



Effect of adding limestone on the metallurgical properties of iron ore pellets



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ABSTRACT

In order to produce high-quality pellets with good reducibility and superior softening and melting properties, certain additives are important. One of the most common fluxing materials for iron ore pellet production is limestone, which is mainly calcium oxide (CaO). In this study, the effect of adding limestone on the metallurgical properties (reducibility, swelling, cracking, softening temperature, Low-Temperature Disintegration, Cold Crushing Strength) of acid iron ore pellets was investigated using a comprehensive set of metallurgical laboratory tests.

The dynamic reducibility test under unconstrained conditions showed a higher final degree of reduction in limestone-fluxed pellets compared to non-fluxed ones. Also in the reduction–softening test under load, the fluxed pellets reduced to a higher final degree of reduction, although they started to soften at a somewhat lower temperature. Swelling and cracking of the pellets during dynamic reduction were slightly increased by the addition of limestone, but not remarkably. Adding limestone slightly decreased the Cold Crushing Strength and increased the formation of fines in the hematite to magnetite reduction stage in the LTD test. However, all four parameters (CCS, LTD, swelling, and cracking) are within the acceptable range for blast furnace use.

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1. Introduction

In general, the main types of pellets for the purposes of making iron are acid, basic and fluxed. In order to produce high-quality pellets, certain additives are important. The most common fluxing materials for iron ore pellet production are limestone (CaCO₃), dolomite (Ca,Mg(CO₃)₂) and olivine (Mg₂SiO₄), but sometimes magnesite (MgCO₃) is also used. Fluxing agents are used not only to enhance slag formation, but also to improve softening and melting properties and to increase the reducibility of the burden materials before softening (Dwarapudi et al., 2012; Nogueira and Fruehan, 2003; Umadevi et al., 2011). In this study, the focus was placed on limestone as an additive in the production of iron ore pellets and its effect on pellet properties.

Some researchers have already studied the effect of basicity on the properties of iron ore pellets. One example is Umadevi et al. (2011), who carried out basket trials with iron ore pellets with basicity ranging from 0.08 to 1.15 in order to understand the effect of adding limestone on the microstructural, physical and metallurgical properties of iron ore pellets. In their study, the Tumble Index (TI) and the Cold Crushing

Strength (CCS) increased with the increase in pellet basicity, while the Reduction Degradation Index (RDI) initially decreased, and then increased again with the increase in pellet basicity. The optimal value for blast furnace performance was a basicity of 0.33. In the study by Loo and Bristow (1998a), high-basicity pellets showed higher reducibility and lower degradation than other pellets.

There are a variety of standard tests for characterizing the metallurgical properties of iron ore materials for blast furnace use. ISO 7215 (2007) specifies a method to provide a relative measure for evaluating the extent to which oxygen can be removed from iron ores when reduced under the conditions prevailing in the reduction zone of a blast furnace. The test portion of 500 g is isothermally reduced in a fixed bed at 900 °C in CO–N₂ gas for 180 min. The degree of reduction is calculated from the oxygen mass loss after 180 min.

Swelling of the pellets occurs simultaneously with reduction and is common in the operation of the blast furnace. ISO 4698 (2007) provides a standard for measuring the free-swelling index when pellets are reduced in an unconstrained bed under conditions resembling those in the reduction zone of a blast furnace. The test involves heating 18 pellets in a size range of 10–12.5 mm to 900 °C and reducing them isothermally for 60 min using a reducing gas consisting of 30 vol.% CO and 70 vol.% N₂ with a total volume flow rate of 15 l/min. The average increase in volume is an indicator of the amount of swelling.

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Table 1
Chemical composition of the pellets.

Pellet grade	Non-fluxed	Fluxed
Component	Content [wt.%]	
Fe _{tot}	65.6	63.8
FeO	0.2	0.6
CaO	0.51	3.20
SiO ₂	4.62	4.61
MgO	0.15	0.18
Al ₂ O ₃	0.38	0.34
S	0.011	0.061
K ₂ O	0.109	0.100
N ₂ O	0.061	0.052
CaO/SiO ₂	0.11	0.69

Due to the increased porosity of pellets, normal swelling can be advantageous for the reduction process (Singh and Björkman, 2004), while abnormal swelling detracts from the mechanical properties of the pellets, thus increasing the generation of dust and fines, which lowers the permeability of the pellet bed and makes operating problems more likely to occur (Bahgat et al., 2009). The degree of size degradation of iron ores in the low-temperature reduction zone of a blast furnace can be evaluated according to the ISO 13930 (2007) standard test, which is carried out isothermally at 500 °C in a gas atmosphere consisting of 20.0 vol.% CO, 20.0 vol.% CO₂, 2.0 vol.% H₂ and 58.0 vol.% N₂ with a total gas volume flow rate of 20 l/min. The standard test gives a relative measure for evaluating the disintegration of the iron burden materials when hematite is reduced to magnetite, namely the percentage of the +6.3 mm fraction after reduction (Loo and Bristow, 1998b).

ISO 4700 (2007) specifies a method for measuring the compressive load required to cause breakage of pellets. The CCS test indicates the ability of pellets to withstand both the load during storage and handling and the load of burden material in the blast furnace. In the test, a single pellet in a size range of 10.0–12.5 mm is compressed at a specific speed. One test portion comprises at least 60 pellets selected randomly from the test sample. The compression is repeated for all pellets in the test portion. The Cold Crushing Strength is calculated as the arithmetic mean of all the measurements obtained. According to the standard, the standard deviation of the measurements must also be presented. An acceptable level for the CCS value of the pellets used in the blast furnace varies in literature from 150 daN (Geerdes et al., 2009) to 200–230 daN (Dwarapudi et al., 2010, 2011, 2012). Furthermore, Geerdes et al. (2009) point out that a little lower average compression strength has no drawback for the blast furnace process as long as it is not caused by an increased percentage of very weak pellets (<60 daN).

It is generally known that in shaft furnaces iron-bearing materials are exposed to increasing temperature and mechanical load under reducing conditions. Due to mechanical stress caused by upper layers, iron-bearing material layers contract and finally collapse during melting. The behaviour of iron-bearing materials during contraction and melting is dependent on the chemistry and structure of the burden material and on reducing conditions, i.e. temperature, mechanical load, and reducing gas composition (Sterneland and Lahiri, 1999).

In shaft furnaces, it is desirable that the burden holds a lumpy packed structure to as high a temperature as possible, and that the temperature range of the start of softening to melting (known as the cohesive zone) is as narrow as possible (Matsui et al., 2003). ISO 7992 (2007) is a standardized Reduction under Load (RUL) test which provides a relative measure for evaluating the structural stability of iron ores when reduced under the conditions prevailing in the reduction zone of a blast furnace. A test portion weighing 1200 g is isothermally reduced in a fixed bed in a tube made of heat-resistant steel at 1050 °C under a static load in a CO–H₂–N₂ gas atmosphere until a reduction degree of 80% is obtained. As a result, the reduction curve is obtained, the differential pressure at 80% reduction is calculated, and the change in the height

of the test bed at 80% reduction is measured. Because of the relatively low test temperature, liquid phases do not form when using traditional iron-bearing materials and the focus is only on the reduction of iron oxides under mechanical and chemical stress.

Sterneland et al. (2003) found the softening and melting behaviour to be the same in the RUL laboratory test as in the experimental blast furnace (EBF) located in Luleå. However, the progress of reduction down through the burden of the experimental blast furnace was similar, but not identical, to the results of the RUL experiments. Thereby, they concluded that the experimental conditions must be carefully chosen in order to be able to simulate reduction, softening and melting with laboratory experiments. Thus, in this paper, dynamic gas composition – temperature profiles simulating blast furnace conditions have been preferred to standard isothermal tests to study the effect of adding limestone on the metallurgical properties of iron ore pellets.

2. Materials

Acid iron ore pellets with 4.6 wt.% SiO₂ manufactured by Severstal Resources in Karelia were used in the investigations. Both test pellets were produced in a laboratory-scale pelletizing drum and fired in sample baskets set in the middle of the sintering belt on the same production line as commercial blast furnace pellets. One set of pellets was fluxed slightly with limestone (CaCO₃) and was labelled “non-fluxed”, while the other one was highly limestone-fluxed and was labelled “fluxed”. The CaO content of the pellets was 0.51 wt.% and 3.20 wt.%, respectively. Chemical analyses of the pellets are presented in Table 1. The contents of CaO, MgO, Al₂O₃ and S were measured by XRF and the SiO₂ content by a gravimetric method. Furthermore, the total iron content (Fe_{tot}) and the oxidation stage of the iron were measured by a titration method, and the content of alkaline components (K₂O and Na₂O) by FAAS. The total iron content of the fluxed pellets was slightly lower than that of the non-fluxed pellets due to the higher amount of flux. The divalent iron (FeO) content of the non-fluxed and fluxed pellets was 0.2 wt.% and 0.6 wt.%, respectively. The higher divalent iron content in the fluxed pellets corresponds to a higher proportion of magnetite in the pellets and is an indicator of the sintering conditions. The size distribution of the pellets was quite similar (see the results of the sieve analysis in Fig. 1). Most of the pellets were in the 10.0–12.5 mm size fraction.

The photomicrographs showing the internal structure of the pellet core in the fired non-fluxed and the fluxed iron ore pellets are shown in Fig. 2. The microstructure has been photographed with FESEM (Zeiss Ultra Plus) and the phases were identified by FESEM with an EDS detector. In the fluxed pellets, there are more macro-pores and fewer micro-pores compared to the non-fluxed pellets. A high amount

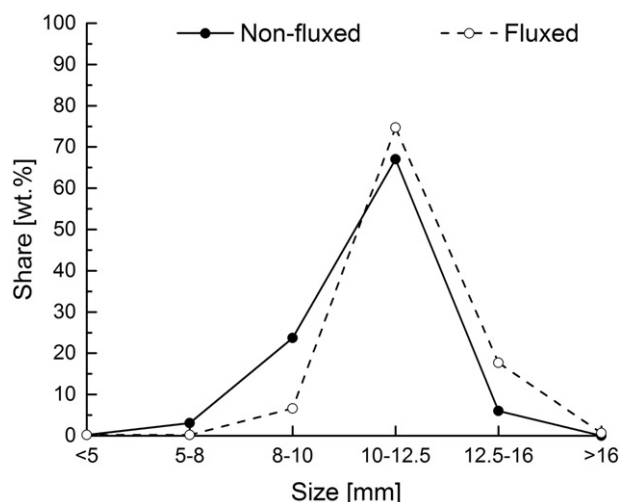


Fig. 1. Size distribution of the pellets.

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