled by grinding the raw material finely, increasing the cement content, and adding .....(cont.)

Examiner/Supervisor
Prof. Bo Björkman

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