USE OF BORON BASED BINDERS IN PELLETIZATION OF IRON ORES

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ABSTRACT

USE OF BORON BASED BINDERS IN PELLETIZATION OF IRON ORES

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Bentonite is the most preferred silicate-based binder in iron ore pelletizing. However, it is considered as an impurity due to its high SiO_2 and Al_2O_3 content. The iron-making economy is adversely affected by the addition of bentonite or other silicate-based binders. In recent years, impurity-free alternative binders have been tested in order to replace bentonite or to lower the bentonite dosage. Organic binders yield good quality green and dry pellets. However, they fail to impart enough mechanical strength to the preheated and fired pellets as a result of insufficient slag bonding. Thus, they have not found widespread application in the industry.

The addition of boron compounds into pellet mix is proposed as a potential solution to overcome the insufficient compressive strengths of preheated and fired pellets produced with organic binders. During the experiments, some organic binders and boron compounds were tested as alternative binders to bentonite either alone or in combination, for both magnetite and hematite pellets. The performances of the tested binders on pellet qualities: balling, wet pellet moisture content, drop number, pellet compressive strengths (wet - dry - preheated - fired), dustiness, porosity, mineralogy, morphology, chemical contents, reducibility and swelling index have been compared with the performances of reference bentonite binder.

The results of the tests showed that, the quality of pellets are insufficient when organic binders or calcined colemanite used as binder alone. The former failed to provide sufficient preheated and fired pellet strengths, the latter failed in terms of wet and dry pellet quality. However, good quality wet, dry, preheated and fired pellets could be produced with combination of these two binders.

Calcined colemanite addition into pellets made with organic binders was tested in different dosages (0.25-1.00%). Results showed that with increasing dosage of calcined colemanite both strengths of preheated and fired pellets increased linearly. It was found that as low as 0.50% calcined colemanite addition equally-performed on magnetite fired magnetite pellets at $1300^{o}C$ when compared with the performance of the reference bentonite binder. However, its performance was better on hematite pellets in order to improve the pellet compressive strengths. In addition, stronger pellets could be produced at lower firing temperatures like $1100^{o}C$ with the addition of calcined colemanite. The reason of the improved preheated and fired compressive strengths of pellets bonded with calcined colemanite was due to the physical melting of calcined colemanite at the contact point of iron oxide grains during thermal treatment.

It was found that bentonite bonded pellets fired at $1300^{o}C$ were more reducible than those of produced with calcined colemanite addition. Swelling indices of these pellets were determined in the industrially acceptable limits. The chemical and mineralogical analyses results showed that the combined binders did not contaminate the pellet composition since the organic binders burnt-out without residue and colemanite does not contain much impurity.

Keywords: Iron ore, magnetite, hematite, pelletizing, pelletization, agglomeration, binder, bentonite, organic binder, CMC, boron compounds, colemanite.

ÖZ

DEMİR CEVHERİ PELETLEMESİNDE BOR KÖKENLİ BAĞLAYICILARIN KULLANILMASI

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Bentonit en çok tercih edilen silika bazlı bağlayıcıdır. Fakat bentonit, içerdiği yüksek SiO_2 ve Al_2O_3 dolayısıyla safzılıktır. Demir üretim ekonomisi, bentonit veya diğer silika bazlı bağlayıcıların ilavesi ile olumsuz etkilenir. Son yıllarda, safsızlık içermeyen alternatif bağlayıcılar, bentonit kullanımı yerine veya bentonit kullanımını azaltmak üzere test edilmişlerdir. Organik bağlayıcılar ile yeterli yaş ve kuru pelet kalitesine sahip pelet üretilebildiği belirlenmiştir. Ancak, organik bağlayıcıların, yetersiz curuf bağlanmasından dolayı yeterli önısıtlmış ve pişirilmiş pelet dayanımı sağlamakta başarısız oldukları tespit edilmiştir. Bu yüzden organik bağlayıcılar endüstride yeterince geniş uygulama alanı bulamamışlardır.

Organik bağlayıcıların kullanımı ile karşılaşılan yetersiz önısıtılmış ve pişirilmiş pelet dayanımı sorununu aşmak için pelet karışımına bor bileşikleri ilavesi potensiyel bir çözüm olarak önerilmiştir. Bazı organik bağlayıcılar ve bor bileşikleri, bentonite alternatif olarak gerek yalnız gerekse kombinasyon olarak, manyetit ve hematit peletlerinde test edilmişlerdir. Denenen alternatif bağlayıcıların; topaklanma, pelet nem içeriği, düşme sayısı, basma dayanımı, tozlanma, gözeneklilik, indirgenebilirlik,

şişme ideksi, mineraloji, morfoloji ve kimyasal içerik gibi pelet kaliteleri üzerindeki performansları referans bentonit bağlayıcı performansları ile karşılaştırılmıştır.

Test sonuçları, sadece organik bağlayıcı veya kalsine kolemanit içeren peletlerin yetersiz kalitede olduklarını göstermiştir. Organik bağlayıcılar; yeterli önısıtılımış ve pişirilmiş pelet dayanımı sağlamakta başarısız olurken, kalsine kolemanit, yaş ve kuru pelet kalitesi bakımından yetersiz olmuştur. Ancak, her iki bağlayıcının karışımı ile üretilen peletlerde yeterli kalitede yaş, kuru, önısıtılımış ve pişirilmiş peletler üretilebilmiştir.

Organik bağlayıcılarla üretilen peletlere değişik oranlarda (%0.25-1.00) kalsine kolemanit ilavesi denenmiştir. İlave oranının artmasıyla hem önısıtılımış hem de pişirilmiş pelet dayanımları doğrusal olarak arttığı bulunmuştur. $1300^{o}C$'de pişirilmiş pelet dayanımını artırmada %0.50 kalsine kolemanit ilavesi manyetit peletlerinde aynı oranda bentonit ilavesiyle yaklaşık performans göstermiştir. Ancak, kalsine kolemanit ilavesi hematit peletlerinde dayanım artırmada daha üstün performans gösterdiği belirlenmiştir. Bunun yanında, kalsine kolemanit ilavesi ile $1100\ ^{o}C$ gibi düşük pişirme sıcaklıklarında daha dayanıklı pelet üretilebilmiştir. Kalsine kolemanit ilavesi ile artırılan önısıtılımış ve pişirilmiş pelet dayanımlarının nedeni; kalsine kolemanitin ısıl işlem sırasında demir oksit tanecikleri temas noktalarında eriyerek fiziksel bağ yapmasıdır.

Referans bentonit bağlayıcısı ile üretilen peletlerin kalsine kolemanit ilave edilen peletlere nazaran daha fazla indirgendikleri gözlenmiştir. Bu peletlerin şişme indekslerinin endüstriyel limit aralıklarında oldukları belirlenmiştir. Kimyasal ve mineralojik analiz çalışmalarıyla kombine bağlayıcı ilavesinin pelet kimyasal içeriği ve minerolojisini kirletmediği belirlenmiştir. Bunun nedeni, organik bağlayıcıların yanarak kalıntı bırakmadan yok olmaları ve kolemanitin önemli miktarda safsızlık içermemesidir.

Anahtar Kelimeler: Demir cevheri, manyetit, hematit, peletleme, aglomerasyon, bağlayıcı, bentonit, organik bağlayıcı, CMC, bor bileşikleri, kolemanit.

To my family

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LIST OF ABREVIATIONS

DRI	Direct reduced iron
DR-plant	Direct reduction plant
CMC	Carboxymethyl cellulose
^{o}C	Degree Celcius
cm	Centimeter
mm	Millimeter
µm	Micrometer
ml	Milliliter
l	Liter
sp.gr.	Specific gravity
cm^2	Centimeter square
cm^3	Cubic centimeter
g	Gram
kg	Kilogram
LMW	Low molecular weight
HMW	High molecular weight
PWAT	Plate water absorption test
WPMC	Wet pellet moisture content
WPDN	Wet pellet drop numbers
WPCS	Wet pellet compressive strengths
DPCS	Dry pellet compressive strengths
±P95	95% confidence interval
TGA	Thermal Gravimetric Analysis
XRF	X-Ray Fluorescence Analysis
XRD	X-Ray Diffraction Analysis
SEM	Scanning Electron Microscopy Analysis
W×D×H	Width, Depth, Height for dimensions
kg/p	Kilogram per pellet
lb/p	Pound per pellet
N/p	Newton per pellet
kN/p	Kilo Newton per pellet

CHAPTER 1

INTRODUCTION

1.1 The necessity of pelletizing

Iron is one of the most abundant elements comprising 5.6% of the earth crust (Taylor, 1964). Iron has served man for centuries and iron is the most used metal in industry. Metal iron is produced from iron containing natural ores. The main raw material in iron-steel industry is natural iron ores. Approximately 98% of iron ores is used in steel-making. Most of the natural iron ores are found as iron oxides and iron hydrous oxides. There are sixteen iron oxides with maximum 72.4% Fe and Table 1.1 shows these iron oxides. Sometimes natural iron ores are found as carbonates i.e. siderite ($FeCO_3$) with 43.2% Fe or sulfides i.e. pyrite (FeS_2) with 46.6% Fe and pyrrhotite (FeS) with 57-63.5% Fe.

Table 1. 1 The iron oxides (Cornell, 1996)

Oxides	Oxide hydroxide and hydroxides
Hematite α-Fe_2O_3 Magnetite Fe_3O_4 Maghemite γ-Fe_2O_3 β-Fe_2O_3 ϵ-Fe_2O_3 Wustite FeO	Goethite α-FeOOH Lepidocrocite γ-FeOOH Akaganeite β-FeOOH Schwertmannite $Fe_{16}O_{16}(OH)_y (SO_4)_z.nH_2O$ δ-FeOOH Feroxyhyte δ'-FeOOH High pressure FeOOH Ferrihydrite $Fe_5HO_8.4H_2O$ Bernalite $Fe(OH)_3$ $Fe(OH)_2$

Hematite and magnetite are the main iron oxides used in the metal iron production. Hematite is the iron ore which occurs most frequently and in the greatest quantities. Hematite has a theoretical iron content of 70.0%. Hematite is also final oxidation stage of indurated (fired) pellets made using other iron oxides.

Magnetite is the second abundant iron containing mineral with a theoretical iron content of 72.4% and its formula frequently also designated as $FeO.Fe_2O_3$.

These natural iron oxide ores can be typically classified as high grade (>65% Fe), medium grade (<65 and >62% Fe) and low grade (<62% Fe) in terms of their Fe contents. High grade massive lump iron oxides (i.e. crushed and sized ore) with acceptable impurity (generally silica and alumina oxides) level can be used directly in smelting processes. Blast furnaces or direct reduction plants are used for smelting iron ores to produce metal iron.

However, high grade iron ores which can be used directly in these reduction processes to produce metallic iron are not abundant in earth's crust to supply the increasing need of iron-steel industry. The available reserves of high grade iron ore appears to be inadequate for the future development of the steel-making industry. Therefore, exploitation of low grade iron ores after enrichment is one method to obtain blast furnace feed. Low grade iron ores with impurity gangue minerals containing e.g. Si, Al, Ca, Mg, Na, K, P and S compounds can be upgraded to an acceptable chemical composition through concentration (enrichment).

Enrichment of naturally low grade iron ores is accomplished by grinding and concentration stages. In grinding process, the iron ore is ground into fine particles so that the iron minerals can be liberated from unwanted gangue components. In concentration stage, the iron minerals can be separated from unwanted gangue minerals commonly silica and alumina oxides. The concentration techniques applied for enrichment of iron oxides are generally magnetic separation or flotation. Grinding and liberation process leaves the iron ore in a finely ground state (e.g. 100% minus 106 μm or generally 80% minus 44 μm) that is not easily transported or readily processed in iron-steel making facilities. Therefore, a size enlargement

operation is necessary to agglomerate the finely ground concentrate into agglomerates. In metallurgy, sintering and pelletization (or pelletizing) are the most applied size enlargement techniques.

1.2   A brief description of pelletizing

Originally the pelletizing process was developed in the United States of America to treat the ultra-fine mineral dressing products obtained from the upgrading of Mesabi ore. The pelletizing process has been developed to provide a blast furnace feed product with iron contents of about 65 percent (Ball *et al.,* 1973).

Iron ore concentrates with very fine particle size can be converted agglomerates by applying sintering or pelletizing techniques. However, sintering cannot be applied efficiently because of too fine particle size of iron ore concentrates. Such materials can lead to problems such as high fuel consumption and low specific output when sintering is applied. Therefore, the most commonly employed agglomeration technique is pelletizing for such a fine sized concentrates. The agglomerates produced by the pelletizing process are called *pellets*.

Pellets are balls produced from iron ore concentrates and natural high grade iron ores of different mineralogical and chemical composition with some remarkable properties such as;

- Uniform size distribution within a main range of 9-16 mm diameter,
- High and even porosity,
- High iron content more than 63% Fe,
- Practically no loss on ignition or volatiles,
- Uniform mineralogical composition in the form of an easily reducible hematite or hematite-bearing compounds,
- High and uniform mechanical strength,
- Low tendency to abrasion and good behavior during transportation,
- Sufficient mechanical strength even at thermal stress under reducing atmosphere (Meyer, 1980).

The pelletizing of iron ore process is essentially based on the formation of wet pellets by rolling a finely ground iron ore or concentrate to which a binder (usually bentonite) is added together with a critical amount of liquid (usually water). The newly formed pellets should have strengths high enough to survive transportation. In iron ore pelletizing, three binders are generally accepted:

- Bentonite, naturally occurring clay found in deposits of varying qualities around the world.
- Hydrated lime produced by the calcination of limestone or inorganic materials.
- Organic binders, either natural or synthetic, such as the cellulose based materials.

Pellets can be produced from magnetite concentrates, hematite concentrates, natural ore fines, artificial magnetite and pyrite cinders. Many pelletizing plants worldwide use magnetite and hematite as iron oxide sources. The investigations on the use of pyrite cinder or pyrite ash were conducted by (Mohamed *et al.*, 2003 and Tuğrul *et al.*, 2006 and 2007). Use of a binder is necessary to bind the iron ore grains in wet and dry condition. Binders play an important role in the success of pelletizing process.

Bentonite is the most common binder in iron ore pelletization. Bentonite has proven to be the most effective binder owing to its high water adsorption capacity and dry film strength. It is commonly used at a addition level of 0.5-1.5% by weight of iron ore.

Bentonite, useful as explained above, however, because of its acid constituents (SiO_2 and Al_2O_3), it is considered as an impurity. These acid oxides are known for their adverse effects on the iron-steel making economy. Bentonite, while long considered to be the industry conventional binder, has the disadvantage of adding unwanted silica into the pellet chemistry. Some forms of sodium bentonite are known to contain more than 65% SiO_2 by weight. Besides the adverse effect on pellet chemistry, this additional silica blocks the porosity of the pellet inhibiting the flow of reducing gases into the interior regions of the pellet. This lowers the reducibility of

pellets, increasing;

    a) the energy requirements in the steel-making process and,

    b) the costs for handling and disposal of increased slag levels.

The disadvantages of these unwanted impurities upon using bentonite are summarized in literature. For instance, the addition of 1% bentonite, containing 85% $SiO_2+Al_2O_3$, decreases the pellet's iron content 0.6% (de Souza, 1984). In another study, authors found that the addition of 1% bentonite decreases the iron content by about 7 kg/ton of iron ore (Kater, and Steeghs, 1984). An increase in the silica content of pellet charge by 1% (abs.) leads to an increase in the unit cost of making the steel by $4-7 (U.S.)/ton (Chizhikova *et al.*, 2003). In the case of direct reduced pellets, every percent of acid gangue addition is associated with an increased energy consumption of 30 kWh/ton (Heerema *et al.*, 1989). By having lower gangue concentrations in the pellet, substantial improvements in energy and flux consumptions can be realized in iron making processes. Cost savings in energy/flux for each 1.0% reduction in silica can reach $2.50 (U.S.)/ton of hot metal making (Schmitt, 2005).

Inorganic materials not containing silica, like hydrated lime; have a slight advantage over bentonite when silica levels are the primary concern of steel makers. However, most of them are incapable of controlling water during pelletization, and do little contribution to the cohesive/adhesive forces required to form and maintain green pellet integrity. This results in poor quality green balls that are fragile and easily broken, lowering production rates in iron making facilities. Furthermore, due to the massive amounts required for basicity control and pelletization, some inorganic materials can contribute to spalling of pellets decreasing the quality of the finished pellet product. The Inorganic materials tested as binders in iron ore pelletizing have been discussed under the title 3.5.

Organic binders, on the other hand, offer the perfect alternative to the conventional bentonite binder. In recent years, organic binders have been tested/used in order to eliminate the negative effects of bentonite or other silicate based binders. Organic binders which burnt out at relatively low temperatures with virtually no residue are

the most widely tested binders. However, organic binders have not found widespread application in the industry. Although, they give good results for green and dry pellets but they fail to impart enough strength to the preheated pellets. The organic binders and their usage in iron ore pelletizing will be discussed under the title 3.4.

1.3   Objective of the thesis

In view of the adverse affects of bentonite, many researchers attempted to find viable alternative binders to bentonite. Organic binders have attracted attention as they are known to have good binding properties. The results from the studies conducted on the use of organic binders showed that good quality green and dry pellets can be produced with organic binders. However, they could not provide sufficient strength to the preheated and fired pellets as a result of reduced slag bonding (Kater and Steeghs, 1984, de Souza *et al*., 1984, Goetzman *et al.*, 1988, Arol *et al.*, 1989, Arol 1997, Sivrikaya and Arol 2008, Sivrikaya and Arol 2009, Sivrikaya and Arol 2010, Sivrikaya and Arol 2011). Slag bonding is especially more important in pelletizing of hematite ores due to lack of strengthening mechanism through oxidation. As such, organic binders have hitherto failed to be an alternative to bentonite, except a few cases of straight grate pelletizing furnace system, where there is no dynamic pellet bed. In recent years efforts have been focused on improving the preheated and fired strength of pellets produced with organic binders.

The aim of this thesis has been to propose the addition of a slag bonding/strength increasing constituent into pellet feed to provide pellet strength with the use of organic binders. Addition of boron compounds into pellet mix has been thought as a potential solution to improve the lower preheated and fired compressive strengths encountered with the use organic binders. In this context, boron compounds known with lower melting points have been considered as an additive in conjunction with organic binders. Organic binders and boron compounds were tested as binder either alone or in combination.

In order to determine the performances of tested alternative binders, the following raw materials are used to produce pellets during pelletizing experiments;

- Three iron oxides (two magnetite concentrate and one hematite ore),
- Two bentonite samples (both sodium bentonites),
- Three organic binders (CMC, dextrin, corn starch),
- Three manufactured organic based binders (polymers),
- Four different boron compounds (colemanite, tincal, borax pentahydrate and boric acid),
- Four different combinations of organic binders and colemanite.

The influences of several dosages of binders and different heating temperatures on compressive strength of pellets are comparatively studied. The main interest of this study is to answer the questions given below.

- Can boron compounds be used as binder alone for iron ore pelletizing?
- What is effect of boron compounds addition on pellet quality especially on compressive strength of pellets?
- Can boron compounds addition improve compressive strength of pellets when used together with organic binders?
- Can boron compounds and organic binder combination be an alternative to bentonite binder in point of all pellet quality.
- Can firing temperature be reduced to get industrially sufficient compressive strength with addition of boron compounds?
- What is the effect of boron compounds addition on physico-chemical pellet properties such as porosity, mineralogy, morphology, reducibility, swelling etc.
- What is the effect of boron compounds addition on pellet chemistry?
- What is the bonding mechanism of boron compounds addition into the pellets?
- What is the dustiness mechanism of product pellets by a novel equipment?

CHAPTER 2

IRON ORE PELLETIZING

2.1 Principle steps for the production of iron ore pellets

The iron ore pellets are the properly sized agglomerates which can be converted to metal iron in any smelting processes. There are a few methods to produce metal iron in industry. The entire complex iron ore preparation showing alternative routes for agglomeration and metal iron production is given in Figure 2.1.
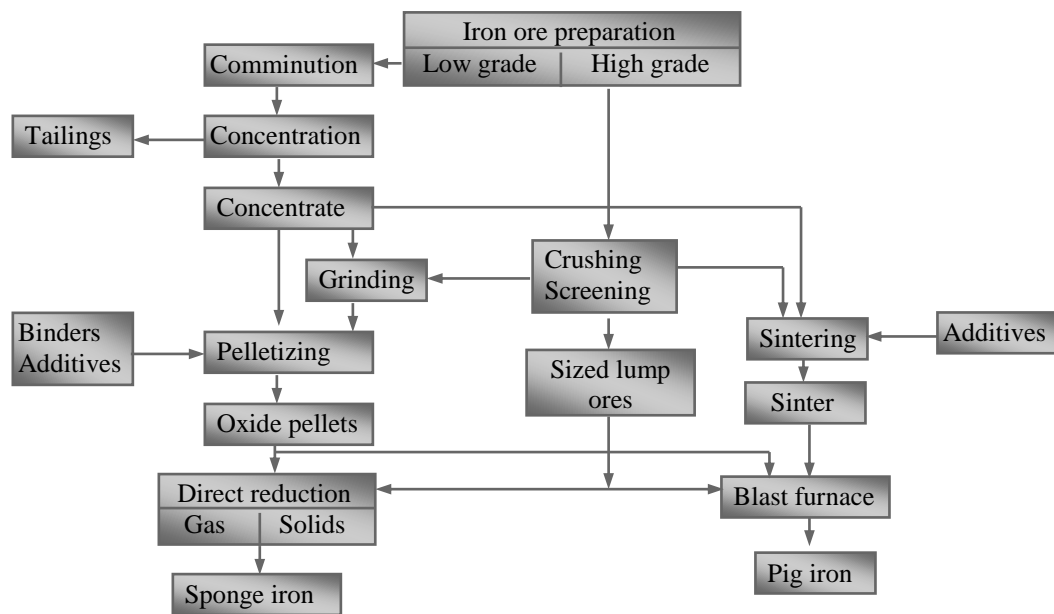
Figure 2. 1 Alternative routes of complex iron ore preparation for agglomeration and metal iron production (redrawn after Meyer, 1980)

The pelletizing of iron ore process is essentially based on the formation of wet pellets by rolling a finely ground iron ore or concentrate to which a binder (usually

bentonite) is added together with a critical amount of liquid (usually water). The green balls are dried, preheated and fired, all under oxidized conditions, to a temperature 1250-1340°C. As a result, oxide bridging, grain growth, and some slag bonding occur, and pellet strength is developed. The pellets are then cooled in air and the sensible heat recovered in the form of hot air used as process air in the previous heating operations. The following steps are basic to the pelletizing process; each step is modified to suit both the equipment employed and the ore being processed (Ball *et al.,* 1973).

1) Raw material preparation (feed preparation),

2) Balling of raw materials (formation of wet pellets),

3) Induration of pellets (thermal treatment or hardening of pellet by heat),

  a) Drying of wet pellets,

  b) Preheating of dry pellets,

  c) Pellet firing,

  d) Cooling of fired pellets.

2.1.1 Raw material preparation : Iron ore concentration plant

The first stage of the pelletizing is the preparation of raw materials. Many of the natural iron ores, secondary raw materials; additives or binders are naturally not suitable for direct using in pelletizing processing. Therefore, preparation of the raw materials involved is required. The aim of the material preparation;

1) Mechanical crushing, grinding, screening, classification. These steps are necessary for both liberation of minerals and gangue and to reach a suitable fineness required for pelletizing,

2) Increasing of the Fe content of the low grade raw material (enrichment or concentration),

3) Removal of undesired impurities (rejecting of gangue).

A flowsheet for both iron ore concentration plant and iron ore pelletizing plant is given in the Figure 2.2. The first part of the figure shows the necessary steps for

upgrading of iron ore extracted from the mine pit. The second part illustrates the common operation units of an iron ore pelletizing plant. In this example, drum pelletizer for balling and travelling grate furnace is used for thermal treatment of pellets. The detail for a pelletizing plant is given in the following part.
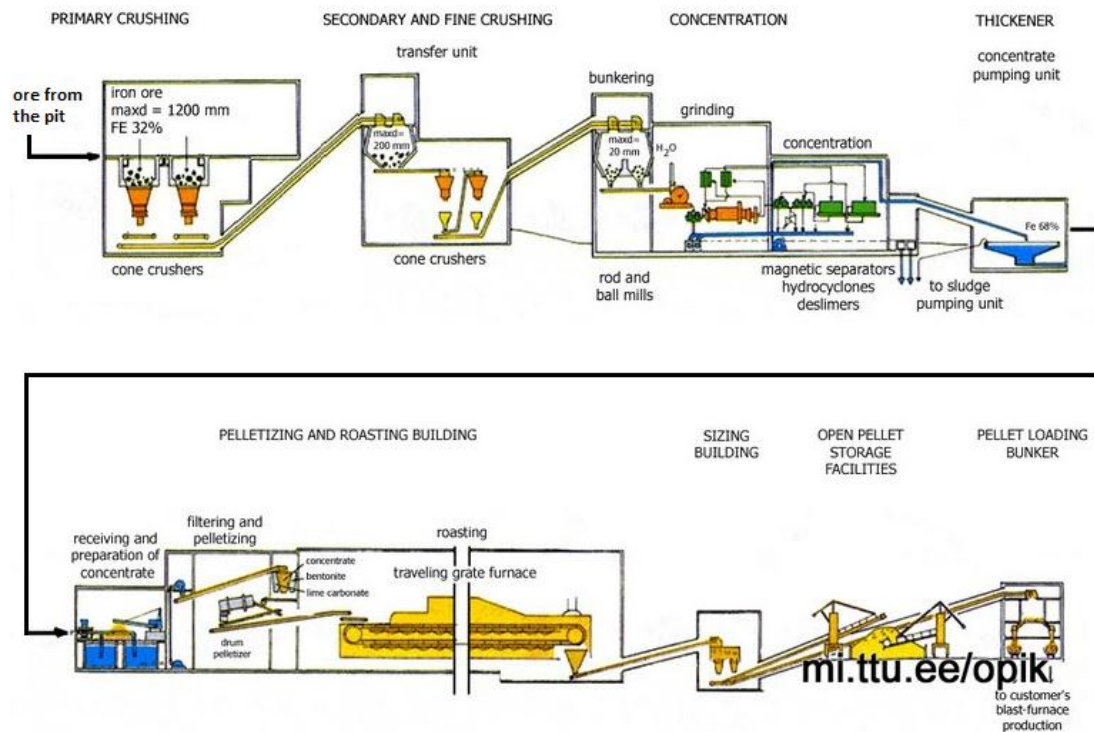
Figure 2. 2 Iron ore concentration and pelletizing plant flowsheet (Figure taken from http://mi.ttu.ee/opik and edited for page orientation, last visited on 10/02/2011)

2.1.2 Iron ore pellet production : Pelletizing plant

There are two different types of raw materials in the production of iron ore pellets. One of them is iron containing minerals: iron oxides. The other is binders and additives comprise mostly raw materials low in or free from iron, which is exclusively used as;

- Binders for facilitating the pellet production by balling,
- Binders and additives for improving the physical-mechanical quality,
- Additives for modifying the metallurgical properties of pellets. Metallurgical

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change by basic additives decreases the energy consumption of the succeeding process stages.

In Figure 2.3 a typical pelletizing plant with general operational units is shown. Magnetite concentrate slurry from concentration site is sent to the dewatering units and the concentrate with suitable moisture content is stored in bins. Binder or sometimes additives are added to this concentrate and then mixed. Mix pellet feed material is sent to the balling units; pelletizing drum or disc. In this illustration, pelletizing is carried out with balling drum and thermal treatment is done with travelling grate and rotary kiln furnace system. Balling of the raw materials is explained in the following part.
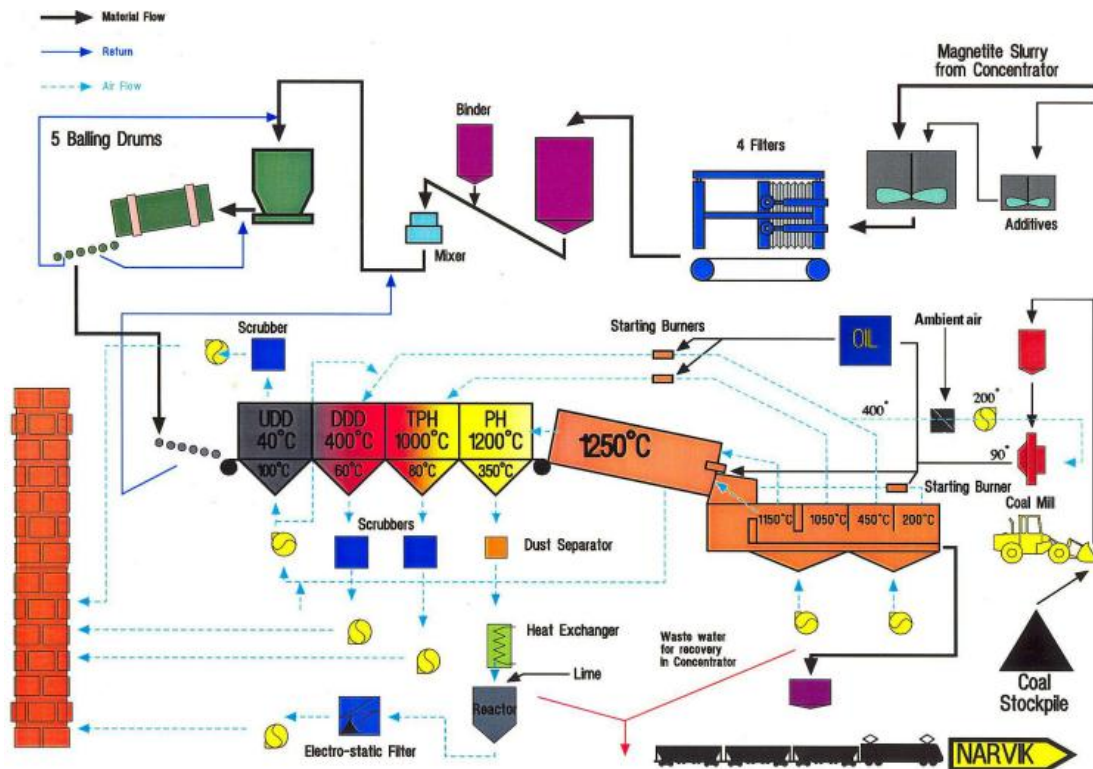
Figure 2. 3 Flow scheme for a typical pelletizing plant (Forsmo, 2007: scheme for the Luossavaara-Kiirunavaara AB (LKAB) Kiruna, Sweden pelletizing plant KK3)

2.1.3 Balling of the raw materials

In the second step of pelletizing after raw material preparation, a mixture of iron ore or concentrate with adequate size distribution, a wetting liquid, generally water, balled/rolled in a suitable mechanical equipment. **Balling**, in particularly iron ore pelletizing, is defined by Pietsch, 1991 as any agglomeration method producing more or less spherical pellets by tumble or growth agglomeration. Agglomerates can be formed by two different balling units in iron ore industry: balling/pelletizing disc or drum. Industrial scale balling disc and balling drum can be seen in Figure 2.4. The agglomerate formation is similar to snow-ball growth by layering with the help of rotation of the disc or drum vessel. These agglomerates so produced are called **green balls, green pellets** or **wet pellets**. During this operation, use of binders is common to improve properties of wet and then product pellets. The conventional binder is bentonite clay for iron ore pelletizing in industry. It is possible also to add additives at this stage to change the metallurgical properties of the product pellets, e.g. limestone or dolomite.

Figure 2. 4 Industrial scale **A)** balling disc **B)** balling drum (http://www.metso.com, last visited on 10/02/2011)

Wet pellets from the balling equipment are sent to the rolling conveyor and rolling screens to transport and to reject the undersize materials. **Roller conveyor** was developed to solve the handling problem of wet pellets. It consists of multi rolls individually driven and carrying wet pellets from balling equipments to the

subsequent operation. Rolling screen is similar equipment and a part of the roller conveyor works as rolling screen. Figure 2.5 shows an industrial size rolling conveyor and rolling screen. There are gaps between individual rolls adapted to the undersize particles to be separated. These undersize materials are recycled to the circuit after crushing together with fresh feed. The pellets with desired size generally 9-16 mm in diameter are sent to the drying zone of the thermal treatment unit.
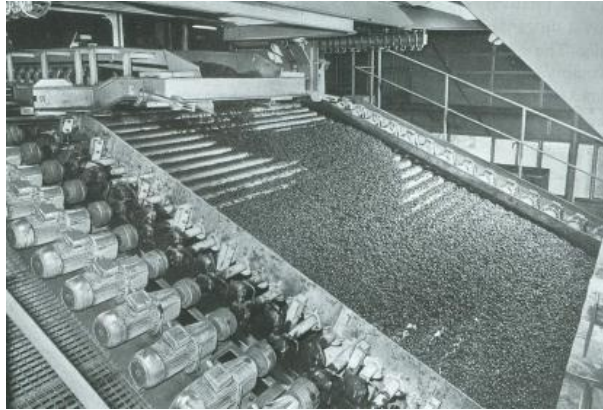
Figure 2. 5 Industrial size rolling conveyor and rolling screen (Meyer, 1980)

2.1.4 Balling mechanism and green ball strength

The feed material may be dry grains or a wet cake according to its preparation. Most concentrates are available as filter cake (concentrate with moisture). If dry solid particles come into contact with water, the ore surface is wetted. The ore particle is coated with a water film, as is shown in Figure 2.6, phase A. In many places, the wet particles touch each other. Due to the surface tension of the water film, liquid bridges are formed, phase B. as a result of the movement of the particles inside balling unit and of the combination of individual water droplets, each containing one or several ore grains, the first agglomerates are formed, phase C. in the interior of the loose agglomerate, the first liquid bridges appear among a large number of voids still existing. The liquid bridges hold the particles together as in a network. Loose balls are formed. With the further supply of water the agglomerate condense. More and more water is layered in the interior and the agglomerates become denser, phase D. At this stage of green ball formation, the capillary forces of the individual liquid

bridges are essentially active. The optimum of this ball-formation phase is attained when all pores are filled with liquid but the latter does not yet uniformly coat the whole agglomerate, phase E. The effect of the capillary forces is clearly shown by Tigerschiöld and Ilmoni, 1950 in Figure 2.7. Concave liquid surfaces form on the outer pores and capillary suction is holding the ore particles together. The final stage is exceeded, when the solid particles are fully coated with a water film. Now, the surface tension of the water droplets containing the solid particles becomes fully active, Figure 2.6, phase F (Meyer, 1980).
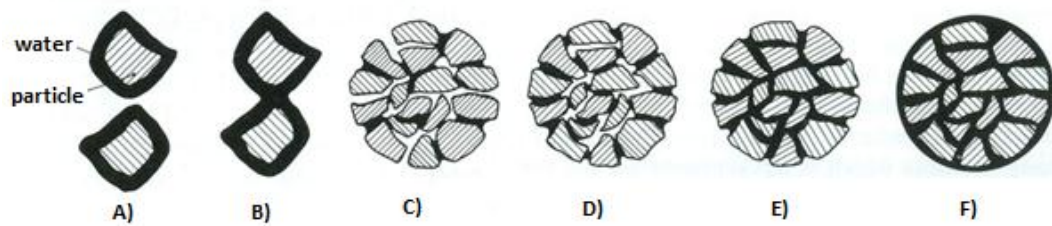
Figure 2. 6 Influence of water addition on green pellet formation (Meyer, 1980).
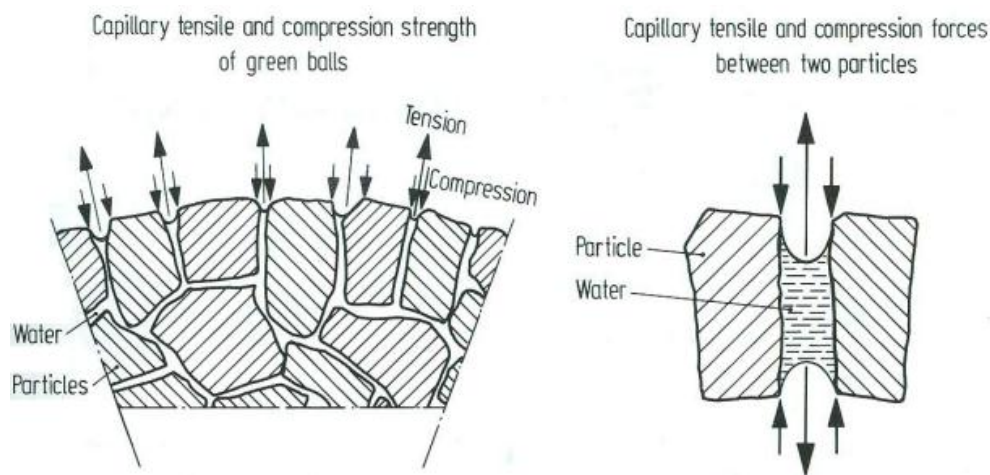
Figure 2. 7 Influence of capillary forces on bonding (Tigerschiöld and Ilmoni, 1950)

Figure 2.8 shows the alternative green ball formation in a balling system. According to Sastry and Fuersteneu, 1973 the following methods, as shown in Figure 2.8 adopted by Meyer, 1980.

a) Layering of very fine particles to others and thus formation of an agglomerate,

b) Conglomerating of smaller balls already existing resulting from relative motion and a certain pressure,

c) Layering on and incorporation of minor fragments from damage green balls into existing sounds one,

d) Incorporation of fine-grained abraded material from weak pellets into the surface of stronger pellets.

A) Layering   B) Sticking   C) Breakage   D) Abrasion
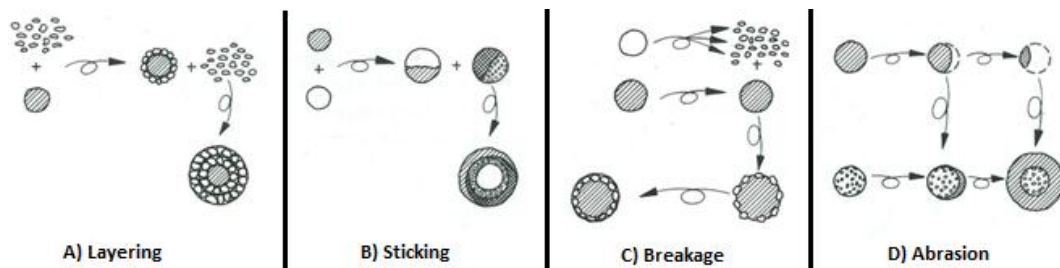
Figure 2. 8 Alternatives for green pellet formation (Meyer, 1980 after Sastry. and Fuerstenau, 1973).

Important bonding factors for the green pellet formation and the properties of green pellets described by Rumph, 1962 and he divided into the following groups:

1) *Physical forces*, such as van der Waals', magnetic or electrostatic force.

2) *Surface-dependent factors*, such as particle size, particle size distribution, particle shape and crystalline structure.

3) *Material-dependent factors*, such as wettability, adsorptive capacity due to porous structure, availability of swelling components, chemical properties in primary ores or by-products after previous treatment.

4) *Capillary forces and surface tension* during the addition of liquid binders, such as water or others.

2.1.5 Induration of pellets

The green pellets strength is hardly sufficient and should be increased by applying heat hardening treatment. Green pellets then undergo a thermal treatment in the third

step to produce durable product pellets. Thermal treatment or heat hardening of pellets, can also be named ***induration of pellets***, consists of three sub-stages;

1) Drying stage (250-400°C),
2) Preheating stage (400-1200°C) and
3) Firing stage (1200-1350°C).

2.1.5.1 Induration equipments

Green pellet strength is increased by heat hardening processes. Three different induration furnace systems have been developed for induration of pellets;

1) Shaft furnace,
2) Straight grate and
3) Travelling grate and Rotary kiln processes.

2.1.5.1.1 Shaft furnace

The shaft furnace had been used for several centuries for the smelting of ores and the burning of lime. Because of their high thermal efficiency and ease of operation they were the first, both in Sweden and USA, to be adopted for iron ore pelletizing (Pietsch, 2005).

Wet pellets or lump iron is introduced through the top of the shaft furnace. As the pellets descend through the furnace by gravity flow, they are heated by hot air. Wet pellets moves through the all thermal zones towards the bottom of the furnace and discharged. Shaft furnace has a good thermal efficiency and relatively simple operational requirements. Figure 2.9 shows a typical shaft furnace and the temperature profile of shaft furnace. The hot gases and pellets move concurrently in the shaft furnace.

In this system pellets should be resistant to thermal shock, since the sintering zone is located about only 50 cm below the top of the pellet bed. The green pellets are

quickly dried and preheated at preheating zone. This system is developed for the induration of pellets, however, used mostly for magnetite pellets. Magnetite pellets reduce the heat requirements since the oxidation is an exothermic process, so the heat control of furnace is easy for magnetite pellets. Nevertheless, the shaft furnace has lost importance. The advantages and disadvantages of shaft furnaces for in duration of iron ore pellets were summarized in Table 2.1 by Pietsch, 2005.
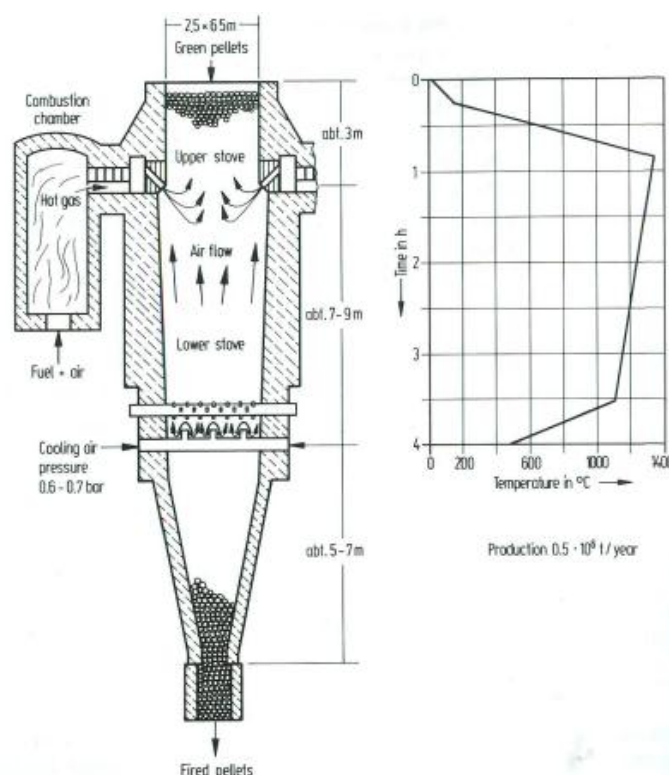
Figure 2. 9 A schematic view and temperature profile of shaft furnace (Meyer, 1980)

Table 2. 1 Advantages and disadvantages of shaft furnaces for induration of iron ore pellets (Pietsch, 2005)

Advantages	Disadvantages
Simple design Small number of moving parts Refractory lining of entire furnace Intensive heat exchange Feasible for low production capacity Best for magnetite pellets	Little chance of influencing process stage Low flexibility Charge is in constant movement Pellets must be of highest quality Limited production capacity High fuel consumption Commonly disrupted flow pattern (lumping) Inconsistent product quality

2.1.5.1.2 Straight grate furnace

In this furnace, a stationary bed of pellets are loaded on a straight travelling grate. Pellets are moved on the grate through the drying zone, preheating zone, firing zone and cooling zone. Hot gases are sent to the pellet bed to heat in heating zones and fresh air is sent onto the pellets in last grate to cool them. A schematic diagram of straight grate pellet induration system can be seen in Figure 2.10.

In this system, the pellets have no critical transfer points to survive or a need for high preheat strength as they are basically motionless on the pellet grate. The only pressures being exerted on the pellets come from the upper layers of the pellet bed itself and from airflows created by the process fans (Schmitt, 2005).
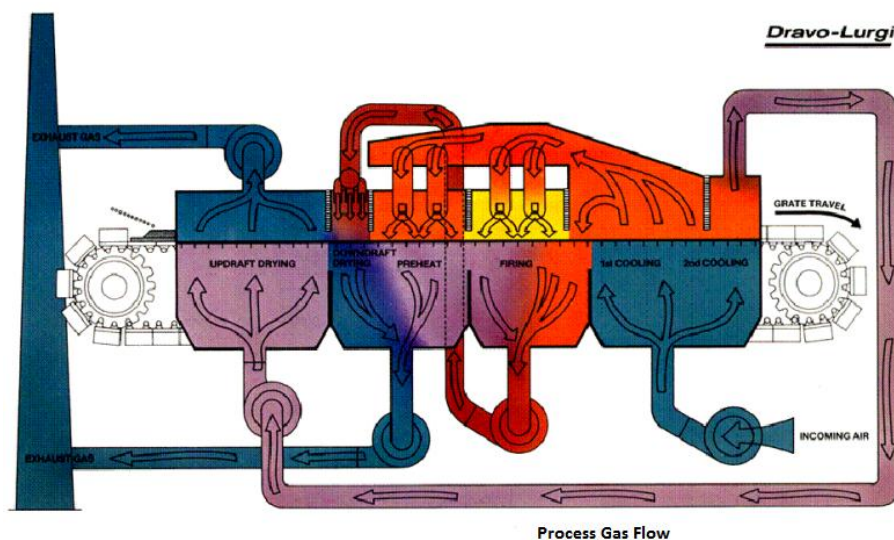
Figure 2. 10 A schematic diagram of straight grate pellet induration system (Schmitt, 2005)

2.1.5.1.3 Travelling grate and rotary kiln system

In travelling grate and rotary kiln system (Figure 2.11), the wet pellets are transported on a stationary grate. Drying and preheating is completed in this stationary grate. Reactions such as removal of chemically bonded water, decomposition of some minerals (gangues or flux additives like carbonates), coke

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combustion if added and oxidation of magnetite to hematite take place in this zone. Most of the oxidation takes place in the preheating zone if the magnetite pellets are used. Preheated pellets are then sent to a rotary kiln for firing by radiation heat to the required temperature. Firing in rotary kiln is more homogenous than straight grate system since the pellets are rolled in the kiln evenly. The fired hot pellets move in to a cooler part, generally an annular cooler in grate-kiln system.
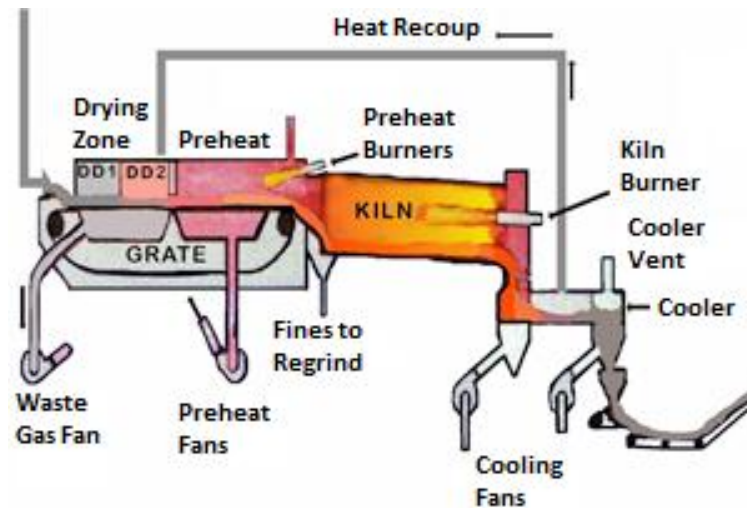
Figure 2. 11 A schematic diagram of travelling grate and rotary kiln system (http://www.d.umn.edu/scse/feature/davis.html, last visited on 10/02/2011)

Thermally treated pellets in one of induration furnace systems explained above are called *fired pellets* or *hardened pellets*. These pellets after cooling stage are called *product pellets* and afterward they are ready to store and transport to the smelting facilities (reduction furnaces).

2.1.5.2 Drying of wet pellets

Drying is usually a part of the heat hardening process. Drying starts on the first section of the induration furnace when the hot air and combustion gases flow over wet pellets. The moisture of the wet pellets commences to evaporate evenly on the surface of pellets.

During this drying phase, the drying velocity is no longer constant but decrease. As soon as the capillary water evaporates, the drying procedure is terminated. However, if the wet pellets contain hygroscopic or chemically-combined water, the drying procedure only continues when the temperature of the drying medium is enough to dissociate the compounds. The velocity of this third drying phase is again lower. The drying procedure of such a wet pellet, which also contains hygroscopic water, is given in Figure 2.12 (Meyer, 1980).
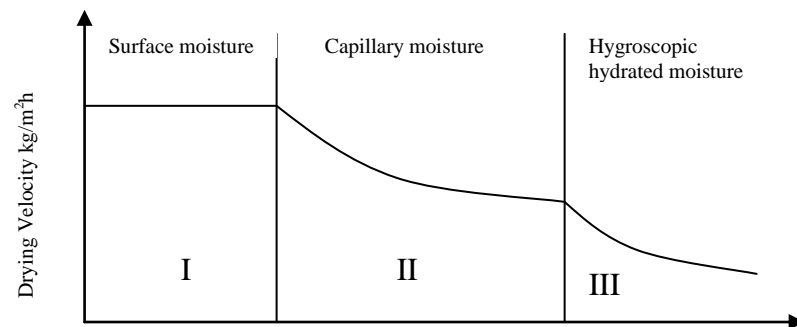
Figure 2. 12 The drying procedure of such a wet pellet, which also contains hygroscopic water (Meyer, 1980 after Krischer and Jaeschke, 1961)

2.1.5.3 Preheating of pellets

The preheating zone is the thermal link between the drying and firing of pellets. It directly follows the temperatures of the drying zone. According to the ore type involved, the temperature ranges from 300-400°C to 1200°C by a continual and controlled heat supply (Meyer, 1980). During preheating decomposition of hydrates, carbonates or sulfates as well as roasting of sulfide compounds may take place. The most important reaction, for iron oxides except hematite, in the preheating zone is oxidation; to conversion of magnetite to hematite. Oxidation is the main strengthening mechanism to provide the mechanical strength to the pellets by recrystallization and crystal growth. In addition, oxidation also plays a significant role on the reducibility characteristic of pellets.

2.1.5.4 Firing of pellets

The last thermal process before finished pellets are produced is firing of preheated pellets. Firing just starts after preheating temperatures about 1100-1200°C and the pellets are heated to an optimum temperature for each ore type and temperature is maintained for a controlled period. This temperature is just below the melting temperature but within the reactivity range of gangue components and additives (Meyer, 1980). Normally firing temperatures in the region of 1250-1350°C are sufficient to produce pellets of the required quality. Higher temperatures are to be avoided, as they lead to overslagging of the pellets and also spontenous reversion of hematite to magnetite with loss in pellet quality (Ball, *et al.,* 1973)

The reactions occurring in preheating zone proceed in the firing stage of pellets;

   a) Completion of the oxidation of magnetite and grain growth,
   b) Chemical reactions between the gangue constituents of the pellets, whether present as naturally occurring constituents or as additives, which may also involve reaction with the iron constituent.

2.1.6 Strengthening and bonding mechanism of fired pellets

Pellets attain their mechanical strength during thermal treatment, namely preheating and firing cycles. The preheating and firing process should be so designed that various physical and chemical changes take place at the appropriate time to avoid harmful interactions, or loss of useful heat, and terminate at the optimum firing temperature to produce pellets with the required properties.

In several studies carried out primarily with iron ore pellets from industrial plants, it was found that two major thermal bonding systems are key mechanisms for the strength and quality of pellets. The two factors which impart strength to the pellets are summarized by Ball *et al.,* 1973 and Meyer, 1980 in literature.

   a) Change of the crystalline structure during firing either by crystal

transformation and growth upon oxidation of magnetite to hematite or by crystal growth when hematite is used only. Mineral grain growth, essentially a physical process in which the smaller particles consolidate into larger ones with resulting loss in surface energy - this process may take place in solid state or through a liquid melt medium, and

b) The reaction of slag-forming constituents which are either present as gangue in natural ores or concentrates or added before the pelletizing, such as binder, acid oxides, basic additives such as limestone or dolomite. Basic components react with acid components and under certain conditions also with iron oxides. Thus, slag or crystal bonding is achieved as a result of the melt formation.

The iron ores or concentrates to be pelletized have a certain amount of gangue or additives which even at low percentages react with each other by the formation of intergranular melting phases. As transport medium, these phases may play an important part for the growth of iron oxide crystals.

The conglomerates, arising during the formation of wet pellets and their drying, are stabilized by thermal treatment and are further consolidated. The consolidation is achieved by energy supply during preheating and firing. The solid reacts with each other in conformity with natural laws. The reaction proceeds below the melting temperature while new solid phases are formed. Such reactions of fine crystalline and pulverous material develop in dependence on the energy supplied during the temperature rise in various stages;

- First, an activation occurs in the crystal lattice which can be recognized in the interface. A rearrangement of the molecules takes place. The particles draw closer together with strength beginning to increase.
- During the further temperature rise, the mobility of the ions in lattice increases. A lattice diffusion occurs which leads to rearrangements, vacancies are occupied and inclusions are eliminated.
- The dislocations intensify and involve adjacent crystals in the diffusion.

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- Crystal bridges are formed between the individual ore grains. The bridges lead to a consolidation of the conglomerate.

- A rearrangement of the crystal lattice and a recrystallization occur the bridge formation changes to a bridge bonding. The recrystallization intensifies the latter.

- A further energy supply causes the rounding of grains. The pores between the ore grains become smaller.

The latest phase would be melting which, however, has to be avoided because, in this case, individual pellets would no longer be exist. This reaction development is well known from solid state chemistry and physic (Meyer, 1980).

CHAPTER 3

USE OF BINDERS IN IRON ORE PELLETIZING

The use of a binder is necessary or sometimes compulsory to bind the particle grains of the iron ore together during pelletizing processes: balling, drying and before completion of firing step. Numerous types of materials have been considered for use as binders during the development of iron ore pelletizing process, with an objective of finding the material that would produce the highest quality pellets at the lowest possible cost. A comprehensive review about binders in iron ore pelletizing was published by Eisele and Kawatra, 2003. They classified the binders that have been used in industry or tested in laboratory as follows;

- Clays and colloid minerals,
- Organic polymers and fibers,
- Cement and cementations materials,
- Salts and precipitates,
- Inorganic polymers

3.1   Function of binders

Binders serve to improve properties of pellets in wet, dry or indurated/fired condition; as listed below:

- Promoting and facilitating - balling of iron ores in pelletizing drum or disc;
- The improvement of green, dry, preheated and fired pellet strength;
- Overcoming the problems associated with balls sensitive to heat in the drying

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stage, i.e. increase in shock temperature of green balls;

- Enabling the production of good quality pellets to be attained at lower temperatures;
- Improving the properties of the fired pellets (Ball, *et al.,* 1973).

During the development of the pelletizing process, a great number of organic and inorganic substances were tested with regard to their suitability as binders. However, only bentonite, slaked lime, limestone and dolomite are used. Binders which are deleterious or contaminate the pellet composition or give off pollutants to the waste gas of pellet plant are no longer taken into consideration (Meyer, 1980).

3.2 Binding system of binders

The binding system or mechanism of agglomeration is divided into five major groups in Table 3.1 by Pietsch, 2005. Figure 3.1 describe pictorially these binding mechanisms.

Table 3. 1 Binding mechanism of agglomeration (Pietsch, 2005)

I	**Solid bridges** caused by	1- Sintering 6- Drying 2- Partial melting a- Recrystallization 3- Chemical reaction (dissolved substances) 4- Hardening binders b- Deposition 5- Recrystallization (colloid particles)
II	**Adhesion and cohesion forces**	1- Highly viscous binders 2- Adsorption layers (<3nm thickness)
III	**Surface tension and capillary pressure**	1- Liquid bridges 2- Capillary pressure

IV	**Attraction forces between solids**	1- Molecular forces
		     a- Van-der Waals forces
		     b- Free chemical bonds
		     c- Associations (non-valence); hydrogen bridges
		 2- Electric forces (electrostatic, electrical double layers, excess charges)
		 3- Magnetic forces

V	**Interlocking forces**	

a		Sinter bridges (I-1) Partial Melting (I-2) Crystallization of soluble substances (I-5 and I-6-a)
b		Chemical reactions (I-3) Hardening binders (I-4) Highly viscous binders (II-1) Adsorption layers (<3nm thickness) (II-2)
c		Liquid bridges (III-1) Hardening binders (I-4) Crystallization of soluble substances (I-5 and I-6-a) Deposition of suspended particles (I-6-b)
d		Molecular forces (IV-1) Electric forces (IV-2) Magnetic forces (IV-3)
e		Interlocking forces (V)
f		Matrix binder (I-3, I-4 and II-1) Capillary forces (conglomerates saturated with liquid) (III-2)

Figure 3. 1 Pictorial representation of the binding mechanisms of agglomeration (Pietsch, 2005)

Holley, 1981 studied the binders and binder systems for agglomeration. Author defined the ***binder*** as any substance that can be used to cause particles to adhere together into agglomerate. Since binders can accomplish this in a number of different ways, they cannot all be used in all possible applications. It is therefore useful to categorize binders in some systematic way. Several different classifications have also been proposed, with one of the most useful being the division of binders into the following five groups.

1. ***Inactive Film:*** The binder forms a sticky layer on the particles which bind them together. The film can bind by capillary forces or through adhesional or cohesional forces. The binding is typically reversible.

2. ***Chemical Film:*** The binder forms a film on the particle surface, which then undergoes a chemical reaction and hardens. The binding is typically irreversible.

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3. *Inactive Matrix:* The binder forms a more-or-less continuous matrix that particles are imbedded in. Often the binder is a material such as a tar, pitch, or wax that is heated or emulsified to make it fluid and then hardens upon cooling or drying. Binders of this type often require high compaction forces and high binder dosages. Binding may be reversible upon heating.

4. *Chemical Matrix:* The binder forms an approximately continuous matrix, which undergoes a chemical reaction that causes it to harden. Binding by this mechanism usually is irreversible.

5. *Chemical Reaction:* The binder actually undergoes a chemical reaction with the material that it is binding, resulting in a very strong bond. This is specific to particular types of material, and binders of this type have not been developed for iron ores (Eisele and Kawatra 2003).

It should be noted that sometimes a single binder can be classified in different ways, depending on its dosage and the details of its application; examples of each of these types of binder are reviewed by Eisele and Kawatra, 2003. Iron ore pelletization currently uses ''inactive film'' binders because they are generally effective at low dosages, bind the particles rapidly without the need to wait for a chemical reaction to be completed, and typically do not require large compaction pressures in order to work.

3.3   Bentonite: conventional binder

Bentonite, a mixture of clay mineral (hydrated alumina-silicate clay), consists of montmorillonite (smectite class mineral) as the major component and small quantities of quartz, mica, feldspar and kaolin. The theoretical formula is given by (Grim, 1968) for montmorillonite as $(OH)_4.Si_8.Al_4.O_{20}.nH_2O$, corresponding to a composition of 66.7% SiO_2, 28.3% Al_2O_3 and 5% H_2O. The actual composition varies from this formula because of substitutions eg. Al^{+3} for $Si+4$ and Mg^{+2} for Al^{+3} in the lattice (Ball, *et al.,* 1973). Typical chemical analyses of some bentonite samples are given in Table 3.2

Table 3. 2 The chemical analyses of some bentonite samples

Sample,%	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI	Reference
Wyoming	65.00	18.00	3.50	2.50	0.43	0.94	2.06	7.40	Ball, 1973
Reşadiye	67.76	16.86	4.17	1.38	0.73	2.19	3.62	2.93	XRF
Lake Superior	58.36	21.14	3.96	3.82	0.58	1.43	2.98	6.75	XRF

The basic crystal structure of montmorillonite is drawn by Grim, 1968 and re-drawn by Eisele and Kawatra, 2003 and shown in Figure 3.2. It has a lattice structure arranged in layers which is capable of absorbing great water quantities between the individual layers. On such occasions the distances between the lattice layers increase considerably. The mineral swells. This swelling property and the high thixotropic behavior are the most important characteristics for its bonding capacity (Meyer, 1980).
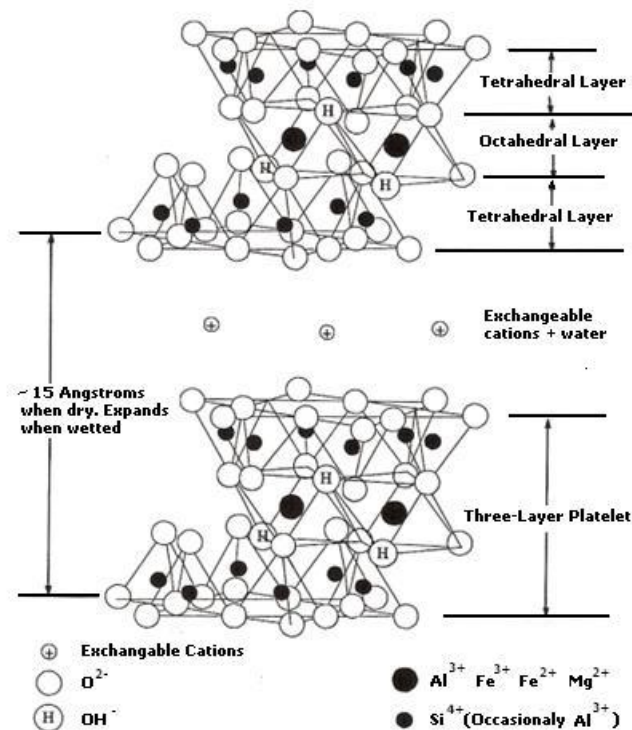
Figure 3. 2 Structure of the smectite crystal. Each clay platelet consists of three layers: two layers of silica tetrahedral and an octahedral alumina/magnesia layer joining them. Platelets are loosely bonded by counterions (typically sodium or calcium) between them. In the presence of water, the counter ions hydrate, causing the clay to expand (Eisele and Kawatra, 2003)

The most successful and widely used binder is bentonite. Bentonite has found the widest application in the pelletizing process and has played a major part in the development of successful balling techniques (Ball, *et al.,* 1973). Bentonite dosages were given in literature as 0.5 to 1.5% by weight of iron ore concentrate (Ball *et al.,* 1973, Meyer, 1980, Pietsch, 2005)

Bentonite absorbs water and, hence, controls ball growth while imparting some plasticity to pellets. This property is important for handling of green pellets from a point to another during process. Upon drying bentonite gives additional strength to pellets owing to dry film bonding of mineral grains.

Ripke and Kawatra, 2000 summarized the effect of bentonite clay as binder in pelletizing after Ball, *et al.,* 1973

- Bentonite absorbs moisture, allowing for higher moisture concentrate feeds to be pelletized.
- Clay layers expand and disperse, when added into iron ore concentrate, from the hydration of exchangeable interlayer cations, throughout the concentrate transforming into a matrix that bonds the ore particles together.
- Bentonite is well dispersed and provides an even moisture distribution to the wet pellet as it grows.
- During drying, bentonite increases the drying rate by providing a pathway for the moisture to be removed through.
- It has been reported by Ball, *et al.,* 1973 that bentonite may result in "slag bonding" that improves the strength of the fired pellet.

The essential parameters affecting the high barite iron ore concentrate pelletizing process were studied using normal and activated bentonite as binder materials by Mohamed et al., 2003. They investigated the properties of green, dried and fired pellets using chemical and X-ray analyses. The average compressive strength of fired pellets 1.5% normal bentonite and fired $1300^{o}C$ for 25 min exceeded 200 kg/p. However, they found that lower compressive strength value for pellets made with addition of activated bentonite. Furthermore, it was reported that the productivity of

green pellets decreased when activated bentonite was used as binder alone.

The use of bentonite binder in iron ore pelletizing is useful as explained above. However, bentonite is considered as an impurity due to its high SiO_2 and Al_2O_3 contents (see Table 3.2). These acid oxides are known for their adverse effects on the iron-steel making economy. Here are a few examples collected from literature:

- For instance, the addition of 1% bentonite, containing 85% $SiO_2+Al_2O_3$, decreases the pellet's iron content 0.6% (de Souza *et al*.,1984).
- In another study, authors found that the addition of 1% bentonite decreases the iron content by about 7 kg/ton of iron ore (Kater, and Steeghs, 1984).
- An increase in the silica content of pellet charge by 1% (abs.) leads to an increase in the unit cost of making the steel by \$4-7 (U.S.)/ton (Chizhikova *et al*., 2003).
- In the case of direct reduced pellets, every percent of acid gangue addition is associated with an increased energy consumption of 30 kWh/ton (Heerema *et al*., 1989).

The main disadvantage of bentonite and other binders based on silicate minerals is that they add silica to the finished product pellet. Since the purpose of iron ore processing is to remove silicate minerals from the ore, adding silicates back in the form of binder is counterproductive. This has prompted long-term interest in developing or discovering binders that contain no silica. Particular attention has been devoted to organic binders, which include a variety of carbon-based polymeric or fibrous compounds (Eisele and Kawatra, 2003). Because of good binding properties without contaminating the product pellets, organic binders have attracted attention among researchers. The use of organic binders in iron ore pelletizing and some results are discussed in detailed in the following part.

3.4   Organic binders and manufactured organic based binders

Organic binders offer the perfect alternative to conventional bentonite binder since they do not contaminate the chemical composition of pellets. In recent years, organic binders have been tested in order to eliminate the negative effects of bentonite or other silicate based binders.

Organic binders are based on the cellulose and carboxymethyl cellulose structures, which are illustrated in Figure 3.3. Some of these binders have a substantial sodium content because of their inclusion of sodium in some of their anionic side groups. Because sodium can be troublesome in the blast furnace, this is an undesirable feature that should be kept in mind when using these binders. In the Bureau of Mines study, the physical properties of pellets bonded with 0.10% carboxymethyl cellulose (CMC) were comparable to pellets bonded with 0.50% bentonite. The highest values for the wet drop test were achieved with the CMC binders with the highest PWAT values at about 8% pellet moisture. These binders can be added to the concentrate as either dry powder or as water slurry while still producing satisfactory pellet quality (Eisele and Kawatra, 2003).

Organic binders which burnt out at relatively low temperatures with virtually no or little residue are the most widely preferred alternative binders to bentonite. The advantages of organic binders can be listed as follows;

- They provide sufficient wet pellet strengths,
- They are free from impurities,
- They do not contaminate pellet composition (high Fe and low impurity content),
- Ability to reduce slag level (less flux consumption),
- They provide a more porous pellet structure,
- Higher reducibility due to higher porosity.
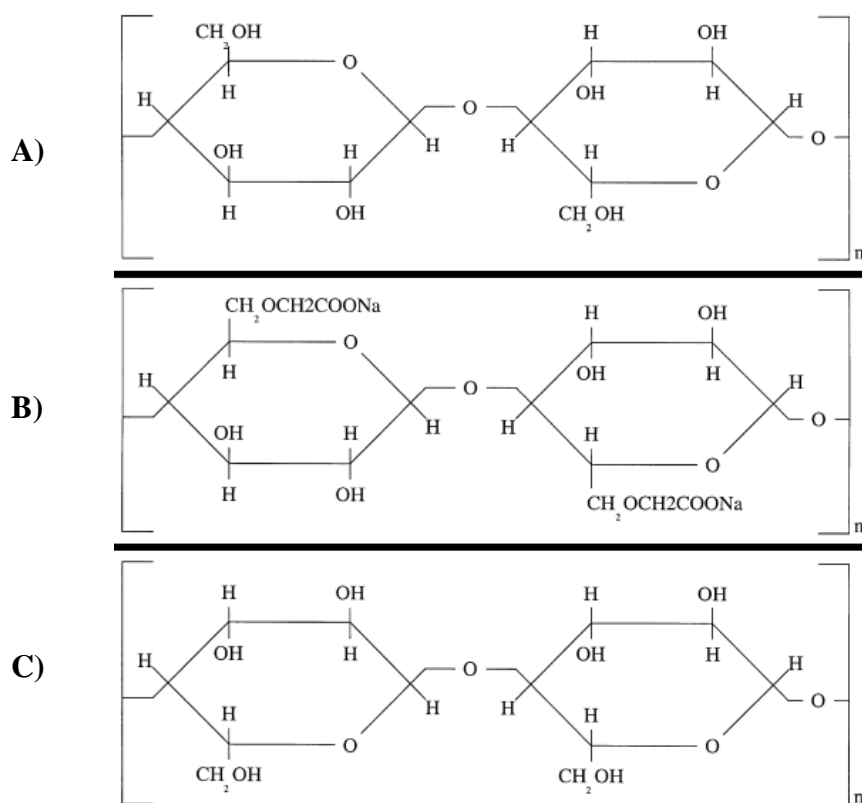
Figure 3. 3 Idealized chemical structures of the repeating base units for **A)** cellulose, **B)** CMC; carboxymethyl cellulose, and **C)** starch. Differences in characteristics of various starch and cellulose derivatives are due to changes in the side groups and chain lengths (Eisele and Kawatra, 2003)

The specific benefits of use of organic binders in iron ore pelletizing are reported by Shmitt, 2005 as follows;

- Higher productivity of the pellet plants, a result from more consistent pellet sizing and superior green pellet properties. Less fines and oversize are rejected from roll screens immediately before the furnace and airflow through the pellet bed is improved. In some plants, pellet production increases of 1000 Mt/day have been reported when replacing bentonite with organic binders.
- Reduced spalling because of the more gradual release of water from the pellets in the drying zones, a particularly troublesome problem for hydrated ores.
- The ability to meet stringent pellet silica specifications at a time pellet demand and production is at record high levels.

- Higher productivity of the concentrator, because there is no longer any need to compensate for the additional silica which is normally added to the pellets by bentonite. By softening the silica specifications in the concentrator, less grinding, lower generation of slimes, and higher overall recoveries.

Although organic binders give good results for green and dry pellets but they fail to impart enough strength to the preheated pellets. Schmitt, 2005 also reported that organic binders have proven themselves at a number of pellet production plants; acceptance at other facilities has been limited to a large extent because of difficulties that can occur during the processing of iron ore agglomerates and the quality of fired pellets. Although, organic binders have some advantages mentioned above, at the same time they can negatively impact the preheated and fired pellet strengths, particularly tumbles indices because of lower slag bonding. The physical quality problem is more pronounced on grate-kiln systems where pellets must have a sufficient preheat strength in order to survive the critical transfer point from grate to kiln. Pellets made with organic binders will typically have only 50% - 75% of the strength of a bentonite pellet at the grate to kiln transfer point because of the absence of low melting bonds created by the bentonite.

Due to reasons explained above, organic binders have not found widespread application in the industry Ripke and Kawatra, 2000 have reported a statistics about the pellet plants in the USA. Eight of the nine plants utilized bentonite clay as a binder, while the ninth plant used an organic binder.

Peridur® is an organic based manufactured binder produced by AkzoNobel that provides pellet makers with a technically advanced alternative to bentonite. Not only does Peridur® function as a consistent and reliable agglomeration aid, it is non-contaminating to the pellets leaving the iron ore pellets with superior metallurgical and chemical qualities. When Peridur® successfully replaces bentonite in the manufacture of Blast Furnace or Direct Reduction pellets significant cost benefits can be achieved in subsequent iron making processes (http://www.akzonobel.com, last visited on 12/01/2011).

The production of acid iron ore pellet for DR using an organic binder was studied by de Souza *et al*., 1984. They comparatively tested the bentonite and organic binder Peridur[®]. It was reported that the pellets produced with Peridur[®] showed to have more round shape and a specially smooth and shiny surface. The green pellet properties shown in Table 3.3 and can be considered good for pellet production. Authors compared the properties of bentonite bonded and Peridur[®] bonded pellets produced in 6 m disc pelletizer. These results are shown in Table 3.4. They concluded that the quality of pellets did not meet the requirements. Peridur[®] could produce satisfactory wet pellets with a small increase in dust production. However, they suggested the use of Peridur[®] as a potential option for the production of pellet for direct reduction. The authors do not mention the numerical data for strength of the fired pellets.

Table 3. 3 Green pellet characteristic with Peridur[®] in different amounts (de Souza *et al*., 1984)

Peridur[®] addition level %	Moisture of green pellets	Green pellet drop number	Compressive Strength kg/p	
			Wet	Dry
0.0700	9.4	2.6	0.95	1.68
0.0500	8.7	2.7	1.11	1.42
0.0475	8.6	2.7	1.09	1.34
0.0450	8.7	2.6	1.14	1.14

Table 3. 4 Properties of bentonite bonded and Peridur[®] bonded wet and dry pellets (de Souza *et al*., 1984)

Binder addition level %	Moisture of green pellets	Green pellet drop number	Compressive Strength kg/p	
			Wet	Dry
Peridur[®] 0.060%	8.3	4.2	1.26	3.2
Bentonite 0.50%	8.6	2.4	0.96	1.3

Arol *et al.*, 1989 comparatively studied the quality of pellets produced with bentonite and selected organic binders namely Peridur[®] CX3, Peridur[®] C-10 and technical grade CMC with magnetite concentrates from Divriği, Turkey. It was reported that drop numbers and wet pellet compressive strength of pellets bonded with organic binders are superior to bentonite bonded ones. The compressive strength of dried

pellets at 400°C also found to be satisfactory. However, compressive strength of pellets produced with organic binders and fired at 1200°C for 120 minutes were found insufficient (Figure 3.4) as organic binders reduce the slag formation resulted in lower fired pellet strength.
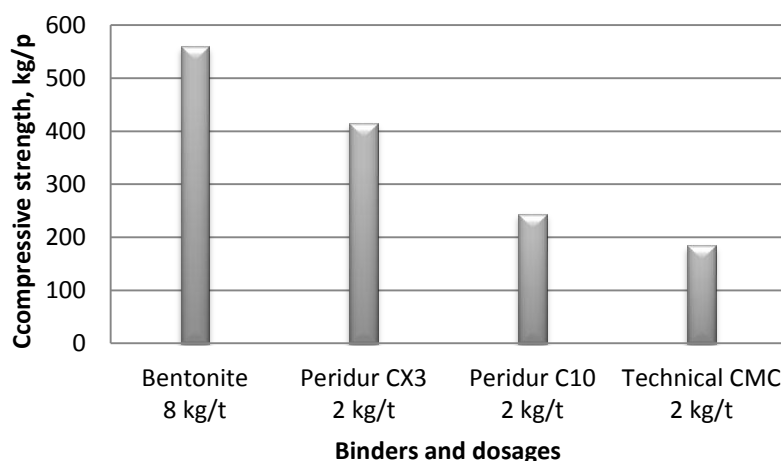
Figure 3. 4 Compressive strength of fired pellets (1250°C, 120 min) produced with selected organic binders (Arol *et al.*, 1989)

The results of the physical and metallurgical properties of product pellets are summarized in Table 3.5. They have found that the compressive strength, before and after reduction, and tumbling resistance of product pellets produced with bentonite were notably higher than those produced with organic binders. Only bentonite binder was found to be satisfactory for industry when these physical properties are considered. However, porosity and swelling of pellets produced with organic binders was larger than those of pellets produced with bentonite. As greater porosity is known to lead to faster reduction, reducibility of pellets with organic binders was found to be greater than that of the bentonite pellets. In addition, one of the advantages of organic binders is that they do not contaminate the pellet composition since they burnt-out with no or little residue during thermal treatment. They also found that the Fe contents of pellets bonded with organic binders are slightly greater than those of pellets with bentonite as a natural consequence of adding no impurity.

Table 3. 5 Physical and metallurgical properties of product pellets produced with selected organic binders (Arol *et al.*, 1989)

Binder and Addition level	Compressive Strength (before reduction) kg/p	Compressive Strength (after reduction) kg/p	Tumbling Test		Porosity %	Reducibility ISO 7215 %	Swelling %
			+6.3 mm	-0.5 mm			
Bentonite 8 kg/t	560	68	94.5	5.3	15	65	8
Peridur® CX3 2 kg/t	415	43	88.0	10.2	22	65	8
Peridur® C-10 2 kg/t	244	19	72.6	22.0	26	68	13
Technical CMC 2 kg/t	185	8	76.9	19.6	34	70	12

(Eisele and Kawatra, 2003) reviewed the commercial organic binders which are intentionally synthesized for agglomeration purpose. In general, these binders have the advantages that they are highly effective, can be specifically designed for binding particular types of particles, and have highly reproducible characteristics. Their main disadvantage is their comparatively high cost relative to other binder types.

A broad range of binders are or have been available from various manufacturers, although they are frequently only identified by name or number, with no identification of their structure. Many of these organic binders have been tested by one of the local iron ore producers, and a summary of the results obtained with several binders is given in Table 3.6.

Qui *et al,.* 2003 and 2004 investigated the use of organic binder; Funa, on balling behaviors of magnetite concentrates. The functions and molecular structure of organic binders for iron ore pelletization were examined. In the work, the basic principles of molecular design, interface chemistry and polymer science as well as failure model of binding systems were studied.

Two organic binders for iron ore pellets have been developed based on the investigation. Pelletizing experiments show that both of them are effective to iron ore pelletization. One of them, Funa, prepared from lignite or weathered coal and with

humates as major constitutes, possesses a netty molecular structure and sufficient carboxylic, hydroxyl and phenolic groups in its molecules. Funa is found less expensive than other organic binders reported before and has been put into industrial production of iron ore pellets in China (Qui *et al.*, 2003).

Table 3. 6 Commercial organic binders summary review (Eisele and Kawatra, 2003)

Manufacturer	Binders	Results
Nalco	Binder F TX-4712=TX-6326	Minipot tests were successful. Binder F is no longer available.
Akzo (Dreeland Colloids, Inc.)	Peridur® 330	Successful as complete replacement for bentonite. Slight deterioration in physical fired pellet quality, improved reducibility. No kiln dusting.
Allied Colloids	FE4, FE8, and combined with soda ash	FE4 satisfactory in minipot but poor balling performance in the plant. FE8 performed well in balling circuit, but minipot results were poor.
Union Carbide	Carbinder 498	When used as partial bentonite replacement, resulted in poor balling and constant surging.
Grain Processing Corp.	GPC-4 GPC-46 GPC-49	All three binders gave good performance with fluxed pellets as a total bentonite replacement but poor performance with unfluxed pellet feed. GPC-46 gave the best minipot sintering results.
American Cyanamid	S-7241 S-7244 S-7242 S-7245 S-7243	All five binders gave good minipot results, but balling characteristics and green ball quality were variable and generally poor.
Weyerhauser	Cellulon	Generally unsuitable because the binder could not be produced with a fine enough size consists.
Glenn Chemical	Mackquadt I-O	Generally good fired pellet quality and poor green ball quality.
Aqualon	AQU-D3217-B (sodium carboxymethyl hydroxyethylcellulose)	Gave good bench balling and miniport firing results as a total bentonite replacement. Some green ball plasticity occurred at higher binder dosage levels.
Sherex	DP 3349-179 (petroleum extracts and paraffinic distillate solvent)	Physical pellet quality was good but ballability was poor and the green balls had excessive surface moisture.

3.5   Other inorganic materials tested as binder

Inorganic alkaline materials have often been tested, but with little success. The results of pelletizing test using some inorganic materials and a specular hematite are published by Ridrigon *et al.*, 1954 and shown in Table 3.7. The dry strength and some fired strength were increased with the addition of such inorganic materials. The mechanism of these effects has not been completely elucidated. The possibility of

chemical reaction between sodium compounds and the iron ore has been postulated by some researchers, however but test work to confirm this proved inconclusive (Ball, *et al.,* 1973).

Table 3. 7 The effect of inorganic materials on pellet strength (Ridrigon *et al.*, 1954, Ball, *et al.,* 1973)

Inorganic binder		Strength kg/p (25 mm in diameter)		
Type	Amount, %	Green	Dry	Fired at 1300°C
without	0.0	1.00	0.30	678
NaOH	2.0	1.15	5.40	1150
Na_2CO_3	3.0	1.20	4.60	1350
K_2CO_3	3.0	0.75	1.50	--
$CaCl_2$	3.0	0.80	2.00	910
$MgCl_2$	3.0	1.30	4.00	320
$MgSO_4$	3.0	0.75	2.70	--

$FeSO_4$ which is added at 0.70% to magnetite concentrate in at L.K.A.B plant in Sweden has been found to be effective. Sodium chloride, which is added to the pellets in which sea-water is used to make the green balls, has been tested in Hamersley plant in Australia (Ball, *et al.,* 1973).

Fly ash based binders (FBB) were tested (Eisele *et al.*, 1997, Kawatra *et al.*, 1998a, 1998b and Ripke and Kawatra, 2000) to replace bentonite or reduce the bentonite dosage. Ripke and Kawatra, 2000 aimed to use fly ashes from fluidized-bed combustor since they have high calcium oxide content from addition of limestone to the fired coal to absorb sulfur, and have been shown to be useful as a binder for iron ore pellets. They produced magnetite concentrate pellets with bentonite, fly ashes added calcium hydroxide $(CaOH)_2$ and calcium chloride $(CaCl_2)$ as activator and hardening accelerator, respectively. It was reported that iron ore concentrate pellets produced with up to 50% of the bentonite replaced by fly-ash exceeded minimum industrial specifications for dry compressive strength. However, the pellet strengths decreased proportional to the amount of replacement. When bentonite was completely replaced with fly-ash, the resulting strength was only 20% of the strength with bentonite. They concluded that bentonite is a physical binder, while FBB is a pozzolanic binder.

Ahmed & Mohamed 2005 studied the green, dry and indurated iron oxide pellet properties with bentonite and calcium hydroxide addition. They used binder mixtures consist of 0.4% bentonite, and varying percentage of calcium hydroxide (ranges from 0.5 to 4%). The partially replacement of expensive bentonite with cheap lime hydrate was aimed in the research for pelletizing of iron oxide. The results show that, on using binder mixture composed of 0.4% bentonite and 0.5% calcium hydroxide a deterioration effect of the physicochemical properties of the mill scale pellets was observed. It was reported that increasing percentage of calcium hydroxide in the binder mixture enhanced the properties of pellets.

Tuğrul N. *et al.,* 2006-2007 studied the effects of addition of $Ca(OH)_2$ and $CaCl_2$ in iron ore pelletizing using pyrite ash as iron source. They found that the addition of 1% $Ca(OH)_2$ and 0.2% $CaCl_2$ had increased the effectiveness of 0.5-1.2% bentonite. It was also reported that, the compressive strength of pellets fired at 1200^oC 30 minutes and containing $Ca(OH)_2$ and $CaCl_2$ in addition to bentonite were better (1239.3 N/p - 1785.4 N/p) than those (232.2 N/p - 333.5 N/p) obtained with only bentonite binder. However, these values are not acceptable for fired pellet compressive strength since the minimum required fired pellet compressive strength is 2500 N/p (250kg/p).

de Moraes and Kawatra, 2010 studied pelletizing of magnetite concentrate with some inorganic materials; sodium hydroxide, sodium carbonate, sodium metasilicate sodium tripolyphosphate and an organic binder, CMC. They tested strength of wet-dry pellets and pellet strength after thermal shock in a muffle furnace at 300^oC, 500^oC, 700^oC, and 900^oC for 10 minutes. Results with obtained with different inorganic materials were compared to those obtained with bentonite bonded pellets. It was reported that the bentonite dosage can be reduced from 0.66% to 0.40% with 0.02% NaOH to produce same quality pellets. Although pellets bonded with bentonite shows cracks at all temperatures, there were no explosions during thermal shock test of pellets bonded with bentonite and bentonite + NaOH. The addition of 1.50% sodium silicate improved the compressive strength of pellets. The pellets made with 1.50% sodium carbonate showed better results than pellets bonded with 0.66% bentonite, however, 27% of these pellets exploded during thermal shock.

Inorganic materials do not contain silica have a slight advantage over bentonite when silica levels are the primary concern of steel makers. However, most of them are incapable of controlling water during pelletization, and do little to contribute to the cohesive/adhesive forces required to form and maintain green pellet integrity. This results in poor quality green balls that are fragile and easily broken, lowering production rates at iron making facilities. Furthermore, due to the massive amounts required for basicity control and pelletization, some inorganic materials can contribute to spalling of pellets decreasing the quality of the finished product.

The results reviewed above showed that organic binders produce good quality green and dry pellets. However, they failed to provide enough strength to the preheated and fired pellets as a result of reduced slag bonding (Kater and Steeghs, 1984, de Souza *et al.*, 1984, Goetzman, 1988, arol et al., 1989, Arol 1997, Sivrikaya and Arol 2008,2009,2010, 2011), which is especially more important in pelletizing of hematite ores due to lack of oxide bonding mechanism. As such, organic binders have hitherto failed to be an alternative to bentonite, except a few cases of straight-grate pelletizing, where there is no dynamic pellet bed. In recent years efforts have been focused on improving the preheated and fired strength of pellets produced with organic binders. In this context, boron compounds have been considered as an additive in conjunction with organic binders to improve preheated and fired pellet compressive strength in this thesis.

3.6   Use of boron compounds as binder

Even though organic binders have some advantages over bentonite binder for iron ore pelletizing, they still fail to satisfy all the requirements especially those related to the mechanical strength of preheated and fired pellets. In order to use organic binders successfully, this shortcoming must be overcome. One plausible method is to introduce a slag forming constituent to the pellet mix so that the strength of the pellets would be reinstated as a result of slag bonds formed in pellet structure.

Boron compounds might be the potential additive to organic binders as they are known to lower the melting point of silica glasses (Marshall, 2007). Numerous boron

compounds of natural or synthetic origin can be used for this purpose. Some of the boron compounds can be considered as binder or additive in iron ore pelletizing are; colemanite, tincal, ulexite, borax pentahydrate, boric acid and boron oxide.

The boron compounds tested in iron ore pelletizing by some researchers are given in the Table 3.8. Important characteristics of boron compounds are mentioned in the Table 3.8. None of those boron compounds contain significant amount of SiO_2 or Al_2O_3 which are unwanted impurities for iron pellet chemical composition. Their melting temperatures are relatively low.

The iron ores or concentrates contains varying amounts of SiO_2. On the other hand, the boron compounds have significant amount of boron in their compositions as seen in Table 3.8. Their presence in the pellet mix leads to formation of borosilicate glass bonds. Borosilicate glasses are known for their low melting temperature. Thus, formation of borosilicate glasses is expected to take place at lower temperatures. This occurrence would contribute to the strength of the pellets through slag bonding (Meyer, 1980). Absence of acidic impurities in boron compounds combined with low melting temperature, good thermal and mechanical properties of borosilicate glasses favor the use of boron compounds as slag forming constituents. When used with an organic binder, while the boron compounds render the required properties to preheated and fired pellets, green and dry pellets attain the required quality through organic binders. Hence, combination of an organic binder and a boron compound can be used as binder in place of bentonite in iron ore pelletizing.

Table 3. 8 Some boron compounds used as additives in iron ore pelletizing by researchers

Boron Compounds	Description	Chemical formula	B_2O_3 content %	Melting point	Solubility in water	Specific gravity	Molecular weight g/mol	Reference
Colemanite	Calcium-borate (natural mineral) Dicalcium hexaborate pentahydrate	$2CaO.3(B_2O_3).5(H_2O)$ or $Ca_2 B_6 O_{11} 5(H_2O)$	~43	$986^{o}C$	0.81 g/l @ $25^{o}C$	2.40	411.08	Tektaş, 2003
Calcium-borate	Synthetic calcium-borate		~49	$986^{o}C$	Insoluble	2.40	411.08	Schmit, 2005
Tincal	Sodium-borate (natural mineral) Sodium tetraborate decahydrate, Disodium tetraborate decahydrate Borax decahydrate	$Na_2O.2(B_2O_3) 10(H_2O)$ or $Na_2B_4O_7 \cdot 10(H_2O)$	~36	$62^{o}C$ when heated in closed atmosphere	4.7% @ $20^{o}C$; 65.6% @ $100^{o}C$	1.71	381.37	Mergen, and Tektaş, 2003
Borax pentahydrate	Derivative of tincal Sodium tetraborate pentahydrate, Disodium tetraborate pentahydrate	$Na_2 B_4O_7. 5(H_2O)$	~48	$200^{o}C$ when heated in closed atmosphere	3.7% @ 20°C; 51.2% @ 100°C	1.81	291.35	Tektaş *et al*, 2007
Boric acid	Orthoboric acid Boracic acid Optibor,	H_3BO_3 or $B(OH)_3$		$170.9^{o}C$	4.72 g/100 ml @20 °C; 27.53 g/100 ml @100 °C	1.435	61.83	www. wikipedia. org
Boron oxides	Boron trioxide (the most common form) Boron monoxide Boron suboxide	B_2O_3 B_2O B_6O	Pure	450 °C (trigonal) 510 °C (tetrahedral)	2.2 g/100 ml	2.460 liquid	69.62	www. wikipedia. org

The boron compounds have been proposed as slag forming constituents either alone or in combination with organic binders by some researchers (Köroglu, 1980, Malysheva, 1996, Schmitt, 2005, Sivrikaya and Arol 2008, 2009, 2010, 2011).

Köroğlu, 1980 tested calcined colemanite alone and in combination with bentonite as alternative binder for pelletizing of magnetite concentrate. The magnetite concentrate had 64.70% Fe and 4.22% SiO_2. The binder dosages, firing temperature and fineness of magnetite concentrate were investigated as operation parameters for the quality of pellets. Bentonite and calcined colemanite dosages were in the range of 0.5, 1.0, 1.5, 2.0% and 1, 2, 3, 4, 5, 6 and 7%, respectively. It was reported that, the calcined colemanite as a binder alone is insufficient with regard to wet and dry compressive strength quality, as seen in Figure 3.5. It was also reported that, increasing firing temperature from $1200^{o}C$ to $1350^{o}C$ increases the compressive strength of the pellets produced with bentonite or calcined colemanite. The test results obtained with different calcined colemanite dosages showed that increasing addition level of calcined colemanite from 1% to 7% increases the compressive strength of fired pellets significantly (Figure 3.6). The researcher tested the combination of bentonite and calcined colemanite in order to produce pellets with both sufficient wet, dry and fired strengths, and meaningful increases in compressive strength of fired pellets were reported (Figure 3.7).
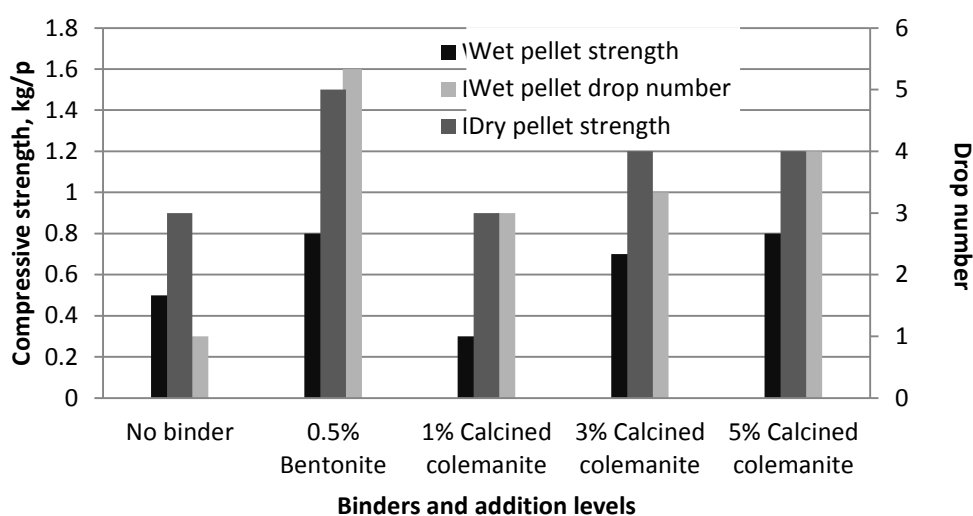
Figure 3. 5 Compressive strengths of wet and dry pellets and drop numbers of wet magnetite pellets made with –200 mesh particle size (Köroğlu, 1980)
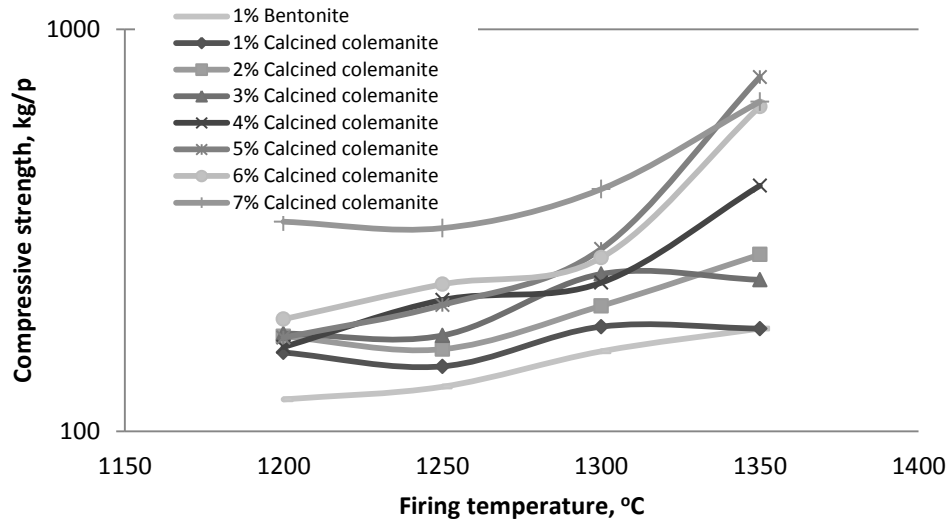
Figure 3. 6 Effect of calcined colemanite dosages on the compressive strength of fired magnetite pellets made with −200 mesh particle size (Köroğlu, 1980)
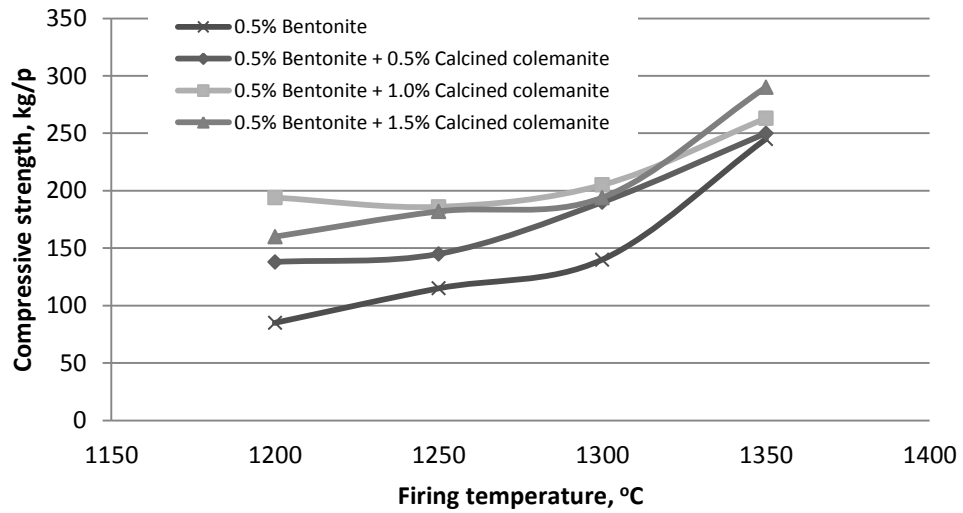
Figure 3. 7 Effect of addition of bentonite and calcined colemanite combination on the compressive strength of fired magnetite pellets made with −200 mesh particle size (Köroğlu, 1980)

Timuçin *et al.,* 1986 investigated the reducibility properties of itabarite ore (99.66% Fe_2O_3) pellets produced with calcined colemanite addition. The particle size of itabarite ore was 70.90% passing 37 μm. Several addition levels of calcined

colemanite were tested and the pellets with 10 mm diameter were heated at a temperature of $800^{\circ}C$. These pellets then were reduced in a tube furnace at $900^{\circ}C$ under CO atmosphere and reducibility of pellets was calculated. They reported that calcined colemanite addition has a catalytic effect on reducibility of colemanite added pellets. While reducibility of pellets with no binder was only 92% after 4 hours, the reducibility of 0.6% colemanite added pellets were reduced completely in 2 hours, as seen in Figure 3.8. The maximum catalytic effect of calcined colemanite was at 0.6%, the greater addition levels decrease the catalytic effect of colemanite.
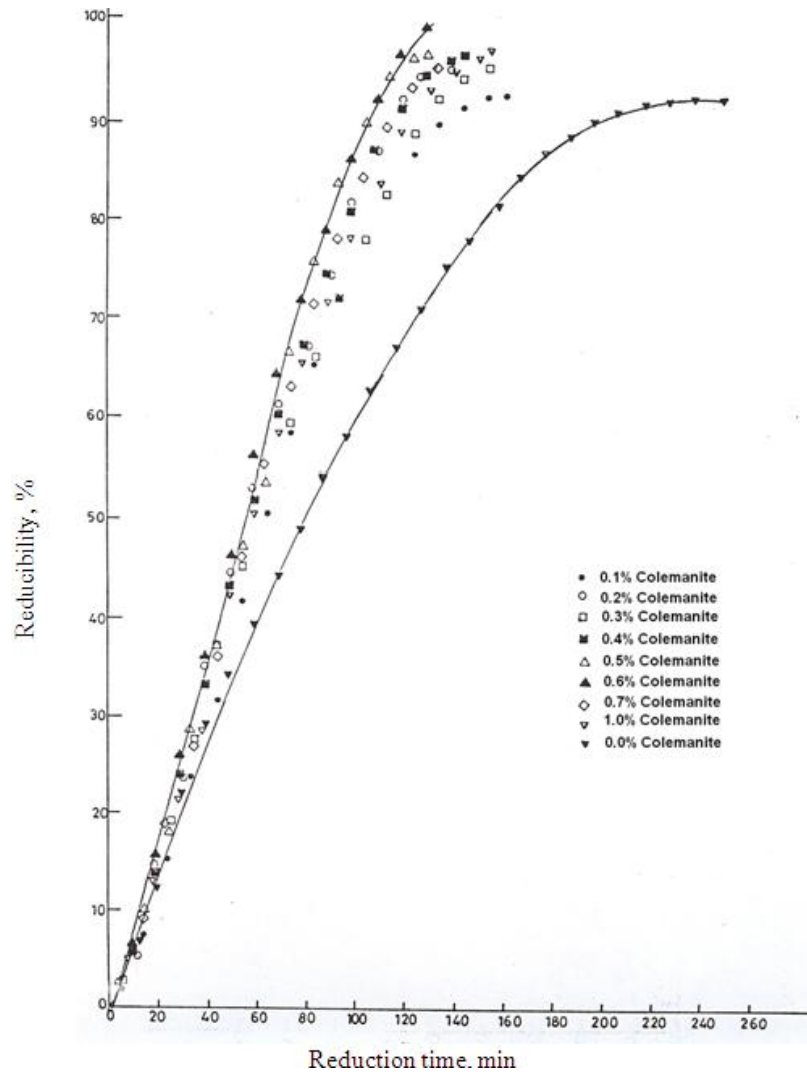
Figure 3. 8 The effect of calcined colemanite addition on the reducibility of itabarite pellets (Timuçin *et al.,* 1986)

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The effect of calcined colemanite and bentonite combination on the reducibility of pellets was also investigated in the same study. It was reported that the catalytic effect of colemanite on reducibility of iron ore pellets was decreased when used together with bentonite Figure 3.9.
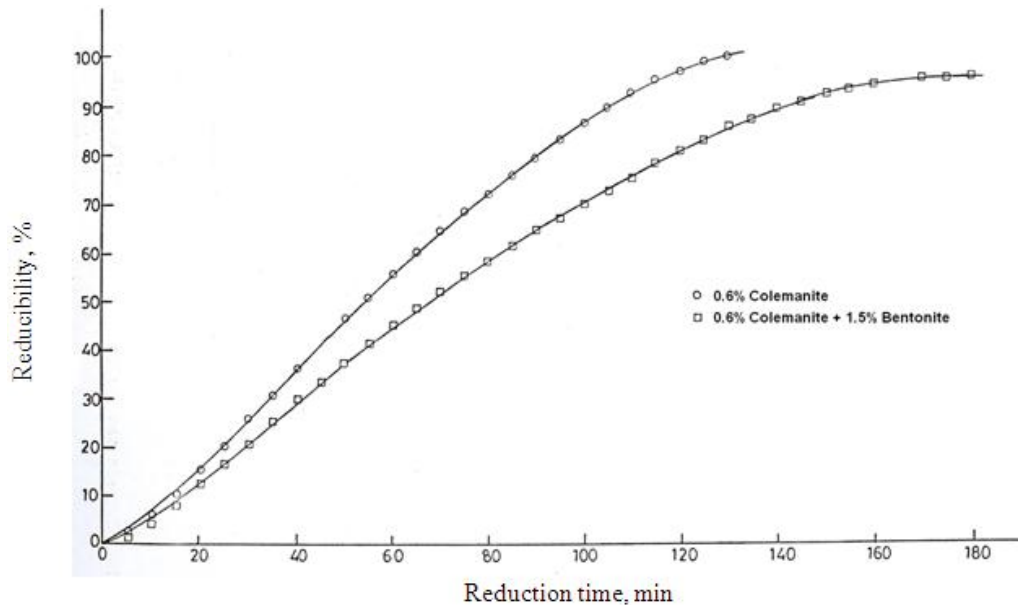
Figure 3. 9 The effect of calcined colemanite and bentonite addition on the reducibility of itabarite pellets (Timuçin *et al.,* 1986)

Guangquan, 1990 studied the shaft furnace pelletizing test of iron ore concentrate with addition of boron oxide. He investigated the effect of boron oxide addition into iron ore pellets on blast furnace operation. It was reported that;

- Firing temperature of pellets with the addition of 1.5-2.0% of boronic eluted dust can decrease by 70-100°C,
- Quality indices of pellets can be improved obviously: fired pellet compressive strength 2000-2200 N/p, ISO strength up to 84-86%,
- No degradation phenomenon occurred after reduction,
- Tumbler strength after reduction increased by 13.8%,
- Results of 100m^3 blast furnace operation during 15 months indicated that: blast furnace productivity has increased from 1.4 t/(m^{3}day) to 1.74 t/(m^{3}day),
- Coke rate has decreased from 716 kg/t to 630 kg/t.

Malysheva *et. al.,* 1996 studied the effect of boron on the quality of iron ore pellets. Experiments were designed to clarify the actual mechanism of the effect of boron on the strengthening of fluxed pellets. Researchers used chemically pure boron oxide (B_2O_3) as boron compound. They reported that boron has beneficial effect at all stages of metal production and the quality of pellets was increased. Pellets with bentonite and weight percentage of B_2O_3 in the charge (0.0, 0.3, 0.5, 2.0) were formed and fired. However, bentonite dosage was not mentioned in the report. The basicity of pellets was $CaO/SiO_2=1.2$ and firing temperature range was from 600 to 1300^oC. It was reported that the strength of green pellets markedly increased: from 0.8 kg/p to 1.5, 2.0 and 5.0 kg/p if boron oxide additions amounts to 0.3, 0.5 to 2.0 wt% respectively. Higher strength of green pellets cuts the costs required for repetitive processing of fines and increases the capacity of plant.

The effect of B_2O_3 addition on fired pellet strength was determined by Malysheva *et. al.,* 1996 and given in Figure 3.10. They also investigated the desulfurization process of pellets and found desulfurization process in B_2O_3 containing pellets is more rapid compared with the pellets without B_2O_3 and takes place at lower temperatures because of the early formation of melt (Figure 3.11).
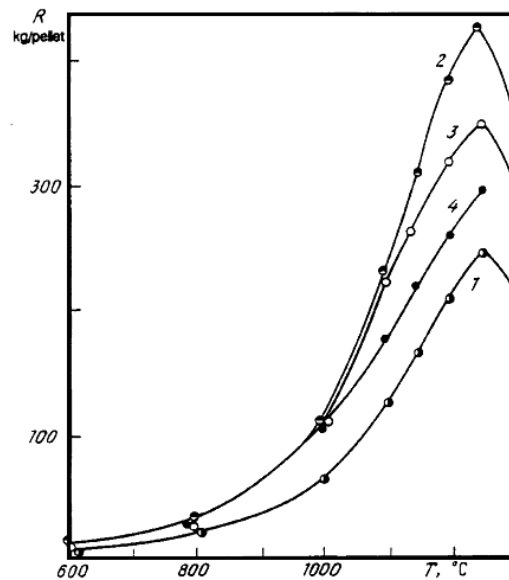
Figure 3. 10 Effect of boron oxide on the strength of pellets fired at different temperatures: (1: without B_2O_3 and 2, 3, 4 : 0.3, 0.5, 2.0 % B_2O_3, respectively) (Malysheva *et. al.,* 1996)

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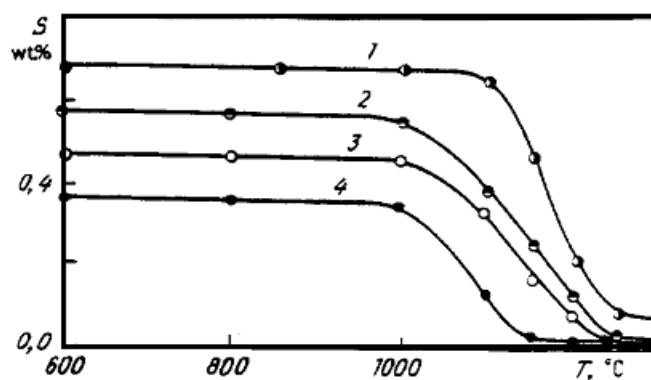
Figure 3. 11 Effect of firing temperature on the residual sulfur content of pellets differing in B_2O_3 content: (1: without B_2O_3 and 2, 3, 4 : 0.3, 0.5, 2.0 % B_2O_3, respectively) (Malysheva *et. al.,* 1996)

Schmitt, 2005 studied the addition of some boron containing compounds to the organic binder Peridur[®] to improve physical quality of pellets. He used for different iron oxides (a magnetite-hematite blend concentrate, a specular hematite concentrate, two magnetite concentrate with flux and without flux) and tested colemanite, sodium tetraborate pentahydrate, sodium tetraborate decahydrate and synthetic calcium borate as boron compounds alone or in combination with Peridur[®]. The results obtained with pellets produced with boron compound addition were compared with the baselines obtained with bentonite or Peridur[®] alone. The addition levels were 0.04% or 0.05% for Peridur[®] and 0.05% to 0.20% for boron compounds. It was reported that boron compounds increase the physical strength for both preheated and fired pellets, tumble indices, and reduce the sulfur content of fired pellets. In addition to desulfurization, the addition of boron containing compounds to iron ore pellets made from specular hematite has shown the ability to increase reducibility and metallization of DR pellets.

It is believed that the mechanism behind the preheat strength generation is the bonding that occurs when the boron compounds melt and fuse the iron ore grains together at contact points. To demonstrate, bentonite, Peridur[®], and Peridur[®] plus colemanite pellets were sawed in half and photographed under a scanning electron microscope (SEM). The surface of the iron ore grains are shown for bentonite pellets

(Figure 3.12) and Peridur$^®$ plus colemanite pellets (Figure 3.13). The surface of the iron ore grains for those pellets has taken on a more rippled, wave like appearance as if there had been some fusion and/or melting of particles onto the iron ore grain surface. While the pellets made with just Peridur$^®$ (Figure 3.14) have less of this formation. This visual evidence supports the belief that a melt takes places on the surface of the iron ore grains at temperatures less than 1121°C temperature reached in the preheat firing cycle (Schmitt, 2005).
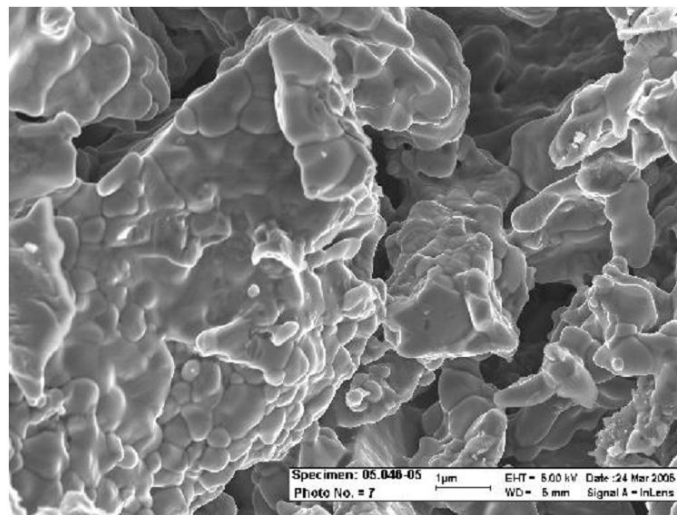
Figure 3. 12 SEM image of preheated pellet at 1121°C made with bentonite (Schmitt, 2005)
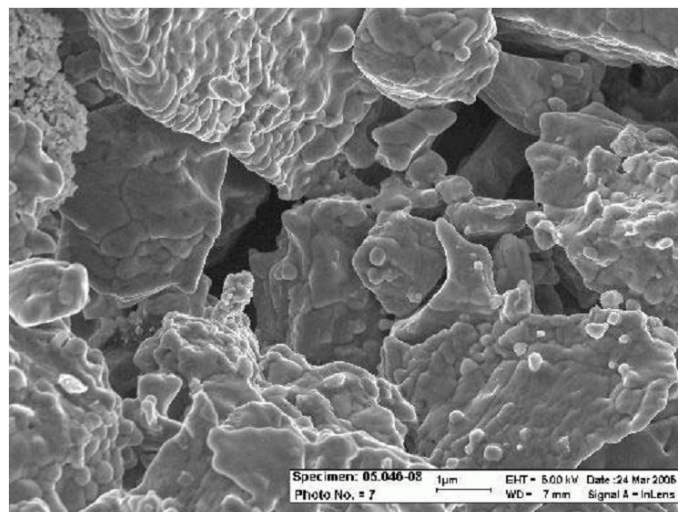
Figure 3. 13 SEM image of preheated pellet at 1121°C made with Peridur$^®$ plus colemanite (Schmitt, 2005)
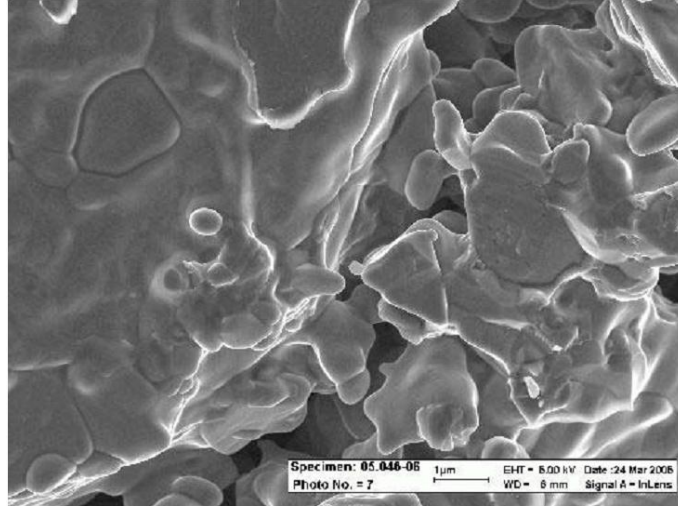
Figure 3. 14 SEM image of preheated pellet at $1121^{o}C$ made with Peridur[®] (Schmitt, 2005)

Coşar, 2006 investigated the use of boron minerals and wastes in iron ore pelletizing in his M.Sc. thesis. He used colemanite, borax, ulexite and borax tailing as additives to bentonite in pelletizing of Divriği magnetite concentrate in the study. The addition levels were 0.7% and 0.05% to 0.20% for bentonite and boron compounds, respectively. It was reported that boron minerals had negative effects on pellet compressive strength when compared to the results obtained with bentonite bonded pellets. In addition, the pellet strength decrease was found to be higher when the addition level of boron minerals was increased from 0.05% to 0.20%. The reason of the lower strength was due to direct addition of boron minerals to the pellet feed. If they are added directly (without calcination) to the pellet feed, they will cause spalling or even explosion of pellets during thermal treatment. Therefore, a pre-calcination process must be applied to the boron minerals before adding to the pellet feed.

The spalling of pellets can be explained by the decrepitation of boron minerals since they contain considerable amount of chemically bonded water in their structure. Decrepitation, shrinkage and expansion of boron minerals, namely colemanite, ulexite and borax under heat treatment were presented by Şener 1991, Şener and Özbayoğlu 1995, Çelik *et al.,* 1994,1998, Arslan *et al.,* 1999, Özbayoğlu *et al.,* 2001.

Industrial test data are published by Akberdin and Kim, 2008 regarding the production (at Sokolovsk–Sarbaisk mining and enrichment enterprise) and blast-furnace smelting (at Magnitogorsk metallurgical works) of boron-alloyed iron-ore pellets (500000 t). Authors did not mention about the borate ore, they only gave the percentage of borate ore addition and the calculated percentage of B_2O_3 in the pellets. It was reported that, thanks to the presence of boron;

- Compressive strength of the fired pellets is increased by 18.5%,
- Compressive strength of pellets after reduction is doubled,
- Limestone consumption is reduced by 11%,
- Bentonite consumption is halved,
- Dust content of the gases in the last section of the firing machines is reduced by 20%,
- In blast furnace smelting, the yield of low-sulfur ($<0.02\%$) hot metal is increased from 65-70% to 85.1% ,
- Furnace productivity from 2.17-2.20 to 2.27 t/(m^{3}day),
- Coke consumption is reduced by 3-8 kg/t of hot metal,
- The plasticity and stamping properties of 08IO auto-industry steel are improved by microadditions of boron.

CHAPTER 4

DESIRED PELLET PROPERTIES AND TESTING METHODS

The pellet properties or qualities are dependent on the properties of raw materials used in pellet production. Therefore, before pellet properties the main raw material, in this case iron ore concentrate, properties should be examined. Iron ore concentrate properties are discussed below. The main property of the concentrate for balling/pelletizing is the ***ballability*** and defined by Jaroslav, 1988, the ability to produce balls with satisfactory compressive strength. Ballability is an outcome of a variety of properties, which include particle size distribution with the intrinsic specific surface area and particle shape, particle wettability and moisture content are other important properties.

4.1   Iron ore concentrate properties

Naturally fine size iron ores or ground iron ore concentrates are main raw materials for pelletizing process. They should have some significant properties before feeding to the balling equipment. A material preparation stage is obligatory to obtain a suitable balling feed to produce good quality pellets.

The material preparation steps;

Particle size reduction *:* Multi-stage crushing and grinding processes are applied to reduce the particle size of iron ore. Crushing and grinding steps are named also comminution. Particles are liberated after grinding and ground ore is then sent to concentration step for separation.

Concentration : In general iron ores are concentrated to achieve a chemical composition suitable for smelting. Concentration is aimed to upgrade the Fe content to a desired level and to remove the undesired impurities below limits. As the best known process, magnetic separation is applied and sometimes, in addition, flotation is used.

After producing of concentrate, the following properties are determined before pelletizing.

- Particle size distribution (screen analysis),
- Specific surface area measurement (Blaine number),
- Chemical analysis of iron ore or concentrate,
- Moisture content of iron ore or concentrate (filter cake moisture),

4.1.1 Particle size distribution of iron ore concentrate

In order to produce wet pellets from ground iron ores in any balling equipment, the feed size should be less than 200 μm, with more than 60% minus 44 μm (325 mesh). Therefore, grinding operation should be directed to reach such fineness. Three different typical pelletizing feed material size analyses are given by Ball, *et al.,* 1973 in Table 4.1.

Table 4. 1 Three different typical pelletizing feed material size distribution analyses (Ball, *et al.,* 1973)

Pellet feed	Cumulative percentage				
	>76 μm	>59 μm	>37 μm	>20 μm	>10 μm
Magnetite concentrate	18	28	75	90	97
Hematite flotation concentrate	2	2	23	50	70
Limonite ore	25	25	32	50	65

The particle size distribution of feed material can be determined by screen analysis. Determination of size distribution by sieving should be done by following standard ISO 4701:2008. However, screening/sieving method is not effective for finer

particles. Therefore, the portion of the feed larger than 44 μm or 37 μm can be determined by dry or wet screening. The finer part can be determined by other sub-sieving methods. The sub-sieve size material amount plays important role in balling and increasing percentage of finer size increases the wet pellet properties (Forsmo, 2007).

Urich and Ban, 1962 demonstrated that the quality of pellets can also be controlled by the degree of grinding, and this factor is undoubtedly one of the most important aspects of feed preparation. A specular hematite was ground to give products with minus 44 μm contents ranging from 45% to 100%, and these materials were then balled and fired. It was shown in the Table 4.2 that the green ball strength increased with the degree of grind.

Table 4. 2 The effect of the degree of grind on green ball strength (Urich and Ban, 1962, Ball, *et al.,* 1973)

% <44 μm in feed material	Green ball strength	
	lb	kg
45	1.5	0.7
75	2.9	1.3
100	8.6	3.9

The major part of the particles of pelletizing feed is below than the usual size of test screen. Nowadays the computerized laser particle size analyzers are used to determine the particle size distribution.

A more appropriate criterion shows the pellet feed particle fineness is specific surface area of the fine materials and it is explained in the following title.

4.1.2 Specific surface area of iron ore concentrate

The increasing fine material percentage provides a significant contribution to the surface area of the pellet feed material. *Surface area* is the measure of how much exposed area a solid object has, expressed in square units. For pellet feed is

expressed as cm^2/g and cm^2/cm^3 or cm^2/kg. A standard (ASTM C 204-07) is available and this test method covers determination of the fineness of hydraulic cement, using the Blaine air-permeability apparatus. A schematic draw of simple Blaine air permeability apparatus is given in Figure 4.1. The general method to measure the specific surface area is based on the determination of permeability of a sample bed. Blaine air-permeability apparatus is also used to measure the surface area of pelletizing feed. By comparison of standard sample the specific surface area of the unknown material can be calculated.
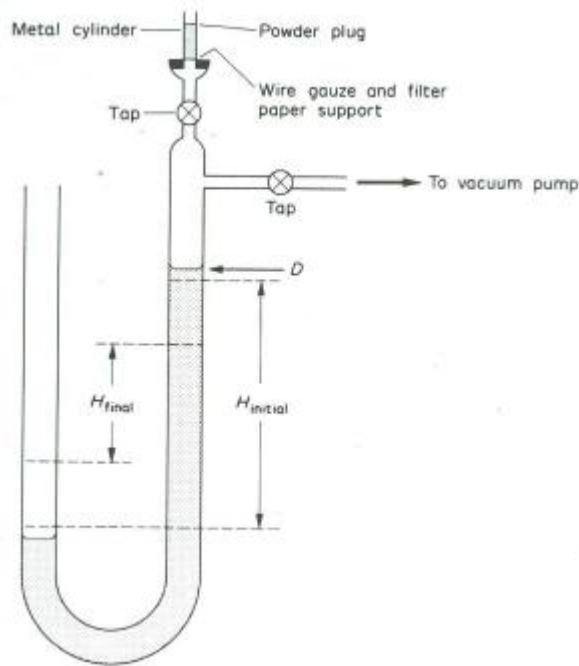
Figure 4. 1 A schematic draw of simple Blaine air permeability apparatus (Ball, *et al.,* 1973)

Blaine air permeability apparatus is a variable-pressure permeability tester, and the measurement of the surface area is based on the time, **t**, required for a specified volume of air to be drawn through the sample bed as fluid in the manometer falls between two fixed levels $H_{initial}$ and H_{final}.

The values found out by measuring the specific surface area are dependent on the type of iron minerals. The usual values for specular iron ores are 1600-1800 cm^2/g and 1600-2300 cm^2/g for magnetite concentrates.

$$\text{Specific surface area} = \frac{K}{\rho} \cdot \left(\frac{e^3}{(1-e)^2} \cdot \frac{t}{\eta} \right)^{0.5} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\textbf{Eq.1}$$

Where;   **K** : a constant for the apparatus,

ρ : specific gravity of the sample,

e : the porosity of the sample bed,

η : the viscosity of the air under the test condition.

At Luossavaara-Kiirunavaara AB (LKAB, Sweden) Kiruna pelletizing plant the specific surface area is measured with a similar permeability method described by Svensson. It is called as the KTH-surface area and the results are given in cm^2/cm^3. The KTH-surface area and Blaine values show a linear relationship. KTH-surface area values can be converted to Blaine by dividing by particle density (typically 5.12 g/cm^3 for LKAB magnetite concentrates) (Forsmo, 2007).

4.1.3 Chemical analysis of iron ore concentrate

Fe grade and amount of gangues of iron ore concentrate are important to produce pellet with a desired composition. Consistent chimerical composition of the product pellets is very important for blast furnace operation as it leads to efficient furnace operation and uniform metal quality. Hence, before pelletizing the pellet feed should meet the minimum requirements decided by blast furnace operation. Iron ore concentrate should contain about 65% Fe with silica and alumina as main gangue constituents. To provide such a desired composition an adequate blending might be required.

Chemical analysis of iron ore concentrate can be determined by titrimetric methods accord to related standards ASTM or ISO (ISO 2597-1 and 2, 2006) in chemistry laboratories. However, nowadays a quick method; X-ray fluorescence (XRF) spectrometers are used to determine the elemental analysis of pellet feed. A chemical analysis for the pellet feed must contain Total Fe, FeO, SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, S, P_2O_5, and TiO_2 contents. A few examples for typical pellet feed chemical compositions are shown in the Table 4.3.

Table 4. 3 Typical pellet feed chemical analyses

Total Fe	SiO$_2$	Al$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	S	P$_2$O$_5$	TiO$_2$	Reference
69.25	0.95	1.01	0.53	0.90	0.05	0.14	0.48	<0.1	<0.01	XRF
65.35	4.72	0.33	0.45	0.42	ND	ND	0.008	ND	ND	Ball, 1973

4.1.4 Moisture content of iron ore concentrate

The pellet feed material preparation steps (grinding and concentration) are generally wet methods. Hence, the product from last operation unit always contains some extra amount of water which needs to be adjusted to an optimum level The wet ground or concentrate slurry may contain 15-20% solid by weight. In thickening the solid ratio is increased up to 60-65% by weight. The moist materials after thickener are generally sent to filtration unit to remove the extra water. A pellet feed from filtration unit with optimum moisture content called as *filer cake* for pelletizing. The optimum moisture content of filter cake should be about 8.5-10% according to the ore type and particle size fineness.

The moisture content of the material to be balled is particularly important, because each specific type of material has a corresponding moisture, normally given beforehand, which is needed for the resultant balls to possess the highest possible strength. The relationships are given in Table 4.4 (Jaroslav, 1988).

Table 4. 4 Moisture of various types of raw materials for balling (Jaroslav, 1988)

Raw material	Moisture for balling, %
Magnetite (Sweden)	9.5
Synthetic magnetite	14.5
Hematite	8.0
Limonite	13.0
Siderite	7.5

Moisture content affects the packing of grains forming the wet pellets. If the moisture is higher than the optimum value, the balling will be affected adversely.

Moisture content of raw materials can be determined accord to ISO 3087:1998 and calculated by;

$$\text{Moisture content of raw material \%} = \frac{(W_w - W_d)}{W_w} * 100 \ldots\ldots\ldots\textbf{Eq.2}$$

Where W_w : weight of raw material,

             W_d : weight of dry raw material.

4.2   Pellet properties

Pellets properties can be classified as;

- *physical properties* such as size and shape, moisture content, drop number, mechanical strength (compressive strength, resistance to tumbling and abrasion), porosity.
- *chemical properties* such as chemical analysis, reducibility.
- *metallurgical properties* (physical properties under reduction condition) such as decrepitation, low temperature break-down under reduction, hot compressive strength, reducibility, swelling, softening, sticking, high temperature permeability.

4.2.1 Size and shape of pellets

The size distribution of the pellets affects the production rates in the blast furnace. Closely sized pellets are essential for a high production rate. Pellets were originally manufactured in the 1.0 inch (25 mm) range, modern practice is to make pellets in the 1/2 inch (12.5 mm) range, and a normal size requirement at the point of receipt is 90% −16+9.5 mm (−5/8 +3/8 inch), with a maximum of 5% −5 mm material (Ball, *et al.,* 1973).

An example about size distribution of pellets is given by Meyer, 1980. The size distribution of pellets, shown in Figure 4.2, as an average of three commercial

samples is remarkable. 80-90% of the pellets should have a diameter of −15 +9mm, the major part of which diameter of −12 +9mm.
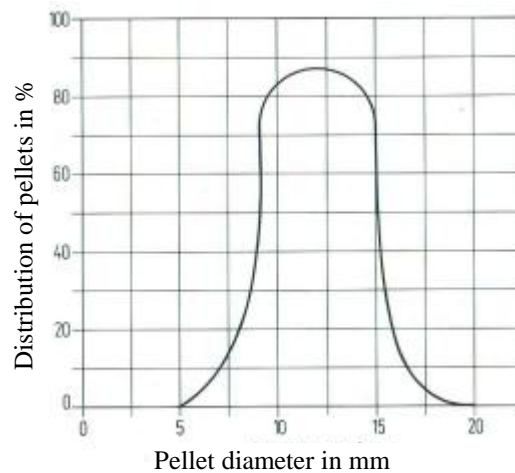
Figure 4. 2 Size distribution of pellets (Meyer, 1980)

Pellets are also classified in terms of their size as basic three groups and size of the pellets can be determined by screening the product pellets with standard size screens.

a) *small size pellets* with a diameter of −8+3 mm can be used in sintering or hydrometallurgical processing,

b) *optimum size pellet* with a diameter of −16+9 mm which is standard size for pellets can be sent to blast furnace,

c) *large size pellets* with a diameter of −30+20 mm used in steel-making facilities.

Pellet size also influences the compressive strength of wet and dry pellets. A study conducted by Rumph, 1958 on pellets made with earthy hematite showed that small pellets yielded lower strength than those of grater diameter. These compressive strengths can be seen in Table 4.5. Therefore closely sized (approximately same diameter) pellets should be produced in laboratory investigations to compare the results correctly.

The spherical/globular shape of the pellets is required since the high permeability of a pellet bed is possible with spherical shape and closely sized pellets.

Table 4. 5 The effect of pellet size on compressive strength of wet and dry pellets made with earthy hematite (Rumph, 1958)

Pellet diameter mm	Wet pellets, kg/p	Dry pellets, kg/p
10	0.82	3.43
12	0.95	3.98
15	1.13	4.14

Pellet size distribution affects permeability of pellet bed in the induration equipment. If pellet permeability is bad due to pellet size distribution, blockages and cold spots may be created along the grade. The low permeability of pellet bed affects the oxidation of pellets adversely. Furthermore, narrow size distribution of pellets is important for good pellet production operation and beneficial for subsequent reduction process in steel-making facilities.

Physical, metallurgical and microstructural properties of pellets have a major influence on their reduction behavior during processing in a blast furnace. The firing time, temperature, oxidation time and oxygen partial pressure are decisive for the structural changes within the pellets; the nature of the changes affects, in turn, the physical and metallurgical properties of the pellets. Based on the above conditions in the induration machine, the fired pellets often have non-uniform phases and structures from the core to the shell of the pellet depending upon their size. The outer part of the pellet differs distinctly from the core. The time difference between the reduction and oxidation of the pellet surface and the pellet core increases with increasing pellet size. For bigger pellets, a concentric duplex and triplex microstructure has been observed. Thus, pellet size has a marked effect on the formation of different phases and microstructure (Umadevi *et al.*, 2009).

4.2.2 Moisture content of wet pellets

Moisture of the wet pellets is the liquid (water) saturated by grains of ore and filling the voids of the grains formed wet pellets.

Wet pellet moisture should generally be in the range of 8.5 - 10% by weight of the iron oxide. The moisture content affects packing of grains, shape and strength of the wet pellets. The shape of pellets with different moisture contents described by Pietsch, 1991 and they are shown in Figure 4.3. If wet pellets formed at an optimum moisture which is slightly below the critical condition and the seeds are wetted with water sprays prior to adding new fresh feed, growth occurs in layers. Often such agglomerates called *onion skin* pellets. Below optimum moisture, either no pellets are formed or the relatively dry agglomerates formed. These pellets have *golf ball* like shape which are brittle and disintegrated during balling. With high moisture, the wet pellets become more and more plastic until, at supercritical moisture. They become mushy and stick to the surface of the balling equipment. These pellets have *raspberry* like shape. At higher than optimal moisture, pieces broken from primary pellets and stick together to produce irregularly shaped *secondary agglomerates*.

A) Onion skin

B) Golf ball   C) Raspberry   D) Secondary agglomerates
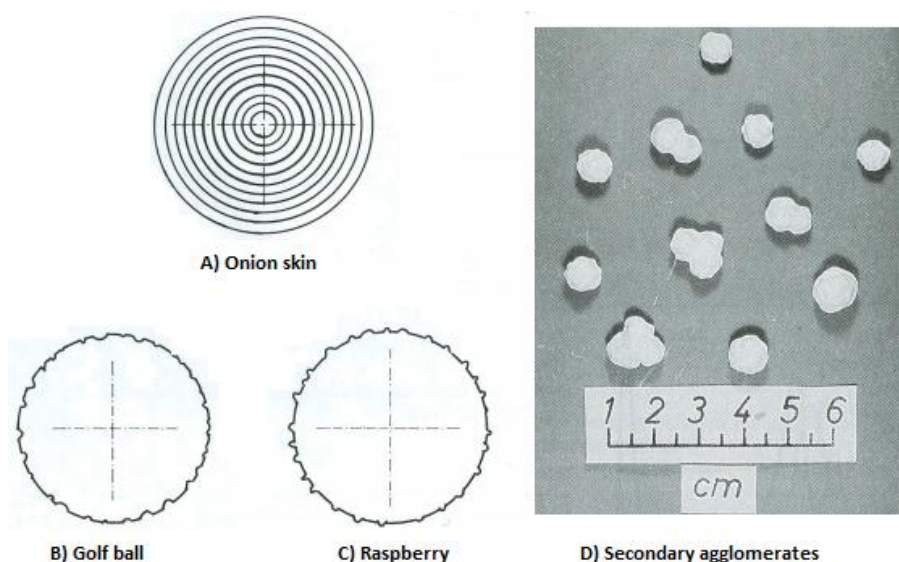
Figure 4. 3 Shape of pellets with different moisture contents; A) with optimum moisture, B) with less moisture, C) with high moisture: raspberry like pellets and D) secondary agglomerates (Pietsch, 1991)

Approximately 100 g or agreed upon representative wet pellets are dried to constant weight at a temperature of 105°C in a drying oven and moisture is determined. Moisture of wet pellets can be determined by same method explained in standard (ISO 3087:1998) and is defined according to the following formula;

$$\text{Moisture content of wet pellets \% } = \frac{(W_w - W_d)}{W_w} * 100 \quad \text{………...} \textbf{Eq.3}$$

Where

W_w : weight of wet pellets,

W_d : weight of dry pellets.

4.2.3 Drop number of wet pellets

Wet pellets produced by balling operation are dropped from one point to another before sending the drying zone of the induration furnace. Therefore, they should be strong enough to reach the drying zone without breaking. One of the quality parameter for wet pellets is drop number.

Drop number or *wet knock* of wet pellets can be defined as ability measure of wet pellets to remain intact during transfer points in pelletizing plant. The drop number indicates how often wet pellets can be dropped from a height of a) 30 cm (12 inch). or b) 46 cm (18 inch) before they show perceptible cracks or crumble.

At least ten green balls are individually dropped on to a platform made with steel plate. The number of drops is determined for each wet pellets. The arithmetical average values of the crumbling behavior of the ten wet pellets yield the drop number. Meyer, 1980 has given the minimum drop number value as 4 according to the experience. As a result, a pellet has to withstand, without any damage, four drops from a height of 46 cm. Satisfactory values according to Ball, *et al.,* 1973, 15 and 6 drops from heights of 30 cm and 46 cm, respectively. Low values are associated with dry, brittle wet pellets while high values can be considered as a result of plastic pellet production.

4.2.4 Compressive strength of pellets

A certain minimum *compressive strength* (or crushing strength) is necessary in order that the pellets can withstand the compression load in the pellet bed on a belt conveyor, drying grate, induration grate, or in a reduction furnace.

Test method for determination of compressive strength of iron ore pellets is described in related standards (ASTM E 382-07 and ISO 4700:2007). Compressive strength test of pellets (wet, dry, preheated or fired) can be carried out by using manual hydraulic press or mechanical press or computerized compression test machines in the laboratories. The average compressive strength of pellets is controlled by compressing of agreed upon number of pellets between parallel steel plates up to their breaking point. The maximum load required to break the pellet can be recorded in kg/p, lb/p, N/p or kN/p automatically by test machines. The mean value of tested pellets gives their compressive strength.

Compressive strength of wet pellets : Wet pellets are loaded on a travelling grate forming a pellet bed. Pellets are subjected to pressure from the upper layer of bed. Therefore, wet pellets should have a minimum strength to remain intact and they should be in spherical shape to prevent good bed permeability.

Wet pellet compressive strength can be determined after formation of wet pellets. Freshly produced wet pellet is located on steel platform of compression test press and loaded gradually with a constant cross-head speed. The maximum load required to break the wet pellet is recorded. The mean value of an agreed upon number of pellets gives the compressive strength of wet pellets. Wet pellet compressive strength is the ability of wet pellets to retain their shape while dropping from balling equipment and during the drying process in induration furnace.

The compressive strength of wet pellets usually lies between 1.0 and 2.0 kg/p (2.2 and 4.4 lb/pellet) (Ball, *et al.,* 1973). Therefore, industrially acceptable minimum compressive strength value for wet pellets should be greater than 1 kg/p or 2.2 lb/pellet.

Pellets having a diameter of 10, 12 and 15 mm have yielded the wet pellet compressive strength 0.81, 0.95 and 1.13 kg/p (Meyer, 1980). It is reported that increasing pellet size increases the wet pellet compressive strength.

Compressive strength of dry pellets : Travelling grate carries the wet pellets through the thermal zones of induration machine: drying, preheating and firing zones. During drying zone of thermal treatment, pellets are subjected to sequential zones of updraft or downdraft drying. Dry pellets in travelling grate furnace are subjected to pressure from hot gases airflow created by process fans and the pressure from pellet bed itself. Therefore, dry pellets should have a minimum strength to withstand these pressures and load during induration. Dry pellet compressive strength is the ability of dry pellets to survive during travelling of the firing process in induration furnace.

Dry compressive strength of pellets can be determined after drying of wet pellets in laboratory oven at a temperature of $105^{o}C$ up to constant weight. Dry pellet is located on steel platform of compression test press and loaded gradually with a constant cross-head speed. The maximum load required to break the dry pellet is recorded. The mean value of an agreed upon number of dry pellets gives the compressive strength of dry pellets.

Acceptable value for minimum dry pellet strength is given by Ball, *et al.,* 1973 as 1.8 to 2.3 kg/p (4.0 to 5.0 lb/p) ad by Ripke and Kawatra, 2000 as 2.2 kg/p (22 N/p or 5.0 lb/p).

Pellets having a diameter of 10, 12 and 15 mm have yielded the dry pellet compressive strengths 3.43, 3.98 and 4.14 kg/p, respectively (Meyer, 1980).

Compressive strength of preheated pellets : Especially, preheated pellets strength is important when pellets are produced with the travelling grate & rotary kiln and cooler technology. As the preheating zone is the thermal link between the drying and firing zones, pellets are preheated in the travelling grate prior to the firing in the kiln. The preheated pellets from the grate are discharged by cascading into the kiln. Therefore, such pellets should be strong enough not to disintegrate during cascading and tumbling in the rotary kiln. In the case of weak pellets, dust and chips generated as a result of disintegration. Weak pellets will cause losses in plant efficiency, in terms of both productivity and quality.

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In the preheating zone, the most important reaction, for iron oxides except hematite, is oxidation; to conversion of magnetite to hematite. Oxidation is the main mechanism to provide the mechanical strength to the pellets by recrystallization and crystal growth. In addition, oxidation also plays a significant role on the reducibility characteristic of pellets. Besides oxidation, decomposition of hydrates, carbonates or sulfates as well as roasting of sulfide compounds found in the ore may take place.

Preheated compressive strength of pellets can be determined in laboratory by preheating of dry pellets in laboratory furnace at desired temperatures (400-1000°C). Preheated pellets after cooling are tested for compressive strength. The maximum load required to break the preheated pellet is recorded. The mean value of an agreed upon number of preheated pellets gives the compressive strength of preheated pellets.

There is no specific compressive strength limit for preheated pellets. However, they should have a strength greater than those of dry pellets until discharging from travelling grate on which no dynamic load for pellet disintegration. When the pellets start to cascade from the travelling grate to rotary kiln, they should have a sufficient strength withstand to break. This strength should be a value which is equal or greater than that of obtained by a conventional binder without breaking problem. Therefore, any alternative binder should provide a preheated strength at least equal or greater than those of conventional binder performance. Because of that, comparative test are usually carried out by researchers in literature.

Compressive strength of fired pellets: Pellets can gain their maximum strength in firing zone after completion of oxidation, recrystallization and formation of slag phase. Fired pellets after cooling stage should have a minimum strength to withstand the load during storing, loading and transportation from the pelletizing plant to iron making facilities. In addition product (fired) pellets should withstand against pressure in reduction furnaces.

Fired compressive strength of pellets can be determined in laboratory after firing of dry pellets in laboratory furnace at different temperatures; 1200-1350°C according to

experiment parameter. Fired pellets are cooled and located on steel platform of compression test press and loaded gradually with a constant cross-head speed. The maximum load required to break the fired pellet is recorded. The mean value of an agreed upon number of fired pellets gives the compressive strength of fired pellets. Pellets consumers demand a minimum strength value for product pellets. According to Meyer, 1980, minimum average value of about 204 kg/p (2000 N/p) is required. Ball, *et al.*, 1973 has given the minimum compressive strength value for fired pellets as 250 kg/p (550 lb/p). İsdemir Iron and Steel Company, Turkey demands also minimum compressive strength 250 kg/p from pellet suppliers.

4.2.5 Tumbling and abrasion indices of pellets

One of the strength indicator of product pellets is tumbling and abrasion indices. The tumbling and abrasion indices are measured primarily by a procedure carried out in a drum with lifters revolving at a certain times with a certain speed. This test is carried out in a tumbler apparatus accord to standards ISO, ASTM or JIS.

Tumbler apparatus (ASTM E279-97(2005)), as shown in Figure 4.4, shall be a circular drum 914 mm (36 inch) in inside diameter and 457 mm (18 inch) in inside length constructed of steel plate at least 6.3 mm (1⁄4 inch) in thickness. The drum has two equally spaced steel angle lifters shall be solidly attached longitudinally inside the drum.

11.3 kg (25 lb) pellet sample is utilized for a single test. The drum is rotated at 24±1 rpm for a total of 200 revolutions. Then all of the material is removed from the drum and hand sieved on 6.3 mm (1⁄4 inch) and 600 μm (30 mesh) sieves. The amount of these materials are weighed and recorded separately. The percentage of +6.3 mm (+1/4 inch) material is called *tumbler index* or *strength index* and the percentage of −600 μm (−30 mesh) material is called *abrasion index* or *dust index.*

In USA −6.3 mm (−1/4 inch) also known as *chip index*. A dust index of 5% and a chip index 6% are regarded as adequate for the treatment to which pellets are subjected (Ball, *et al.,* 1973). Typical results obtained for good pellets with the

ASTM procedure are +1/4 inch (+6.3 mm) index 92-97% and −30 mesh (−600 µm) index 2.5-5.0%
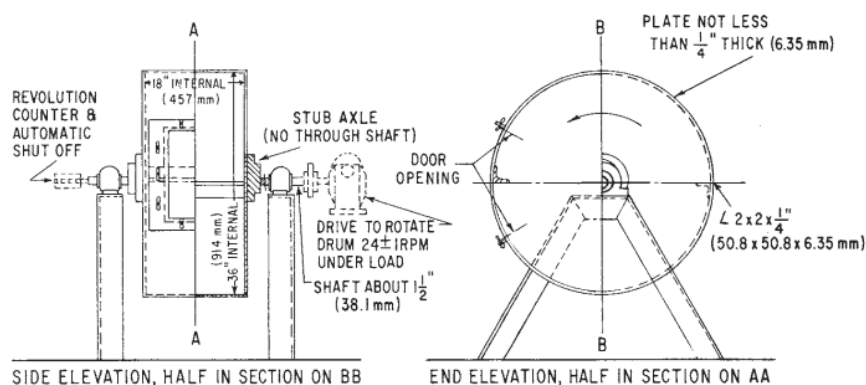
Figure 4. 4 Tumbler apparatus to determine the Tumbler and abrasion indices of pellets (ASTM E279-97:2005)

4.2.6 Dust generation of pellets

Iron ore pellets should have sufficient mechanical strengths against degradation in all stages of pellet production. Besides having the strength, pellets should generate less dust during operation since the process efficiency and the equipments are affected adversely by dust. Dust is also problem for product pellets since they abrade during transportation to the reduction furnaces. Moreover, dust is considered as lost and a problem for environment since they are becoming airborne in plant or during transportation. Therefore, increasing the mechanical strength and decreasing the dust generation of pellets are necessary for better operation and handling of pellets.

The breakdown of taconite pellets at iron ore facilities is a primary source of airborne dust. During breakdown, the pellets produce coarse pellet fragments and a very fine powder. To better understand the problem of airborne dust at iron ore facilities, the breakdown kinetics was studied by Copeland and Kawatra, 2005 and Copeland *et al*., 2009. The apparatus they used was a sieve-shaker with 3 mesh sieve on top and 35 mesh sieve on bottom. 100 to 1000 g dry pellets placed on 3 mesh sieve and the sieve-shaker run for 15 minutes. The fines generated after test are reported and the particle size distribution analysis carried out on fines.

The kinetics of dust generation is strictly dependent on the nature of the pellets, production process and handling conditions. Different pellet-breakdown properties lead to different PM_{10} (particles 10 µm in diameter or smaller) and $PM_{2.5}$ (particles 2.5 µm in diameter or smaller) quantities (Copeland and Kawatra, 2005).

Authors also used a novel dust tower to evaluate how well a suppressant functioned in reducing airborne dust from iron ore. The procedure involved taking the treated pellets and fines and dropping them through a counter-current air stream. The air stream was passed through a filter to remove airborne particles. The weight of the particles collected on the filter paper was reported as the amount of airborne dust generated. Pellet breakdown studies revealed that as much as 43% by weight of the fine particles were 10 µm in diameter and smaller (material regulated by the U.S. Environmental Protection Agency) (Copeland and Kawatra, 2005 and Copeland *et al*., 2009). A diagram of dust tower used in the research is given in Figure 4.5. This dust tower is unique in that it simulates material handling while allowing for direct airborne fine particles measurements.
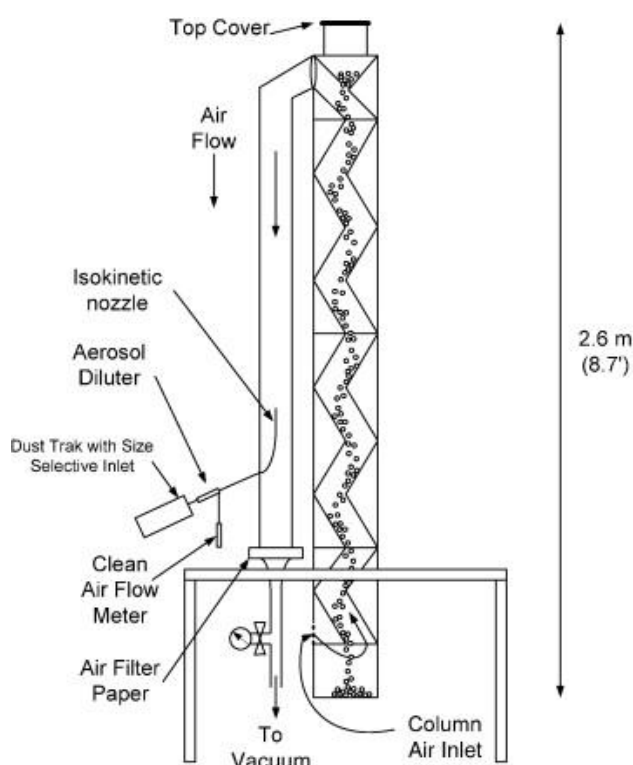
Figure 4. 5 MTU dust tower setup with Dust Trak® meter. Air was drawn through the tower at a constant rate of 9 l/s. Diagram is taken (Copeland and Kawatra, 2005)

4.2.7 Porosity of pellets

Porosity is an important fundamental property of green balls and fired pellets, and plays an important role in each stage in the pelletizing process. Porosity is governed by the particle size and distribution of the feed material; however, it is affected by moisture content of green balls and retention time in balling equipment.

Porosity has an important part in the drying mechanism, since the steam produced, during drying of green balls by means of hot gases, leaves the green balls via pores. In subsequent firing process, the rate of oxidation and the grain growth are directly related to the pore size and distribution.

Pellets with high porosity are desirable for the reduction of iron oxide pellets to iron in the blast furnace to be rapid. **Porosity** is defined by Lodge, 2010, a measure of the open space, or pore volume, within the pellet that is accessible to the reducing gases. The reduction is a heterogeneous reaction that requires first the adsorption of the reducing gas, typically carbon monoxide, on the solid surface of the iron oxide. The larger the pellet's porosity the more surface area there is for the initial adsorption step.

The porosity of pellets (P) is determined by measuring the true specific gravity with benzene or kerosene in a pycnometer. The apparent specific gravity is measured with mercury according to replacement method (Meyer, 1980).

$$\text{Total porosity of pellets, } \varepsilon, \% = \frac{(D-d)}{D} * 100 \text{........................} \textbf{Eq.4}$$

Where : D : true specific gravity of pellet,

              d : apparent specific gravity of pellet.

Typical porosities for green and dry pellets from high grade material are in the range 31-36%, whilst a porosity of 22-30% for fired pellets is associated with good reducibility (Ball, *et al.,* 1973).

Specific gravities can also be determined by some instrumental methods e.g air or gas displacement pycnometers. The instruments like mercury porosimeters are also available to measure the bulk volume of the porous substances.

Recent porosity determination of individual pellet has been done by Lodge, 2010 by measuring of the skeletal volume and the envelope volume of the pellet. Helium pycnometer is the method of choice for the measurement of the skeletal volume, whereas volumetric displacement of dry material is now the preferred method for the envelope volume

Forsmo and Vuori, 2005 reported that at LKAB in Sweden, mercury porosimeter was replaced by the GeoPyc instrument, in which the sample volume is measured by packing in silica sand. The green pellets are strengthened by spraying with a fast-drying lacquer before measurement. They used the absolute density of particles in the calculation of the green pellet porosity. They concluded that reproducibility of the GeoPyc instrument is ±0.3%-unit and easy to use, therefore, the problematic handling of mercury is avoided.

4.2.8 Reducibility of pellets

Reducibility is one of the important characteristic of fired pellets in blast furnace in which they converted to metal iron. ***Reducibility*** is the ease with which oxygen can be removed from the pellet composition in reducing atmosphere. Reducibility data give idea about the fuel consumption in blast furnace and the optimum size range for the charge material.

The number of static-bed reducibility tests is manifold but, Linder rotating furnace procedure which may be regarded as one of the pioneer methods for the most widely used modern tests. The Linder test was designed to determine reducibility and break-down during reduction of 500 g sample with 200 g coke. The furnace rotates at 30 rpm for 5 hours (0 - 2 hours @700°C and 2 - 5 hours @1000°C) by various reducing gas compositions with a flow rate 15 l/min. The reduced sample is analyzed for reducibility and break-down. However, this test does not completely simulate to blast

furnace operation, therefore some modified versions of this test are used to determine reducibility (Ball, *et al.,* 1973).

Gakushin reducibility test method is a static bed type test, shown in Figure 4.6. Dry 500 g sample is heated to 900°C under nitrogen, and then the reducing gas test is passed for 3 hours through the sample bed with a flow rate 15 l/min. The reduction of the sample is calculated by loss weight recorded by a sensitive balance. Besides reducibility data, test is also used to measure;

- the breakdown occurring during reduction,
- volume changing of pellets after reduction (swelling),
- tumbling and abrasion indices of pellets after reduction.
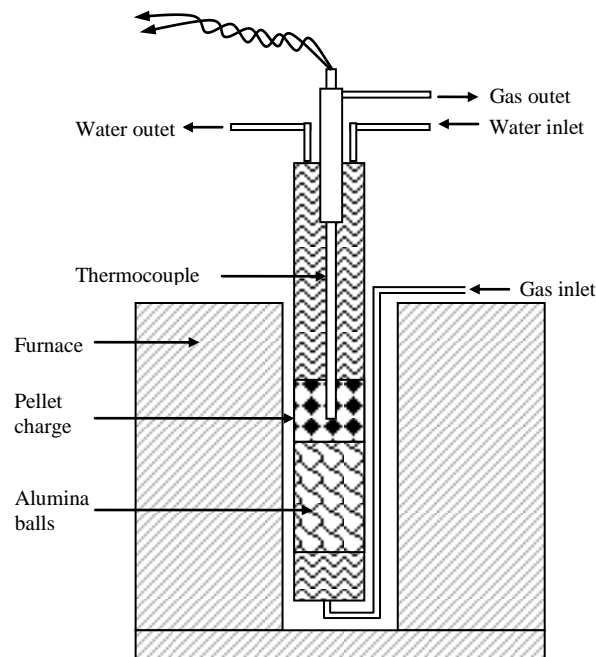
Figure 4. 6 Gakushin reducibility test apparatus for pellet reduction

The Gakushin method has been modified to determine reducibility in which the test conditions are more or less same. The modified tests are;

- Chiba reduction test,
- Verein Deutsher Eisenhüttenleute (VDE) method,

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- Centre National de Recherches Metallurgiques (CNRM) method,
- Non-isothermal test: Aufheizverfahren method.

The typical reducibility test results by reviewed by Ball, *et al.,* 1973 for fired pellets;

- Linder test index : about 50% reduction
- Gakushin test   : about 60% reduction
- Chiba test   : reducibility index of 2.5-3.0 mm/hour
- VDE test   : rate of reduction of 0.6-1.0 %/minute when the pellet is
   60% oxidized

The international standard test for determination of the reducibility by the rate of reduction index reducibility, (R40) (ISO 4695:2007) and determination of the reducibility by the final degree of reduction index (ISO 7215:2007) (relative reducibility) are published by ISO.

The degree of reducibility can be calculated by the weight change of the pellets as shown in Eq.5. Or the degree of reducibility can be calculated by the change of oxygen percentage of the pellets before and after reduction.

$$\text{Reduciblity of pellets, R, \%} = \frac{(M_0 - M_r)}{O} * 100 \quad \text{.......................} \textbf{Eq.5}$$

Where M_0 : weight of pellet sample prior to reduction test,

M_r : weight of pellet sample after reduction test,

O : amount of the oxygen associated with the iron in the pellet sample before reduction.

From the above equations, percent reduction was calculated as a function of time by Akşit, 2004. Researcher obtained R% at the end of 3 hours, which is a measure of reducibility for different samples, are given in Table 4.6. Reducibility curves for the experimental Erdemir samples are presented graphically in Figure 4.7.

Table 4. 6 Reducibilities of some iron ore/sinter/pellet samples at the end of three hours (Akşit, 2004)

Sample	Major Iron Minerals	Reduction,% (3 hours)
Erdemir Lump Ore	Hematite	43.4
Erdemir Pellet A	Hematite	66.6
Erdemir Pellet B	Hematite	78.7
Erdemir Sinter	Hematite & Magnetite	77.6
Kesikköprü	Magnetite	40.0
Divriği Concentrate	Magnetite	49.0
Divriği (Dumluca)	Hematite &Magnetite	56.0
DivriğiB-Kafa	Hematite &Magnetite	63.0
Divriği Pellet	Hematite	72.5
Akdağ	Hematite	74.0
Attepe	Hematite & Goethite	92.2
Koruyeri	Goethite & Hematite	92.5
Hekimhan	Limonite	91.5
Kardemir Sinter	Hematite & Magnetite	69.6
CVRD	Hematite	67.4
ISCOR	Hematite	43.2
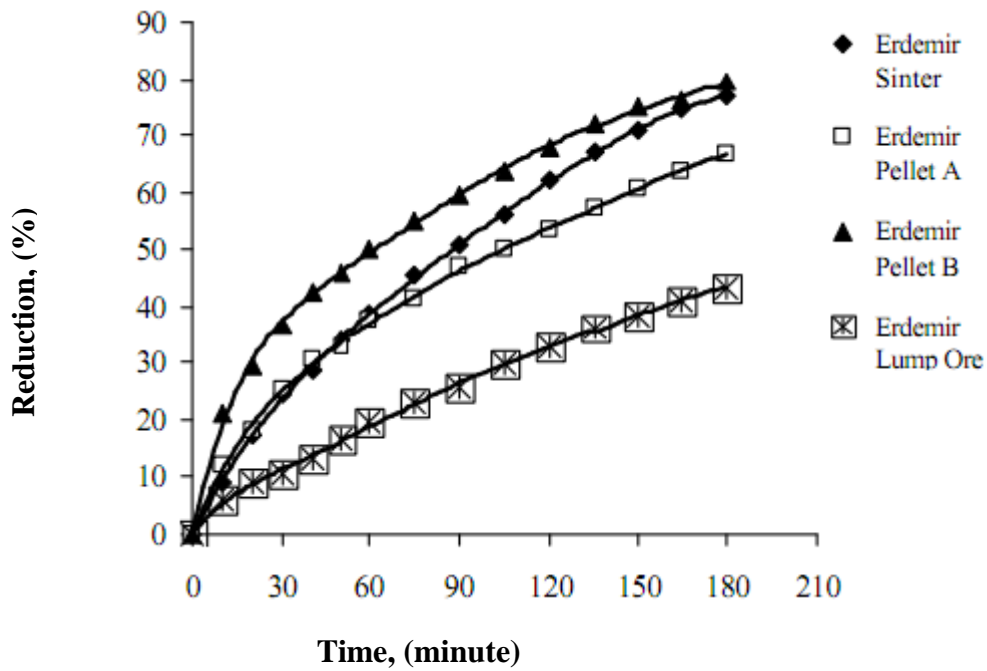
Figure 4. 7 Reducibility of iron ore sinter, pellet and lump ore (Akşit 2004)

4.2.9 Swelling index of pellets

Swelling is the volume change of pellets under reducing condition. During reduction, pellets swell throughout conversion of hematite to magnetite, and roughly swelling increases up to 30%, corresponding to the wüstite formation stage (Ball, *et al.,* 1973). Pellets with a tendency to swell excessively become soft and spongy and sometimes disintegrated into powder in blast furnace. The blast furnace operators recognized that high swelling cause problems in operation like decrease in production rate and efficiency. Therefore, the swelling of pellets should not be greater than an optimum value. According to experience in industry, a maximum 20% swelling is considered optimum for problem-free blast furnace operation.

Different test methods have been proposed to determine swelling. Generally swelling of pellets can be determined by a dilatometer technique. The other method is to measure the apparent volume of the pellets before and after reduction test. The apparent volume of the pellets can be determined by mercury pycnometer.

Determination of the free-swelling index for fired pellet is explained in ISO 4698:2007. The swelling can be calculated by the volume change of the pellets after reducibility test as follows;

$$\text{Swelling of pellets, S, \%} = \frac{(V_r - V_0)}{V_0} * 100 \quad ....\textbf{Eq.6}$$

Where
V_0 : apparent volume of pellet sample prior to reduction test,

V_r : apparent volume of pellet sample after reduction test.

The swelling index up to 20% has been accepted as ***normal swelling*** whereas the higher values are called ***abnormal swelling*** or even ***catastrophic swelling*** (Sharma *et al.,*1990; Nasr *et al.*, 1996). The iron ore pellets exhibit increase in volume during heating due to thermal expansion and reduction, as presented in Figure 4. 8 (Gupta, 2007).
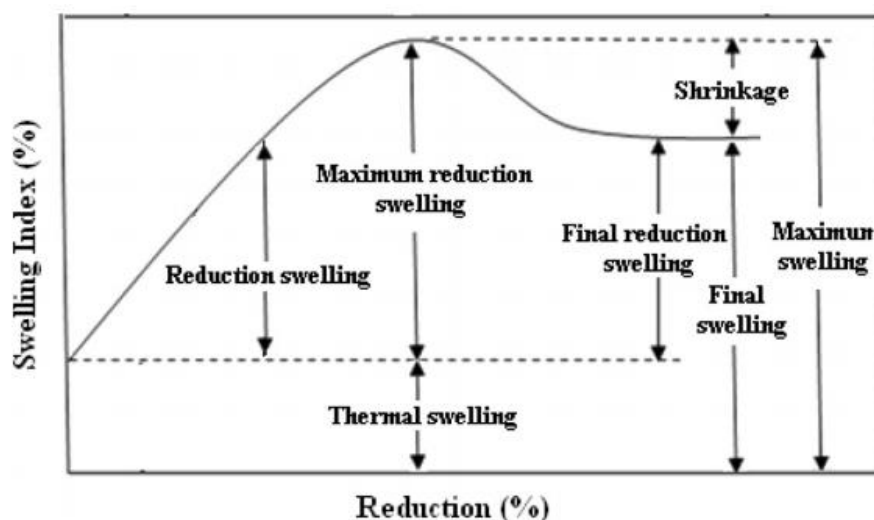
Figure 4. 8 Schematic diagram of swelling behavior of iron ore pellets during reduction (Gupta, 2007)

4.2.10 Chemical analysis of fired (product) pellets

The iron content and the percentage of impurities are important for the indurated product pellets in terms of an economic iron production in the reduction facilities. A chemical analysis of product pellets is carried out and Total Fe, SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, S, P_2O_5 and TiO_2 contents are reported.

4.2.11 Desired pellet specifications by pellet buyers

The product pellets should have specifications explained above to be used in reduction facilities (blast or DRI furnace) efficiently. Desired pellet specifications by İSDEMİR, Turkey (Iskenderun Iron and Steel Company) are given in Table 4.7.

Table 4. 7 The acidic and basic pellet specifications applied by İSDEMİR (http://www.isdemir.com.tr, last visited on 15/05/2011)

Chemical specification (weight % dry basis)				
Fe	65.50	min	S	0.01	max
SiO_2	6.00	max	As	0.005	max
Al_2O_3	1.00	max	Cr	0.05	max
CaO (acidic)	2.50	max	Ni	0.01	max
CaO (basic)	3.00	max	Zn	0.01	max
MgO	1.50	max	Pb	0.01	max
Na_2O	0.05	max	Cu	0.01	max
K_2O	0.05	max	Sn	0.005	max
TiO_2	0.50	max	Mo	0.005	max
Mn	3.00	max	V	0.02	max
P	0.06	max	Moisture	3.0%	max
Basicity	0.25 (acidic pellets)		0.60-1.00 (basic pellets)		

Physical specification		
Size distribution (ASTM E 389-93)	+16 mm	7% max
	-16 mm +12.5 mm	40% max
	-12.5 mm +9.52 mm	45 % max
	-9.52 mm	8% max
Tumbler test (ASTM E 279-92)	+6.35 mm	95.0% min
	-0.5 mm	5.0% max
Compressive strength	250 kg/p	
Density (ASTM C 373-88)	5.10 g/cm^3	
Low temperature breakdown test (ISO 4696)	+6.35 mm	84.0% min
	-0.5 mm	3.0% max

Metallurgical specification	
Reduction under load (R40) (AS PER ISO DP 7992)	0.75 %/min (acidic pellet) 1.20 //min (basic pellets) ΔP 15.0 mm WG max
Swelling index test (ISO DP 4698)	20% max

CHAPTER 5

EXPERIMENTAL STUDY

Experimental studies were carried out in two university laboratories:

1) Middle East Technical University Mining Engineering Department Laboratory (METUMEL)
2) Michigan Technological University Chemical Engineering Department Laboratory (MTUCEL)

The materials and their characteristics, methods and equipments for material characterization and for the pelletizing experiments are explained in the following sections.

5.1   Materials, methods and equipments

After the physical, chemical and mineralogical characterization of the materials, they were subjected to pelletizing experiments. During the pelletizing experiments five different raw materials are used;

1) Iron oxide samples (two magnetite concentrates and a hematite ore),
2) Bentonite samples (two different sodium bentonites),
3) Natural organic binders (CMC, dextrin and corn starch)
4) Manufactured organic based binders (DPEP06-0007 polymer, Superfloc$^{®}$ A150-LMW and Superfloc$^{®}$ A150-HMW flocculants),
5) Boron compounds (colemanite, tincal, borax pentahydrate and boric acid).

Information and characteristics of these raw materials are given below.

5.1.1 Magnetite concentrate samples

Two magnetite concentrate samples were used as iron oxide source. One of them is from Divriği Iron Ore Mine and Concentrator Plant, Sivas, Turkey and the other one is from a pelletizing plant located at the Lake Superior district, Michigan, USA.

5.1.1.1   Divriği magnetite concentrate

The first magnetite concentrate sample was obtained from Erdemir Divriği Iron Ore Concentrator and Pelletizing Plant, Sivas, Turkey. This sample was taken as moist filter cake from the filtration unit of the concentration plant. The original sample was received on 21/06/2005 and brought to the METUMEL in five big plastic bags and weighed about 250 kg in total (weight of original sample with filter cake moisture).

The original Divriği magnetite concentrate was washed repeatedly with water in order to ensure no impurities mixed by mistake. Afterward sample was filtered, dried first at room temperature and then in a laboratory oven at a temperature of $105^{o}C$ for 24 hour. Dry sample was blended and was divided into four parts by cone & quartering sampling method. One part is divided again by cone & quartering and riffle sampling methods into representative samples. Sampling was carried out in accord with the international standards for sampling of iron ores (ASTM E 877-03 and ISO 3082:2009). Representative samples each about 1000 g were put in individual laboratory plastic bags to use in pelletizing experiments. This magnetite sample was named as "Divriği magnetite" throughout the text.

Particle size distribution was determined on representative sample by both screening with standard laboratory sieves and by laser diffraction method with a particle size analyzer; Microtrac SRA shown in Figure 5.1 (Leeds and Northrup Instruments). Particle size distribution result is given in Figure 5.2 and the amount of the material finer than 44 μm (325 mesh) is 63.68%.

Figure 5. 1 Microtrac SRA particle size analyzer (MTUCEL)
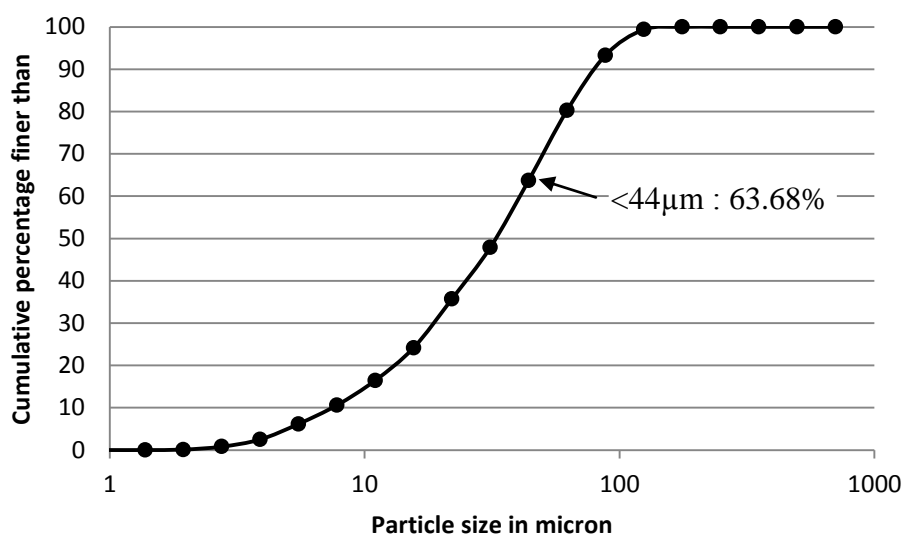
Figure 5. 2 Particle size distribution of Divriği magnetite concentrate (P_{100}: 176.00 μm and P_{80}:61.98 μm)

Specific surface area of original Divriği magnetite concentrate was found 1617 ± 24 cm^2/g. Specific surface area (Blaine number) determination test was done with a Blaine air permeability apparatus shown in Figure 5.3 in accord with the standard (ASTM C 204-07). The Blaine air permeability apparatus consist essentially of a means of drawing a definite quantity of air through a prepared bed of sample of definite porosity. The number and size of the pores in a prepared bed of definite porosity is a function of the size of the particles and determines the rate of airflow through the bed (see also title 4.2.1).

Figure 5. 3 Blaine air permeability apparatus to determine specific surface area of powder material (METUMEL)

Specific gravity (sp.gr.) of Divrigi magnetite concentrate was found 5.10 by pycnometer sp.gr. determination method. During sp.gr. test both distilled water and acetone were used as liquid media.

Elemental analysis of Divrigi magnetite concentrate was performed with Spectro IQ X-ray fluorescence (XRF) spectrometer (Figure 5.4). The results of the chemical analysis of Divrigi magnetite concentrate are presented in the Table 5.1.

Figure 5. 4 Spectro IQ X-ray fluorescence (XRF) spectrometer (METUMEL)

Table 5. 1 Chemical composition of Divrigi magnetite concentrate

Component, weight % dry basis									
Total Fe	SiO$_2$	Al$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	S	P$_2$O$_5$	TiO$_2$
69.25	0.95	1.01	0.53	0.90	0.05	0.14	0.48	<0.1	<0.01

5.1.1.2 Lake Superior district magnetite concentrate

The second magnetite concentrate used in the pelletizing experiment was a magnetite concentrate sample obtained from a mine located at the Lake Superior district, Michigan, USA. Concentrate was received on 28/07/2010 from mine and brought to MTUCEL. Six containers weighing approximately 200 kg in total (weight of original sample with filter cake moisture). The original sample was blended and then divided into 77 representative samples of 2500 g each by cone & quartering and riffling sampling methods (ASTM E 877-03) and sealed in separate plastic bags. Figure 5.5 shows the representative sample preparation procedure. The moisture content of as received magnetite concentrate was 7.51%. This magnetite sample was named as "Lake Superior magnetite" throughout the text.
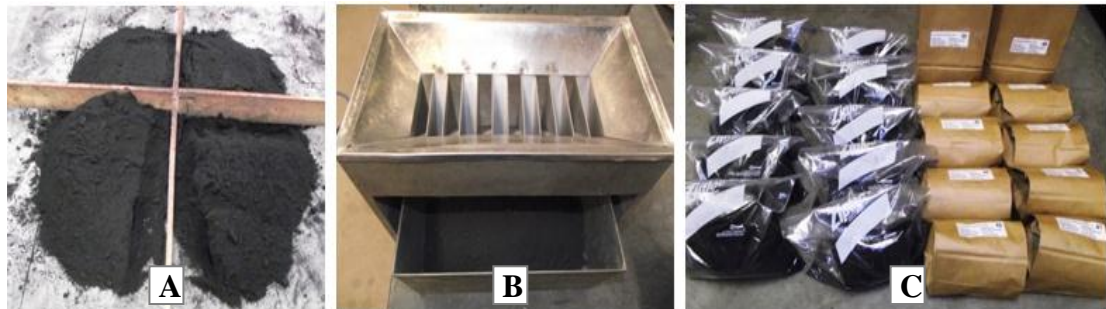
Figure 5. 5 Representative sample preparation procedure **A)** Cone & quartering **B)** Riffling sampling methods **C)** representative samples labeled and stored in separate plastic bags (MTUCEL)

The particle size distribution of Lake Superior magnetite concentrate was determined by SRA Microtrac analyzer. It had a particle size of 96.53% passing 44 μm (Figure 5.6).
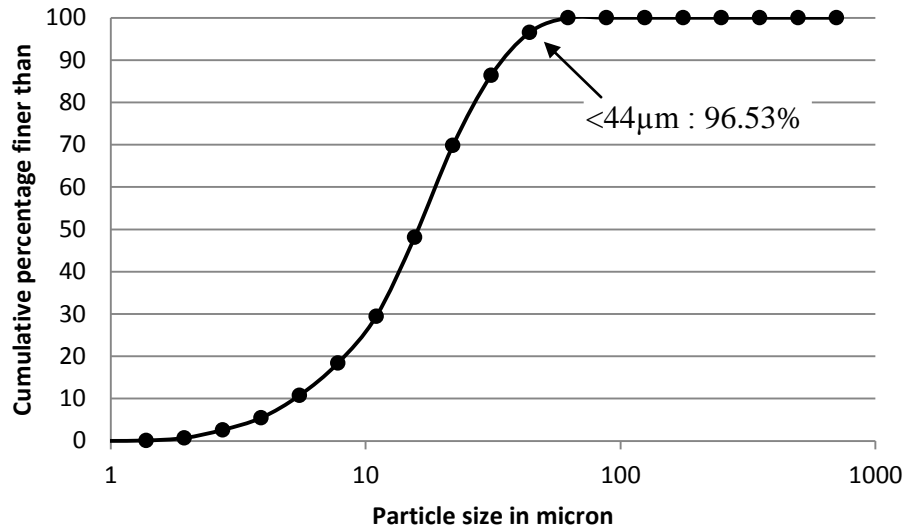
Figure 5. 6 Particle size distribution of Lake Superior magnetite concentrate (P_{100}:62.23 µm and P_{80}:27.60 µm)

Specific surface area measurement carried out by Blaine apparatus and was found 2212 ±38 cm^2/g for Lake Superior magnetite concentrate. Specific gravity of Lake Superior magnetite concentrate was found 4.64.

Elemental analysis of Lake Superior magnetite concentrate sample determined by XRF method and results are shown in Table 5.2.

Table 5. 2 Chemical composition of Lake Superior magnetite concentrate

Component, weight % dry basis									
Total Fe	SiO$_2$	Al$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	S	P$_2$O$_5$	TiO$_2$
65.52	4.87	0.09	0.44	0.37	<0.01	0.02	0.03	0.05	0.01

5.1.2 Hematite sample : Brazilian hematite ore

A Brazilian hematite ore imported by İskenderun Iron and Steel Company, Turkey was obtained from the company. Hematite sample weighing 75 kg in total was brought to METUMEL. The entire hematite sample was blended and divided into

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representative samples of about 1 kg by cone & quartering and riffle sampling methods (ASTM E 877-03). Then each representative batch sample labeled and stored in plastic bags separately. Screen analysis was carried out with representative hematite sample and it had a particle size of 80% minus 850 μm. In order to obtain a suitable particle size distribution and specific surface area for pelletizing, representative hematite batch samples about 1 kg were crushed in roll crusher then ground in a laboratory scale rod mill for different time (see title 6.1). This ground hematite sample was named as "Brazilian hematite" throughout the text.

Particle size distribution was determined by laser diffraction method with Microtrac SRA for ground hematite sample used in the pelletizing experiments. Particle size distribution result is given in Figure 5.7 and the amount of the material finer than 44 μm (325 mesh) is 61.07%.
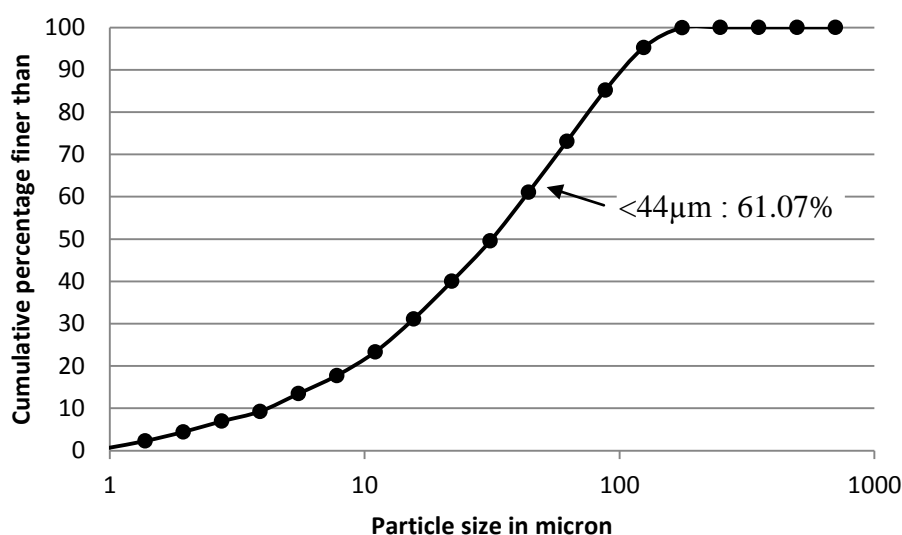
Figure 5. 7 Particle size distribution of Brazilian hematite ore (P_{100}:248.90 μm and P_{80}:76.95 μm)

Blaine specific surface area of the original size (as-received) sample was found 392 cm^2/g. After grinding for an optimum time, it was increased to 1891 ±35 cm^2/g for the ground hematite sample. Specific gravity of Brazilian hematite ore was found 4.90 by pycnometer method with distilled water and acetone as liquid media. Hematite ore chemical analysis was carried out with XRF instrument and results of chemical composition of hematite sample are given in Table 5.3.

Table 5. 3 Chemical composition of Brazilian hematite ore sample

Component, weight % dry basis									
Total Fe	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	S	P_2O_5	TiO_2
66.62	5.71	3.05	0.048	0.017	<0.11	<0.006	0.005	0.16	0.054

5.1.3 Bentonite samples

Two different sodium bentonite samples were used in the pelletizing experiment as conventional binder to set a baseline value to compare the performances of tested binders. One of the bentonites is from Reşadiye, Tokat, Turkey and the other bentonite is from a pelletizing plant in the Lake Superior district in Michigan, USA. The former bentonite sample was named as "Reşadiye bentonite" and the latter as "Lake Superior bentonite" throughout the text.

5.1.3.1 Tokat Reşadiye bentonite

First sodium bentonite sample was taken from Reşadiye region of Tokat, Turkey produced by Karakaya A.Ş. as binder for pelletizing of iron ores. Dry bentonite sample was kept in a plastic container in laboratory to use in pelletizing experiment. The particle size distribution analysis was carried out and the result is given in Figure 5.8. The particle amount finer than 44 μm (325 mesh) was found to be 97.98%. The chemical analysis of Reşadiye bentonite was determined with XRF method and results are given in the Table 5.4.

Table 5. 4 Chemical composition of Reşadiye bentonite

Component, weight % dry basis							
SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI
67.76	16.86	4.17	1.38	0.73	2.19	3.62	2.93
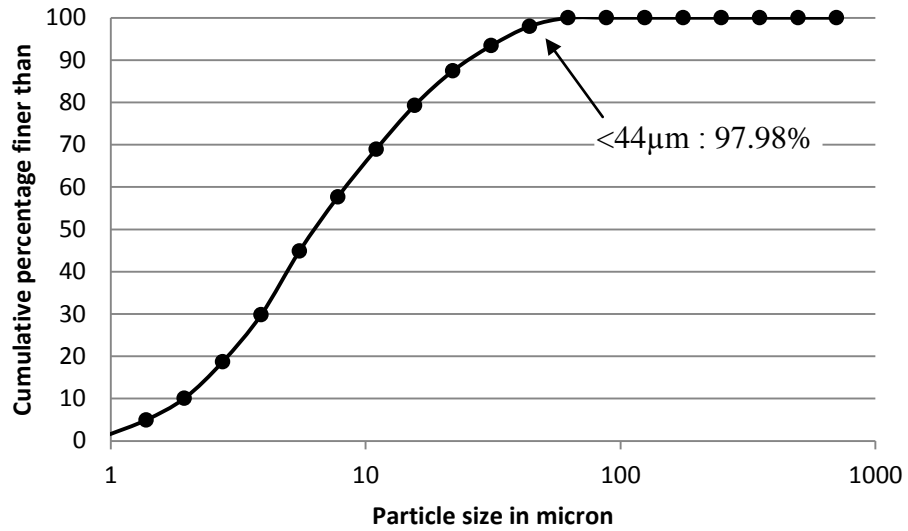
Figure 5. 8 Particle size distribution of Reşadiye bentonite (P_{100}: 88.00 µm and P_{80}:16.13 µm)

5.1.3.2 Lake Superior district bentonite

Second bentonite sample was taken from a pelletizing plant located at the Lake Superior district in Michigan USA. This bentonite is being currently used in this plant for magnetite concentrate pelletizing. The particle size distribution curve is given in Figure 5.9, and shows that the minus 44 µm (325 mesh) material is 95.49%. The chemical analysis of this bentonite sample was determined with XRF method and results are given in the Table 5.5.

Table 5. 5 Chemical composition of Lake Superior bentonite

Component, weight % dry basis							
SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI
58.36	21.14	3.96	3.82	0.58	1.43	2.98	6.75
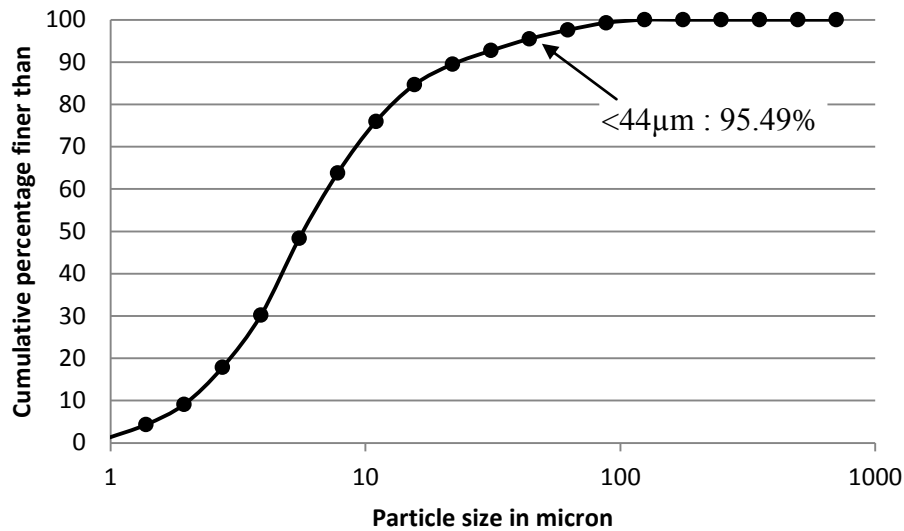
Figure 5. 9 Particle size distribution of Lake Superior bentonite (P_{100}: 124.50 μm and P_{80}:13.11 μm)

5.1.4 Organic binders : CMC, corn starch and dextrin

Three different natural organic materials were tested as alternative binders to conventional bentonite;

1) Technical grade CMC,
2) Food grade corn starch,
3) Dextrin,

Technical grade CMC **:** CMC (carboxymethyl cellulose) is a well known binder for many industries including iron ore pelletizing. CMC is a cellulose derivative with carboxymethyl groups ($-CH_2-COOH$) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. The structure of CMC is given in the Figure 3.3. A few commercial organic binders, manufactured by some chemical companies, for iron ore pelletizing are CMC based binders.

Technical grade CMC was purchased from the local chemical market and tested as organic binder. It was added to the iron oxide concentrate at different addition levels

either powder or as solution with distilled water. The characteristic and screen analysis of CMC used in the pelletizing experiments is given in the Table 5.6. The residue of CMC after burning at $1000^{o}C$ for 30 minutes is only 0.19%.

Table 5. 6 Characteristic and screen analysis of technical grade CMC

Characteristic of technical grade CMC			
Moisture %	10 Max.	**DS**	0.75
Color	White	**pH (1%)**	9.8
Starch	Non	**Viscosity %2-25 C Brookfield**	180cP
Appearance	Dust	**Active material ratio %**	63
Screen analysis of technical grade CMC			
+710μm	**-710μm+355μm**	**-355μm+150μm**	**-150μm+75μm**	**-75μm**
0-1%	0-5%	10-25%	15-25%	75-44%

Corn starch **:** Starch and cellulose are isomers and as such can be expected to have generally similar but not identical properties. Starch derivatives are presented in Figure 3.3. Starches generally are less expensive than cellulose derivatives. They can be used either dry or 'gelled' (cooked in water). Starches are produced from vegetable matter, such as corn, potatoes, or wheat, and their properties vary somewhat, depending on the source (Eisele and Kawatra, 2003).

In this study food grade corn starch was also tested as organic binders. It was bought from the local market. It was used as gel after a cooking process. Predetermined amount of corn starch was put in sufficient amount of distilled water, and boiled in a pressurized autoclave at $140^{o}C$ for 30 minutes. After dissolution of corn starch, this gelled solution was stirred in a mixer to get a uniform mix. The required amount of starch solution was mixed with dry iron oxide. The corn starch has 0.04% residue (almost zero) after thermal treatment at $1000^{o}C$.

Dextrin **:** Dextrins are a group of low molecular weight carbohydrates produced by the hydrolysis of starch or glycogen. Dextrins are mixtures of polymers of D-glucose units. Dextrins are white, yellow or brown powders that are partially or fully water

soluble, yielding optically active solutions of low viscosity. Yellow dextrins are used as water-soluble glues. White dextrins are mostly used in food industry and as a thickening and binding agent in pharmaceuticals and paper coatings (http://en.wikipedia.org/wiki/Dextrin, last visited on 20/05/2011). The dextrin is also mentioned in some patents describing iron ore agglomeration (USA Patent No: 6071325).

A yellow color dextrin sample was purchased from the local market and tested as organic binder. The residue of dextrin after burning at $1000^{o}C$ for 30 minutes is only 0.19%.

5.1.5 Manufactured organic based binders : polymer and flocculants

Three different synthetic manufactured organic based materials are tested as alternative binders;

1) DPEP06-0007 polymer,
2) Superfloc® A150-LMW flocculant and,
3) Superfloc® A150-HMW flocculant.

Ciba© DPEP06-0007 polymer is an anionic copolymer blend and *Cytec Superfloc® A150LMW* (low molecular weight) and *Cytec Superfloc® A150HMW* (high molecular weight) are anionic polyacrylamide flocculants. These manufactured organic based binders were tested as alternative binders. They are intentionally synthesized for agglomeration and flocculation purpose. The former was manufactured and supplied by Ciba Specialty Chemicals Holding Inc. as a commercial agglomeration aid chemical. The latter two are flocculants which are manufactured and supplied by Cytec Industries Inc. The manufactured organic based binders are identified by codes with no identification of their structure. The chemical name of Ciba© DPEP06-0007 polymer is described as 25-55% sodium carbonate in its material and safety data sheet. However, no information about chemical contents was given for Cytec Superfloc® in their material and safety data sheets.

Synthetic organic based commercial binders manufactured by some companies for iron ore pelletizing are generally CMC based binders. These binders can be used as either dry powder or as water slurry. Ciba[©] DPEP06-0007 polymer was added to iron oxide directly as powder since the particle size was suitable. Cytec Superfloc[®] flocculants were used as water slurry after dissolution in distilled water since they are particulate material.

The residue (inorganic-noncombustible part) of Ciba[©] DPEP06-0007 polymer after thermal treatment at 1000^oC is 27.64%. The residues of Cytec Superfloc[®] were found to be 15.36 and 15.65% for low molecular weight and high molecular weight, respectively.

5.1.6 Boron compounds

Four different boron compounds (two natural and two derivatives) were tested as binder alone or together with an organic/manufactured organic binders mentioned above. The boron compounds selected for the study;

1) Colemanite,
2) Tincal,
3) Borax pentahydrate and
4) Boric acid.

5.1.6.1   Colemanite

Colemanite or calcium-borate salt is a natural borate mineral found in evaporate deposits of alkaline lacustrine environments. It is a secondary mineral that forms by alteration of borax and ulexite. Colemanite has a chemical formula $2CaO.3B_2O_3.5H_2O$ or $[Ca_2B_6O_{11} \cdot 5(H_2O)]$ and melting point of 986^oC (Tektaş, 2003).

A colemanite concentrate sample sized $-125+25$ mm (15 kg) was taken from Eti Mine Bigadiç Concentration Plant. The typical chemical composition of colemanite sample is given in the Table 5.7.

Table 5. 7 A typical chemical composition of colemanite concentrate

B_2O_3 %	SiO_2 %	CaO %	SO_3 %	As_2O_3 ppm
41-43	<6.50	26-28	0.50	<50

Preliminary studies carried out at the beginning of pelletizing experiments showed that the addition of 0.50-1.00% boron minerals such as colemanite or tincal into pellet feed caused the pellet spalling after thermal treatment. The spalling of pellets can be explained by the decrepitation of boron minerals since they contain considerable amount of chemically bonded water in their structure. Decrepitation, shrinkage and expansion of boron minerals, namely colemanite, ulexite and borax under thermal treatment were presented by Şener 1991, Şener and Özbayoğlu 1995, Çelik *et al.,* 1994,1998, Arslan *et al.,* 1999, Özbayoğlu *et al.,* 2001. Coşar *et al.*, 2010 studied the effect of boron minerals on pelletizing of iron ore concentrate. They used colemanite, ulexite and borax in the range of 0.05% to 0.20% together with 0.70% bentonite. They concluded that the addition of these boron minerals decreased the fired pellet compressive strength. It is believed that the low fired pellet compressive strength is due to decrepitation of boron compounds during thermal treatment. Therefore, the use of boron compounds in iron ore pellet feed requires a pre-calcination process to avoid pellet spalling and breakage.

The as-received size colemanite concentrate sample was washed, and dried. Dry sample was crushed in a roll crusher and screened from 1000 μm screen. Thermal behavior of colemanite and calcined colemanite (at 550°C) were examined with a thermogravimetric analyzer. The calcination curves obtained from Leco® TGA701 thermogravimetric analyzer is shown in Figure 5.10. TG curves of colemanite and calcined colemanite were obtained using normal atmosphere with a heating rate of 3°C/min from room temperature to maximum 1000°C. The calcination curves of colemanite and calcined colemanite sample can be seen in Figure 5.11.
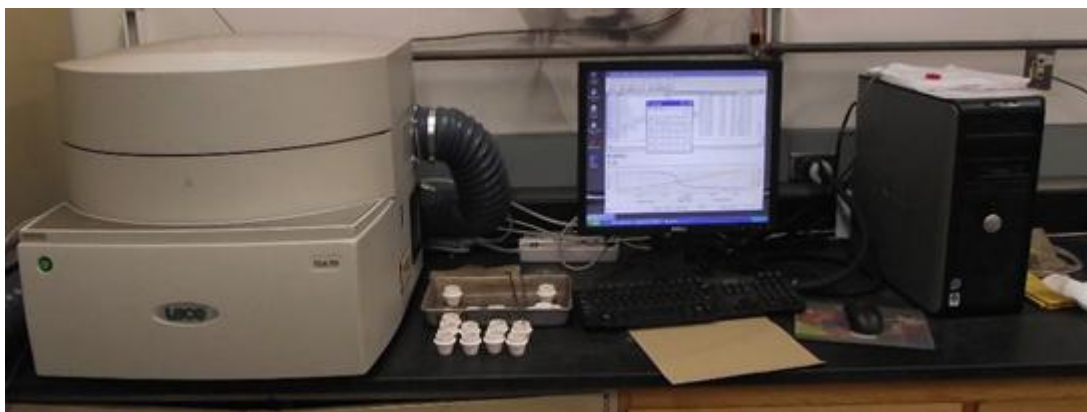
Figure 5. 10 Leco® TGA701 thermogravimetric analyzer (MTUCEL)
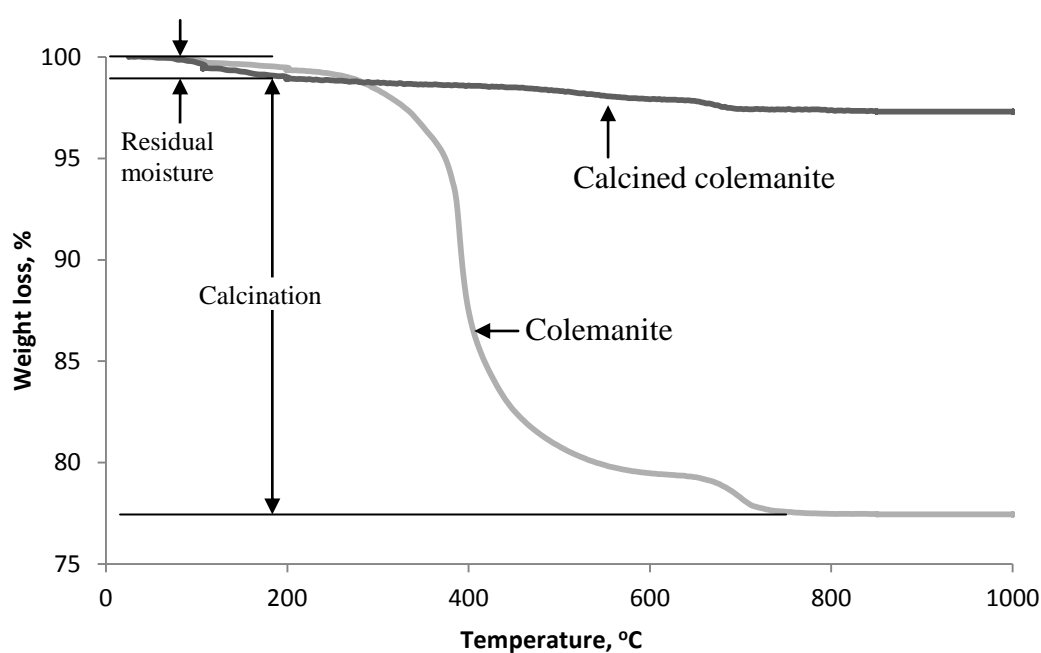
Figure 5. 11 Calcination curves of colemanite and calcined colemanite sample obtained using normal atmosphere and a heating rate of 3°C/min.

Calcination (removal of chemically bonded water) of colemanite was carried out with a crushed and dry sample. However, curves show weight loss due to residual moisture at about 100-110°C. The weight loss (calcination) starts gradually at about 200°C and speeds up at 300°C and the biggest part of the calcination completed at about 550-600°C. After this temperature second weight loss was detected and all chemically bonded water was removed from the body at about 700°C. The reason for

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calcination of colemanite before adding into pellet feed is to prevent pellet spalling and breakage during thermal treatment steps of pelletizing.

Calcined colemanite was ground up to a suitable fineness in a centrifuge ball mill. The particle size distribution curve of ground calcined colemanite is given in Figure 5.12, and shows that the minus 44 µm (325 mesh) material is 73.51%. Ground calcined colemanite with appropriate size distribution was added to iron oxide directly as powder. The specific gravity of the calcined colemanite sample measured with pycnometer using acetone as liquid media was found 1.95.
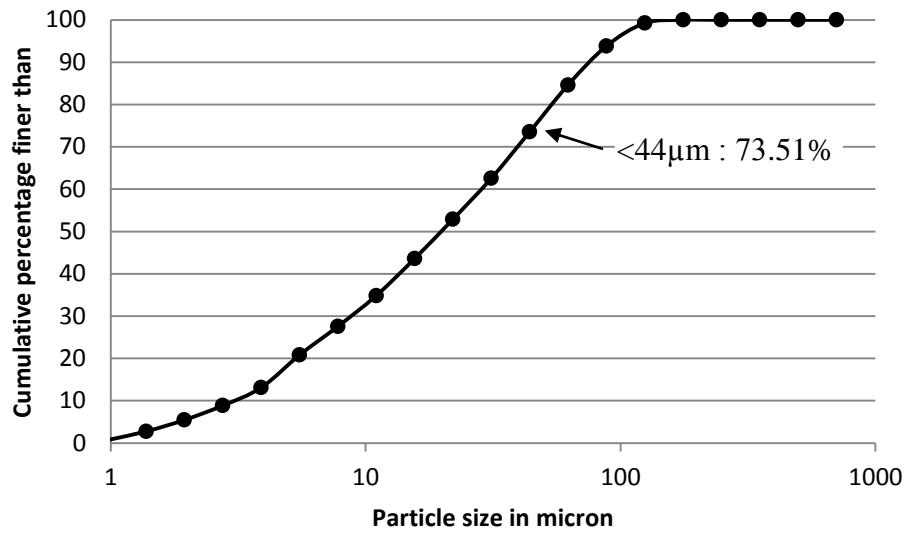
Figure 5. 12 Particle size distribution of ground calcined colemanite (P_{100}: 176.00 µm and P_{80}: 54.67 µm)

5.1.6.2 Tincal

Tincal or sodium borate is a natural boron mineral known as borax decahydrate and a chemical formula $Na_2O.2B_2O_3.10H_2O$ or $[Na_2B_4O_7.10H_2O]$. A typical tincal concentrate contains 36.47% B_2O_3 and 16.24% Na_2O. Melting point of borax decahydrate is 62^oC when heated in closed atmosphere (Mergen and Tektaş, 2003).

A tincal concentrate sample (10 kg) was obtained from Eti Mine Kırka Concentration Plant. The as-received size tincal concentrate sample was crushed in a roll crusher

and ground up to a suitable fineness in a centrifuge ball mill. Ground tincal was used either as powder or a solution.

5.1.6.3 Borax pentahydrate

Borax pentahydrate ($Na_2B_4O_7.5H_2O$) is a boron derivative with about 47.00-48.00% B_2O_3 and 21.25% Na_2O. It has a melting point of 200^oC when heated in closed atmosphere (Tektaş $et\ al$., 2007). Borax pentahydrate weighing 5 kg was taken from Eti Mine Kırka Concentration Plant and this sample contains the minimum B_2O_3 content is 47.76%.

5.1.6.4 Boric acid

Boric acid has the chemical formula H_3BO_3, alternatively written $B(OH)_3$. Boric acid is soluble in boiling water. When heated above 170°C, it dehydrates, forming metaboric acid HBO_2. Metaboric acid is a white, cubic crystalline solid and is only slightly soluble in water. Boric acid melts at about 236°C. Pure boric acid in powder form manufactured by Merck® Chemicals Company was used to see the effect of impurity-free boron compound addition.

5.1.7 Thermal stability of tested binders : TGA Analyses

TGA (thermogravimetric analysis) is used generally to determine thermal stability of materials. The most widely used TGA technique is based on continuous measurement of weight on a sensitive balance (thermobalance) as sample temperature is increased in air or in an inert atmosphere. This is called nonisothermal TGA method. Data are recorded as a thermogram of weight against temperature. Another method is to record weight loss against time at a constant temperature called isothermal TGA method. Isothermal TGA is less commonly used than nonisothermal TGA. Weight loss may arise from evaporation of residual moisture or at higher temperatures it results from decomposition of materials.

Besides providing information on thermal stability, TGA may be used to characterize materials through loss of a known entity. Modern TGA instruments allow thermograms to be recorded on microgram quantities of material.

Thermal stability of binders is important for their weight loss during thermal treatment of pelletizing; therefore, TGA of tested binders were carried out. In order to compare TG curves of alternative binders to bentonite binder, TG curves were obtained with a thermogravimetric analyzer (Leco® TGA701 thermogravimetric analyzer) shown in Figure 5.10.

TG curves of binders were obtained under normal atmosphere with a heating rate of $1\text{-}3^oC/min$ from room temperature to maximum 1000^oC and TG curves are given in Figure 5.13.

Binders are used in TG analyses as they are used in pelletizing experiments (taken from their plastic container and weighed). Therefore binders have more or less residual moisture, and TG curves represent their natural residual moisture (at about 100^oC). Besides residual moisture, loss on ignition and the residue of binders are shown graphically in Figure 5.14. Since the pellets can get their strength during thermal hardening treatment through binders, residues of binders at high temperatures are responsible for binding during thermal treatment.

TG curves show residual moisture, loss on ignition and residue of tested binders as original basis (with natural residual moisture during test). TG curves showed that the natural residual moistures of tested binders. Residual moistures had been drawn away about 100^oC and were found between 0.29% and 10.50%. The residual moisture depends on the condition in which binder is kept.

Loss on ignitions and residues are depend on the substances type; either organic or inorganic. Organic binders or organic based manufactured binders have high LOI with fewer residues. Inorganic binders (borax pentahydrate, calcined colemanite and bentonite) have low LOI with high residues.
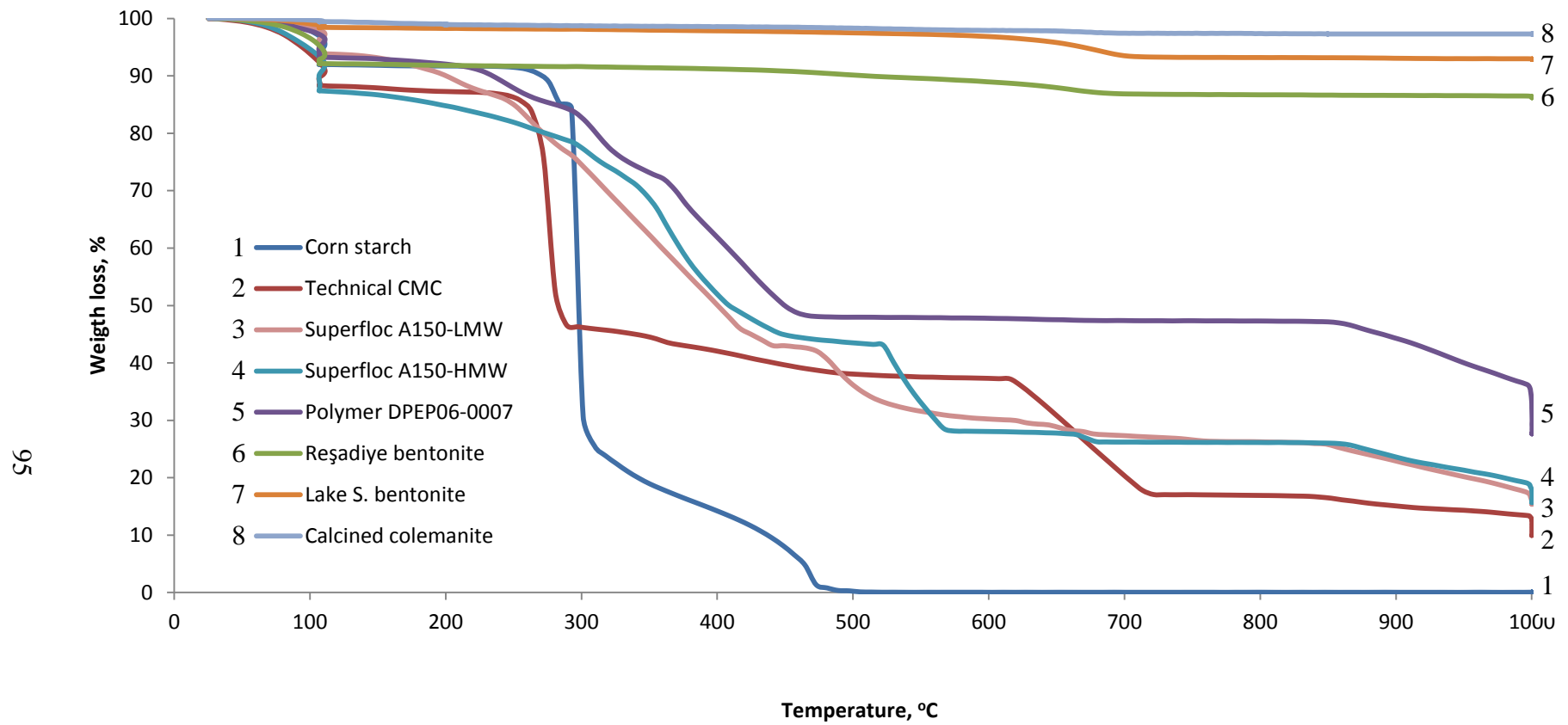
Figure 5. 13 TG curves of binders were obtained using normal atmosphere and a heating rate of 1-3°C/min
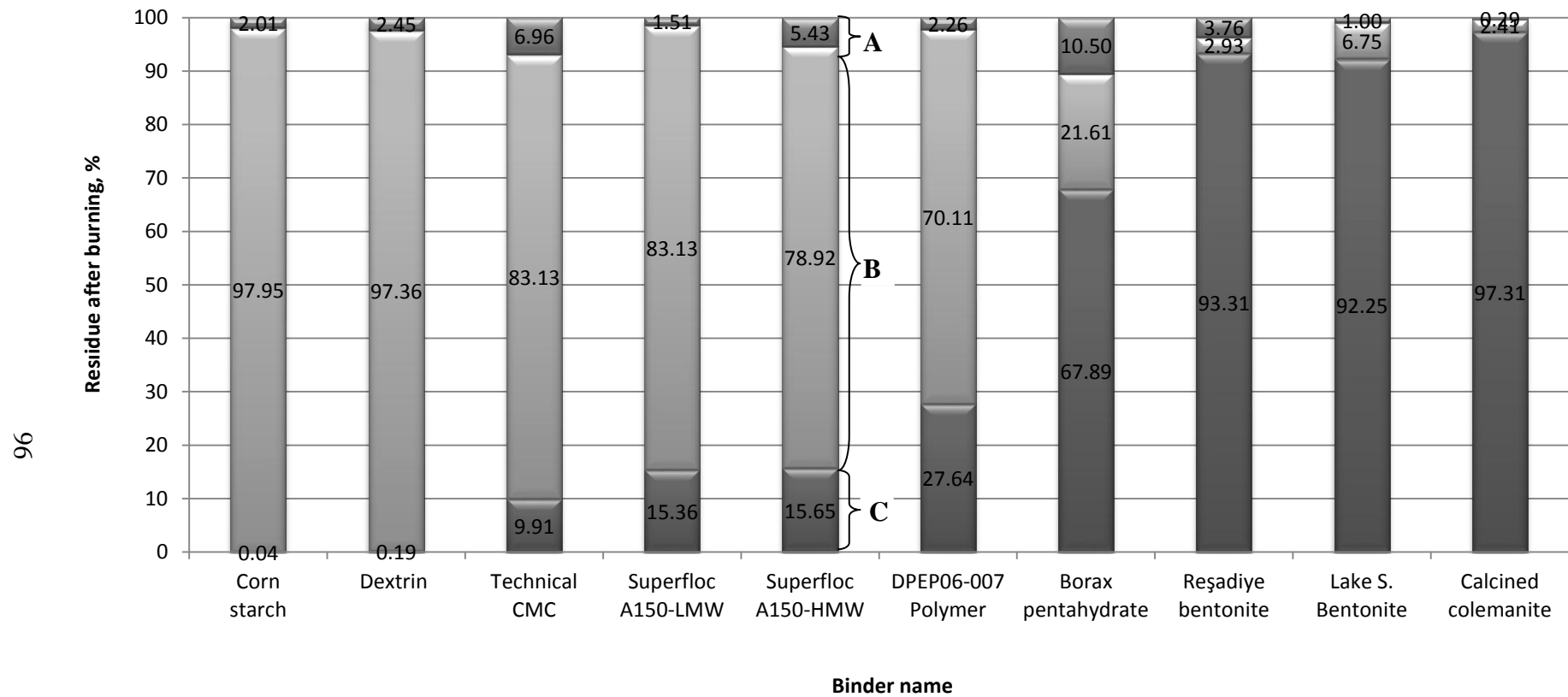
Figure 5. 14. **A**) Residual moisture , **A+B**) loss on ignition and **C**) residue of tested binders determined with TG analyses at 1000°C

Corn starch and technical CMC which are natural organic substances had sharp weight loss at about 300°C showing their burning at this temperature. Typical natural organic binders are burnt-out at relatively low temperature. Corn starch completed burning at 470°C with 0.04% residue. Technical CMC showed another weight loss between 600°C and 700°C and completed burning beyond this temperature with 9.91% residue. This is the reason of low preheated and fired compressive strength of pellets made using organic binders since they burnt out with relatively low residue. Hence, preheated and fired pellet compressive strengths always insufficient with use or organic binders. These results were confirmed many times in previous studies and one more time in the present study.

Organic based manufactured binders; Superfloc® A150-LMW, Superfloc® A150-HMW and DPEP06-007 Polymer had sharp weight loss at similarly about 300°C but not sharp as in corn starch and technical CMC. The weight loss showed a slow decrease; burning of these materials starting at 300°C ending at about 500-600°C. They showed a constant weight up to about 850°C and a gradually weight loss after 850°C up to 1000°C. The residues of Superfloc® A150-LMW, Superfloc® A150-HMW and DPEP06-007 Polymer are 15.36%, 15.65% and 27.64%, respectively.

Bentonite samples from Reşadiye and Lake Superior district showed no big weight loss during TG analyses. They had very small and slow weight loss up to 1000°C. Their residues are determined to be 86.23% and 92.90%, respectively.

On the other hand, boron compounds have higher residue content. While borax pentahydrate has 67.89% residue, the highest residue; 97.31%, was found for calcined colemanite.

As a result, the residues were found in a large interval ranging from 0.04% to 97.31%. While, lower residues with higher LOI as found for organic based binders, the higher residues with lower LOI were found for bentonite and calcined colemanite.

These results show that during and after thermal treatment of pellets, organic binders

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will burn out without or with little residue. Manufactured organic based binders will burn however they still leave small amount of residue. Boron compounds and bentonite will leave the highest residue which will make slag bonding.

In order to observe the physical changing (melting, glass transitions, crystallization etc.) of binders, Reşadiye bentonite, calcined colemanite, borax pentahydrate and combination of calcined colemanite with pure quartz (SiO_2) powder without iron oxides were put in separate porcelain crucibles and heated at 1000, 1100, 1200 and 1300^oC for 20 minutes in muffle furnace. The photos of the binders and mix materials are shown in Figure 5.15.
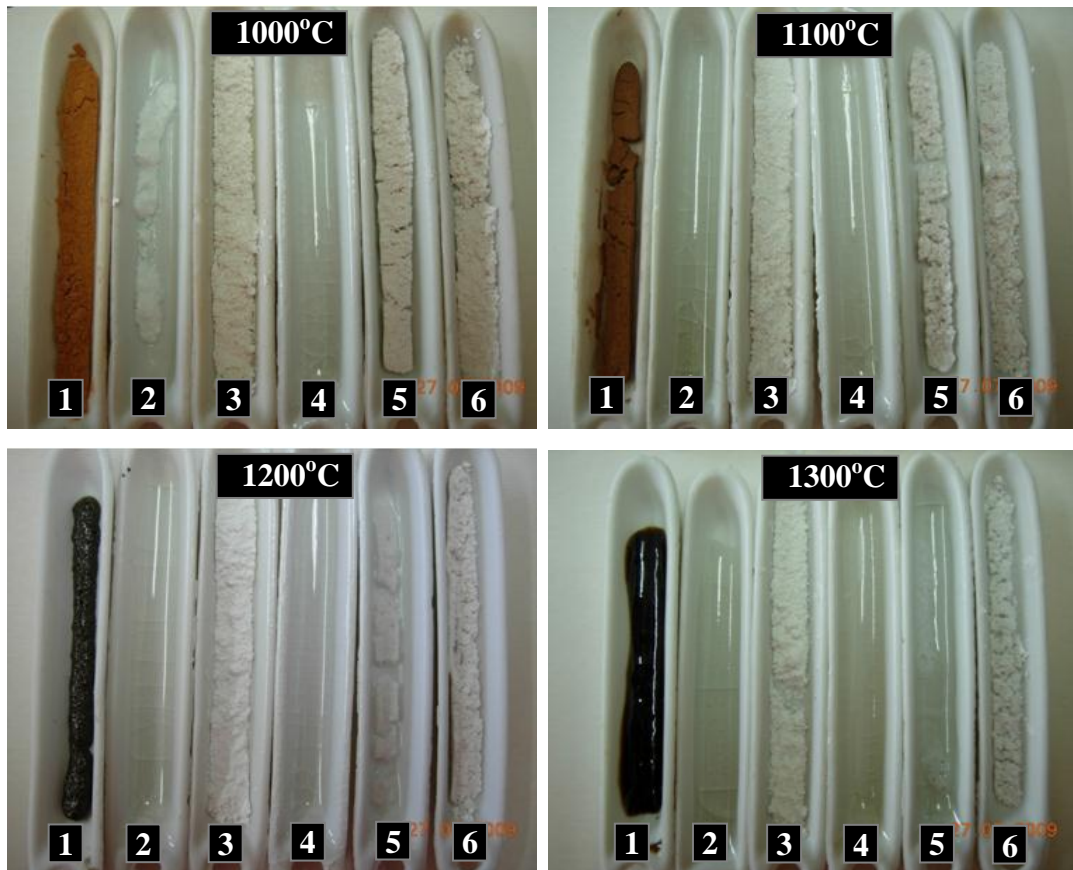
Figure 5. 15. The photos of the binders and mix materials after heating at different temperatures; 1000-1100-1200-1300^oC for 20 minutes. **1)** Reşadiye bentonite, 2**)** Calcined colemanite **3)** Pure SiO_2 powder **4)** Borax pentahydrate **5)** Calcined colemanite plus SiO_2 (ratio:1:2) **6)** Calcined colemanite plus SiO_2 (ratio:1:10).

Since the boron from colemanite and silica from iron ores are expected to form some glassy formation during/after thermal process, the mix of these minerals were prepared synthetically. The ratio of calcined colemanite to pure quartz sand was 1:2 (for low silica iron oxides) and 1:10 (for high silica iron oxides).

It was observed that Reşadiye bentonite did not melt up to $1100^{o}C$, it started to melt $1200^{o}C$ and completely melt at $1300^{o}C$. Therefore, bentonite is expected to increase compressive strength through slag forming via physical melting among iron oxide grains at such higher temperatures.

Calcined colemanite started to melt at lower temperature about $1000^{o}C$ since it has a melting point of $986^{o}C$ and completely melted at $1100^{o}C$. This means calcined colemanite can contribute physical slag forming at lower temperature better than bentonite does.

Borax pentahydrate melted completely at even $1000^{o}C$ since its melting point is $200^{o}C$ when heated in closed atmosphere.

Pure SiO_2 powder did not melt at even $1300^{o}C$ since it has a melting point of 1600-$1725^{o}C$. If one unit calcined colemanite is synthetically added to ten unit SiO_2 (ratio:1:10) the partial physical melting can be seen at $1200^{o}C$. However, if one unit calcined colemanite is added to two unit SiO_2 (ratio:1:2) the physical melting is started at about $1100^{o}C$. This means if boron compounds and SiO_2 are found within pellet feed, the slag forming is achieved with lower temperatures through partial melting on the surface of iron oxide grains.

5.2   Pelletizing experiments

Pelletizing experiments were carried out in METUMEL and MTUCEL. In METUMEL, Divriği magnetite concentrate and Brazilian hematite ore, in MTUCEL Lake Superior magnetite concentrate were utilized as iron oxide sources. Two sodium bentonite samples, different natural and synthetic organic binders and different boron compounds were tested alone or in combination. The procedure for production of wet pellets in both laboratories is explained below.

5.2.1 Laboratory pelletizing procedure

The procedure used to produce the wet pellets was a small scale iron ore pelletizing in laboratory. The laboratory pelletizing experiments were carried out to closely reproduce the conditions that exist in full-scale pelletizing plant.

In METUMEL, about 1000 g dry iron oxides (Divriği magnetite concentrate or Brazilian hematite ore) and a predetermined amount of dry binder were mixed in a mechanical mixer (Figure 5.16 A) for 5 minutes. Then 8% of distilled water by weight of the dry mix was added into this mixture during additional mixing. The binder addition dosages were calculated as percent by weight of the dry iron oxides. In MTUCEL, approximately 2500 g moist Lake Superior magnetite concentrate and a predetermined amount of dry binder were mixed in a kneader-mixer (Figure 5.16 B) at 350 rpm with a 150 rpm orbital motion for 5 minutes. The binder addition dosages were calculated as percent by weight of the moist magnetite concentrate.

Figure 5. 16 **A)** Mixer used in METUMEL **B)** kneader-mixer used in MTUCEL to mix raw materials

Mix material was taken from the mixer and delumped through a 1.68 mm (10 mesh) or 2.40 mm (8 mesh) screen before balling. A small amount of screened moist material was put into the balling disc or drum to form pellet seeds. A laboratory scale balling disc, shown Figure 5.17 A), with 390 mm diameter, 100 mm depth rotating in counter-clock wise direction at 11 rpm in METUMEL, and a laboratory scale balling

drum, shown Figure 5.17 B), with overall diameter 406 mm, mouth diameter 254 mm and depth 178 mm rotating in counter-clock wise direction at 25 rpm in MTUCEL were used to form wet pellets.
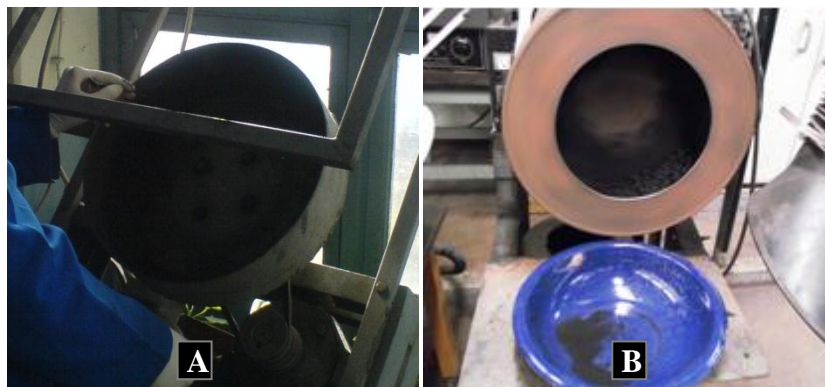
Figure 5. 17 **A)** Balling disc used in METUMEL **B)** Balling drum used in MTUCEL to form wet pellets

After formation of pellet seeds, additional material was fed into disc or drum to enlarge the pellet seeds. During the balling operation, a water mist was applied onto seeds to facilitate the agglomeration of particles and to stabilize the moisture content of wet pellets. Enlarged wet pellets were periodically removed from the disc and drum to control the pellet size and screens shown in Table 5.8 are used for this purpose. Too small or too big agglomerates were crushed and delumped again through 10 or 8 mesh screens and added to fresh feed. This operation was continued until all fresh feed material was converted to properly size wet pellets.

The size of the finished pellets is important since size affects the various reactions within pellets during thermal treatment. With increasing size, the induration intensity, thermo-chemical properties and formation of different phases vary across cross section of pellets. Therefore, the size of the pellets is directly proportional to the time required for reactions. The industrial pelletizing plants produce finished pellets in the size range of 9 to 16 mm. Hence, the pellets were produced in certain size during experiments.

Table 5. 8 Laboratory sieves used to control pellet size

mesh	mm	inch	Laboratory sieves
14	1.168	0.046	
8	2.362	0.093	
6	3.327	0.131	
4	4.699	0.185	
3	6.680	0.263	
	9.423	0.371	
	11.200	0.441	
	12.700	0.500	

The size of wet pellets was controlled by screening the pellets with 12 mm and 10mm special sieves (Figure 5.18) in METUMEL. Therefore, the size of Divriği magnetite and Brazilian hematite pellets were -12+10 mm in diameter.

Figure 5. 18 **A)** 12.0 mm and 10.0 mm special screens to control the pellet size and **B)** wet pellets produced in METUMEL

The size of the finished wet pellets was controlled by screening wet pellets with 12.7 mm (0.500 inch) and 11.2 mm (0.441 inch) standard sieves (Figure 5.19) in MTUCEL. Therefore, the size of Lake Superior magnetite pellets was -12.7+11.2 mm in diameter.

Figure 5. 19 **A)** 12.7 mm (0.500 inch) and 11.2 mm (0.441 inch) standard sieves to control the pellet size and **B)** wet pellets produced in MTUCEL

5.2.2 Moisture content of wet pellets

After producing wet pellets in balling disc or drum, a certain number of wet pellets (20 in METUMEL and 40 in MTUCEL) were randomly selected immediately. The weight of the remaining pellets were recorded and then put in a laboratory oven to dry them at 105°C until constant weight. Laboratory oven used for drying in METUMEL is a direct heating oven with a heating chamber dimension of $45\times40\times65$ cm (W$\times$D$\times$H: width, depth, height), shown in Figure 5.20 A. The other oven used in MTUCEL is an indirect heating oven with a heating chamber dimension of $45\times35\times45$ cm (W$\times$D$\times$H), shown in Figure 5.20 B. These ovens were used to determine the moisture content of wet pellets and to obtain dry pellets. The moisture content was calculated by wet and dry weight difference. Dry pellets were stored in aluminum tray or plastic bags and labeled to use in subsequent tests.

Figure 5. 20 Laboratory ovens used to dry pellets **A)** direct heating chamber used in METUMEL **B)** indirect heating chamber used in MTUCEL

5.2.3 Drop number of wet pellets

10 or 20 wet pellets were used to determine the wet pellet drop number by dropping a single wet pellet repeatedly from a height of 46 cm (18 inch) onto a steel plate (Figure5.21). The drop test for a single wet pellet was continued until a crack was occurred on the pellet and the last value recorded. The mean value was calculated by using all recorded values for each batch experiment and reported with the 95% confidence interval (P95) in the result section.

Figure 5. 21 Steel plates used to determine drop number from 46 cm of wet pellets

5.2.4 Compressive strength of pellets

Compressive strengths of pellets were determined in accord with the method described in the related standard (ASTM E 382-07). A compression test machine consisting of a load cell and a digital controller unit has been constructed in OSTİM. This compression test machine was used in METUMEL, shown in Figure 5.22, to determine the compressive strength of pellets. It has 5000 kg (±0.02%) maximum load capacity and 10 mm/min crosshead speed. The other compression test machine, used in MTUCEL, was a product of MARK-10 Company, shown in Figure 5.23. It has one digital controller unit and two different load cells; maximum 50 lb (25 kg) and maximum 500 lb (250 kg) with a crosshead speed of 40 mm/min. The measurement error for the load cells is given ±0.04% in calibration chart by manufacturer.
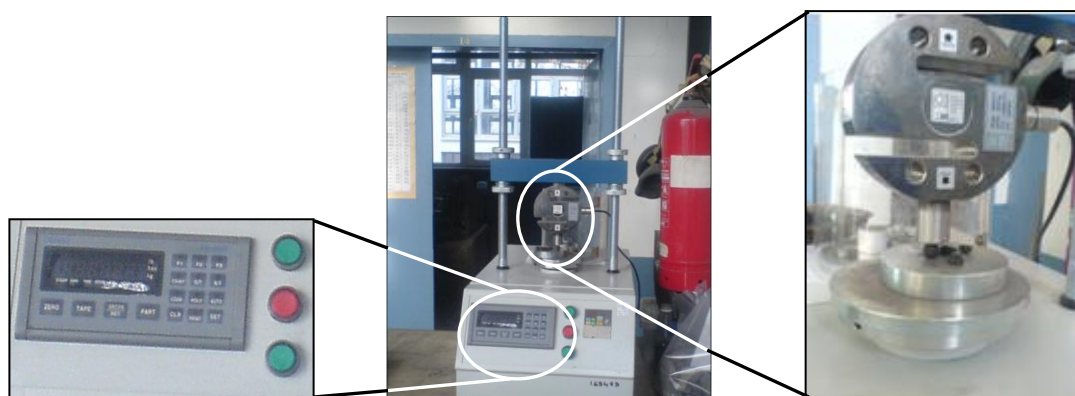
Figure 5. 22 Compression test machine and parts to determine the pellet compressive strength in METUMEL
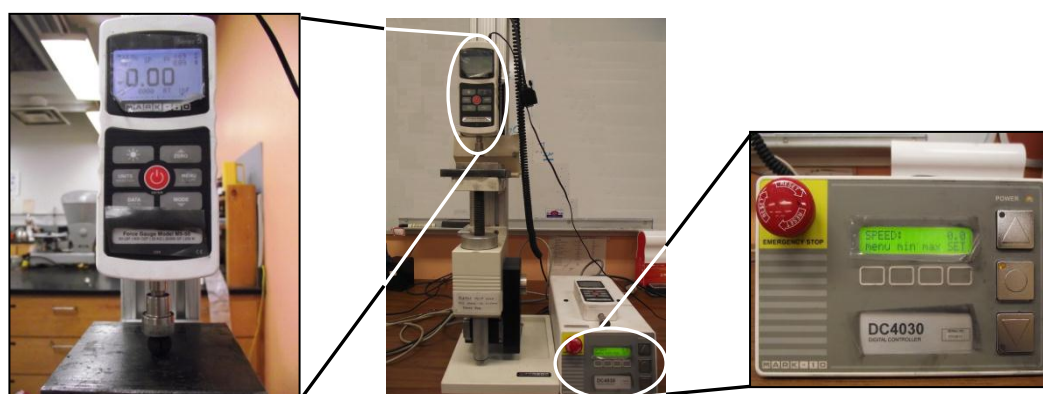
Figure 5. 23 MARK-10 compression test machine and parts to determine the pellet compressive strength in MTUCEL

Wet compressive strength was determined on 10 or 20 wet pellets. Individual wet pellets were compressed using a compression test machine. The peak load required to break the wet pellet was recorded. The mean value was reported with the 95% confidence interval (P95) in the result section.

Dry compressive strengths were determined in accord with the standard after drying of wet pellets at a temperature of 105°C until constant weight. 10 or 20 wet pellets used to determine the dry strengths. Individual dry pellets were compressed using a compression test machine. The peak load required to break the dry pellet was recorded. The mean value was reported with the 95% confidence interval (P95) in the result section.

Dry pellets were preheated and fired at different temperatures to see effect of temperature and performance of tested binders on the strength of pellets. Preheating and firing of dry pellets was carried out in laboratory size muffle furnace, shown in Figure 5.24 A, in METUMEL. The maximum heating capacity of muffle furnace is 1400°C with a heating chamber dimension of 30×55×15 cm (W×D×H). The heating elements of this muffle furnace are silicon carbide (SiC). The heating rate of muffle furnace is about 5°C/min.

In initial experiments with Divriği magnetite concentrate, pellets were preheated at 200, 400, 600, 800 and 1000°C and fired at 1300°C. In subsequent experiments with Divriği magnetite and Brazilian hematite, temperature of 400 and 1000°C were preferred as preheating temperature and 1300°C was selected as firing temperature.

In MTUCEL dry pellets shown in Figure 5.24 C were preheated at 800°C, 1000°C and 1100°C and fired at 1200°C and 1300°C. A laboratory size box furnace, shown in Figure 5.24 B, was used to preheat and fire the pellets. The maximum heating capacity of box furnace is 1300°C with a heating chamber dimension of 20×35×20 cm (W×D×H). The heating elements of this box furnace are molybdenum desilicide (MoSi$_2$). The heating rate of box furnace is about 10°C/min.
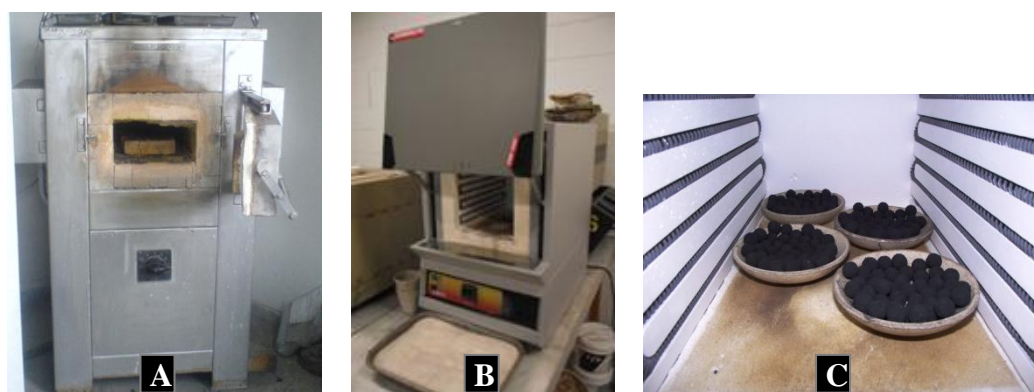
Figure 5. 24 Furnaces used to preheat and fire the pellets **A)** muffle furnace used in METUMEL, **B)** box furnace used in MTUCEL and **C)** dry pellets before firing

Dry pellets were preheated and fired, in one layer in plate type crucibles, Figure 5.25. Preheating and firing of pellets were carried out at different temperatures in normal

atmosphere by following the steps as explained below;

- Dry pellets in crucibles were put in the furnace at room temperature,
- Temperature was set up to desired point, furnace was turned on,
- After reaching the set point, pellets were hold at the set temperature for 20 or 30 minutes,
- After that, furnace temperature was set up to room temperature,
- Pellets were cooled in the furnace overnight.

Figure 5. 25 Dry pellets, in one layer, in plate type crucibles before preheating or firing in furnace

Compressive strengths of preheated and fired pellets were determined by using a compression test machine and in accord with the standard mentioned previously. 10 or 20 thermally hardened (preheated or fired) pellets were used to determine the compressive strengths. Individual pellets were compressed using a compression test machine. The peak load required to break the pellet was recorded. The mean value was reported with the 95% confidence interval (P95) in the result section.

5.2.5 Dust generation of pellets

The dust tower used by Copeland *et al.*, 2009 to evaluate the suppression of airborne particulates in iron ore processing facilities is shown in Figure 5.26. Authors studied the dust suppression of different suppressant on synthetically prepared iron ore pellets and fines from tumbling test. This equipment consists of 11 inclined steel platforms through which pellets drop and knock. One of the dust generation

mechanisms is due to the pellet free-fall drop during operation and transportation. The pellet drop in dust tower can simulate this type of dust generation. Therefore, dust tower can be used for the determination of dust generation.
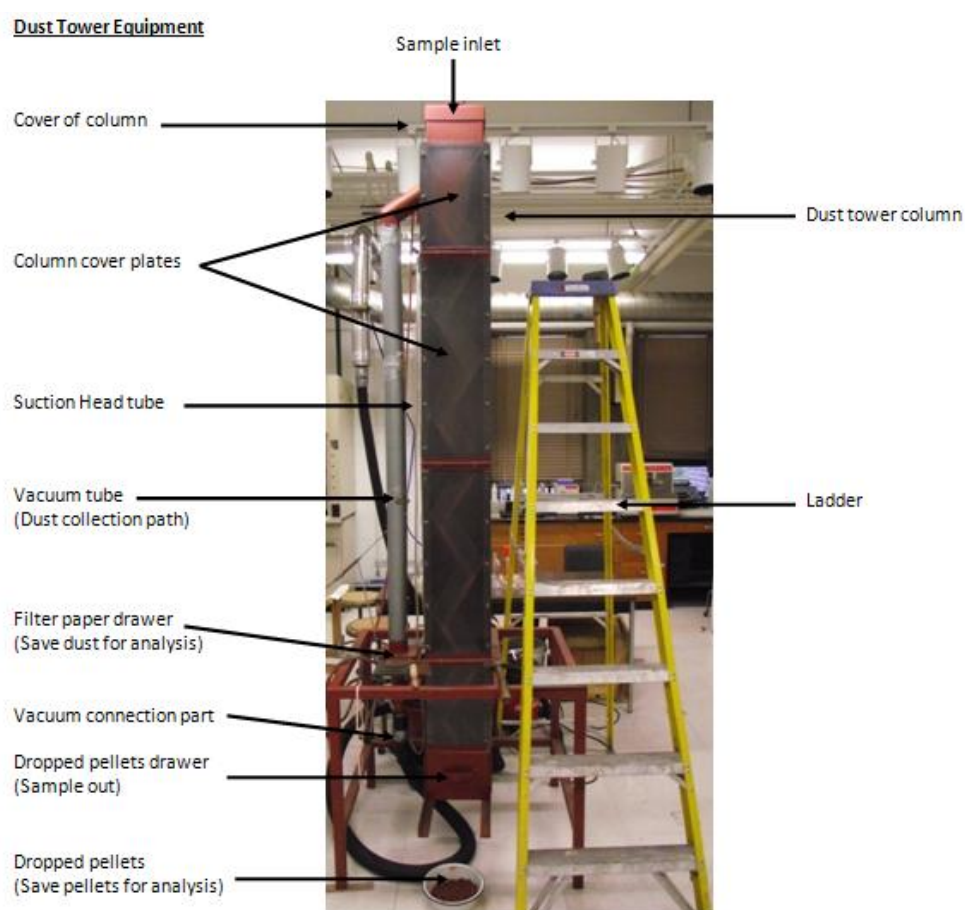
Figure 5. 26 Dust tower used to determine dustiness of fired pellets in MTUCEL

Dust tower was directly used to compare the dust generation of different fired pellets in the scope of this study. Certain amount of pellets (500 – 1000g) produced with different binders were dropped from the top of the dust tower equipment under a certain vacuum condition.

The procedure involved weighing the fired pellets in 500 to 1000 g and dropping them through a counter-current air stream through 11 inclined steel platforms. The air stream was passed through a filter to remove airborne particles. The weight of the particles collected on the filter paper shown in Figure 5.27 was reported as the amount of airborne dust generated. The particle size distribution of the airborne dust

collected on filter paper was determined with Microtrac SRA particle size analyzer.

After dropping the pellets, dropped pellets were taken from the bottom pan of the dust tower equipment and screened from 6.35 mm (3 mesh) and 500 µm (32 mesh) screens to determine the quantities of fines. +6.35 mm, -6.35 mm +500 µm and -500 µm fractions were reported.
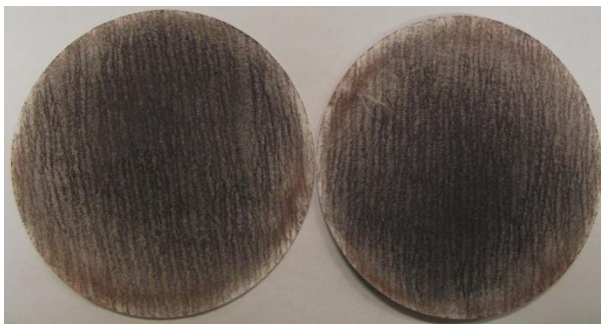
Figure 5. 27 Airborne dust of fired pellets collected on filter paper while fired pellets dropping from dust tower

5.2.6 Microstructure of pellets : SEM Analyses

In order to understand the reason for compressive strength increase of pellets contain calcined colemanite, the microstructure of pellets were examined under scanning electron microscope (SEM, Figure 5.28). The bonding mechanism of combined binders added to magnetite and hematite pellets was tried to be explained by the physical changes (crystal change and crystal growth) in mineral grains of pellets after thermal process.

JEOL JSM-6400 scanning electron microscopy (SEM) was used to obtain micro images of fired (at 1300°C) Divriği magnetite and Brazilian hematite pellets in Metallurgical Department at METU to ascertain the crystal structure changes. Same brand scanning electron microscopy was used for Lake Superior magnetite pellets in Applied Chemical and Morphological Analysis Laboratory at MTU for pellets heated at 800-1000-1100-1200 and 1300°C to see the effect of heating temperature on crystal changes.

Figure 5. 28 JEOL JSM-6400 scanning electron microscopy (SEM) used to take micro image of pellet samples

5.2.7 Porosity of pellets

Porosity of the dry and thermally treated pellets was determined according to method which is based on the measurement of the real/true specific gravity (D) and apparent/bulk specific gravity (d) of the pellets.

True specific gravity (D) of pellets :

In order to determine the true specific gravity, pycnometer was used with distilled water and acetone as liquid media. The pellet sample was ground under 75 µm (200 mesh) in a centrifuge ball mill or a mechanical mortar.

Pycnometer procedure

The empty pycnometer bottle is weighed with lid ($P1$). Dry pellet sample is put in pycnometer bottle and weighed ($P2$). A little distilled water is added into the pycnometer bottle and shaken well to ensure the all sample is wet. Then the pycnometer bottle is filled up with distilled water and weighed ($P3$). After that the pycnometer bottle is emptied and washed. The pycnometer bottle is then filled with only distilled water and weighed ($P4$).

The equation to calculate the true specific gravity of pellets is given below

$$\text{True specific gravity of pellets, } D = \frac{(P2-P1)}{(P2+P4)-(P1+P3)} \quad \text{.................................Eq.7}$$

Where : $P1$: Weight of pycnometer bottle alone in g,

$P2$: Weight of pycnometer bottle + dry powder pellet sample in g,

$P3$: Weight of pycnometer bottle + dry powder pellet sample + distilled water in g,

$P4$: Weight of pycnometer bottle + distilled water in g.

Apparent/bulk density (d) of pellets :

In order to determine the apparent/bulk density (d) of the pellets, the apparent/bulk volume of the pellets must be known. To determine the apparent/bulk volume of the pellets two methods were employed. In one method a mercury pycnometer was used. In the second method bulk volume of pellets was found by immersion of pellets in distilled water after coating with wax paraffin according to ASTM C914-09.

Apparent / Bulk volume of pellets :

A) Mercury pycnometer procedure

Bulk volume of pellets was determined according to the mercury displacement method by using a mercury pycnometer. The procedure involved the weighing of pellets dried at $105^{\circ}C$ (W_p) and put them into the cell of the mercury pycnometer. The bulk volume of dry pellets (V_p) is determined with mercury pycnometer.

$$\text{Bulk/apparent density of pellet, } d = \frac{W_p}{V_p} \quad \text{..Eq.8}$$

Where : Wp : Weight of dry pellets in g,

Vp : Volume of the dry pellets in g.

B) Wax immersion procedure

Envelope/apparent volume of pellets was determined according to ASTM C914-09. The bulk volume of the pellets was found after coating the pellets with wax paraffin and immersing in distilled water. The procedure to measure the volume of the pellets involved the weighing of dry pellet in air, coating with wax and weighing again in air and weighing of coated pellet suspended in water (Figure 5.29).
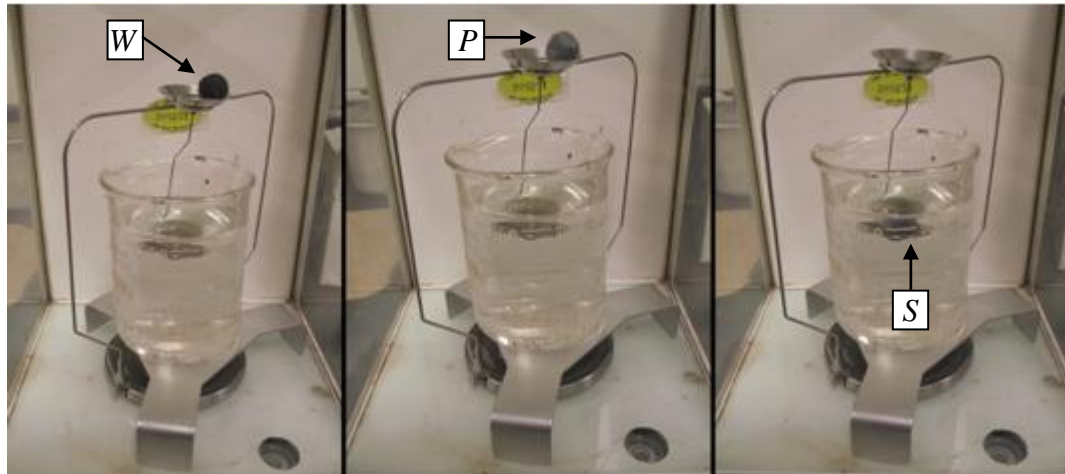
Figure 5. 29 Archimedes principle setup to determine the envelope/apparent volume of pellets according to the procedure of ASTM C914-09

The following equations (Eq.9-12) were utilized to calculate the required volume and density and then Eq.13 was used to calculate the porosity of pellets.

Total volume of the pellet, $\quad V_T \quad = P - S$……………….…......**Eq.9**

Wax volume of the pellet, $\quad V_W \quad = (P - W) / K$…………......**Eq.10**

Envelope/apparent volume of the pellet, $\quad V_E \quad = V_T - V_W$……………….….**Eq.11**

Apparent density of the pellet, $\quad d \quad = \dfrac{W}{V_E}$ ……...…………….…**Eq.12**

Where $\quad$ W : Weight of dry pellet in air,

$\quad$ P : Weight of the dry wax coated pellet in air,

$\quad$ S : Weight of the wax coated pellet suspended in water,

$\quad$ K : Specific gravity of paraffin.

By using the true specific gravity (*D*) and apparent density (*d*) the total porosity (ε,%) of pellets was calculated as follows;

$$\text{Total porosity of pellets,} \quad \varepsilon, \% = \frac{(D-d)}{D} * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\text{Eq.13}$$

5.2.8 Reducibility and swelling index of pellets

The fired pellets with sufficient mechanical strength were subjected to the reducibility test using a vertical split furnace in METU Metallurgical Engineering Department. The reducibility apparatus consisting of a vertical split furnace, a sensitive balance and a control unit was used in the reducibility experiments. The reducibility apparatus and parts are schematically shown in Figure 5.30.

The reducibility of pellets produced with the addition of calcined colemanite was tested and compared with bentonite bonded pellets. The test was carried out in accord with the method described in the related standard (ISO 7215:2007) which is also known as Gakushin method in industry. The test conditions according to Gakushin method, in which pellets are subjected to reducibility shown in the Table 5.9. Table also shows the laboratory test conditions. Instead of nitrogen, argon gas was used as inert gas. The reducibility furnace was heated to 900°C under argon gas atmosphere and then reducibility gas mixture was passed through test sample for 180 minutes period. The reducibility curves of pellets were drawn as percent reducibility versus time. Relative reducibilities of pellets were calculated by weight differences of pellets before and at any time of reduction test.

Table 5. 9 Gakushin and laboratory test conditions for reducibility test

Method	Sample weight (g)	Test gases		Test time (min)	Gas flow rate (l/min)	Test temperature (^{o}C)	Test tube diameter (mm)
		CO (%)	N$_2$ (%)				
Gakushin	500	30	70	180	15	900	60
Laboratory	3.25 avr	30	70 (Ar)	180	0.325	900	50

1	: Split furnace
2	: Weighing unit (sensitive balance)
3	: Control unit
4	: Gas mixing station
5	: Argon tube
6	: CO tube
7	: Fired pellet
8	: Crucible to keep pellet
9	: Ceramic furnace tube
10	: Gas off
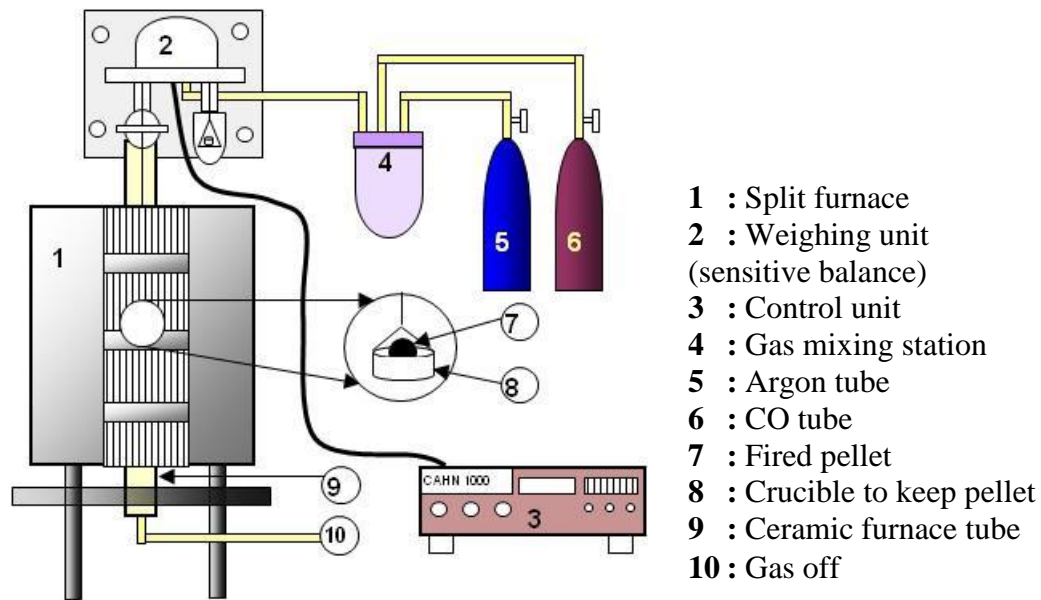
Figure 5. 30 Vertical split furnace and parts for reducibility test of fired pellets according to Gakushin method

Percent swelling of fired pellets was calculated according to Eq.6 as volume change of pellets before and after reducibility test. Pellets used in swelling determination were obtained at the end of 180 minutes Gakushin reducibility method. The apparent volumes of the pellets were determined after coating the pellets with wax paraffin and immersing in distilled water.

5.2.9 Mineralogical (XRD) and chemical (XRF) analyses of pellets

X-ray diffraction studies (XRD) of Divriği magnetite concentrate and Brazilian hematite ore and fired pellets produced with these iron oxides with different binder addition were done using a Rigaku UltimaVI X-ray diffractometer to investigate the possible new compounds formation after binder addition.

Elemental analyses of Divriği magnetite concentrate and Brazilian hematite ore and fired pellets produced with these iron oxides with different binder addition were performed with a Spectro IQ X-ray fluorescence (XRF) spectrometer to examine the chemical composition changes of pellets produced with addition of tested binders.

CHAPTER 6

RESULTS AND DISCUSSION

6.1   Specific surface area of iron oxide samples

The particle size distribution of as-received Brazilian hematite sample was not suitable since it had a particle size distribution of 80% minus 841 μm (20 mesh). Therefore, in order to get a suitable particle size distribution for hematite sample, size reduction processes were applied. Batch of representative hematite samples about 1000 g were crushed in roll crusher then ground in a laboratory scale rod mill for different times (35, 40, 50 and 60 minutes). Besides hematite, Divriği magnetite concentrate was also ground for different times (5, 10, 20 40 and 60) to compare the Blaine surface areas of these two iron oxides. Blaine surface areas of the ground iron oxides samples were determined in accord with the standard (ASTM C 204-07). The results are given in the Figure 6.1.

Blaine surface areas of both iron oxide samples were increased with increasing grinding time. However, the Blaine surface area increase is gradually for Divriği magnetite concentrate since as-received sample already has a sufficient fineness. Blaine surface area of the as-received Divriği magnetite concentrate sample was found to be 1617 ±24 cm^2/g. The Blaine surface area of Divriği magnetite concentrate was increased from 1617 cm^2/g to 2328 cm^2/g after 60 minutes grinding in ball mill.
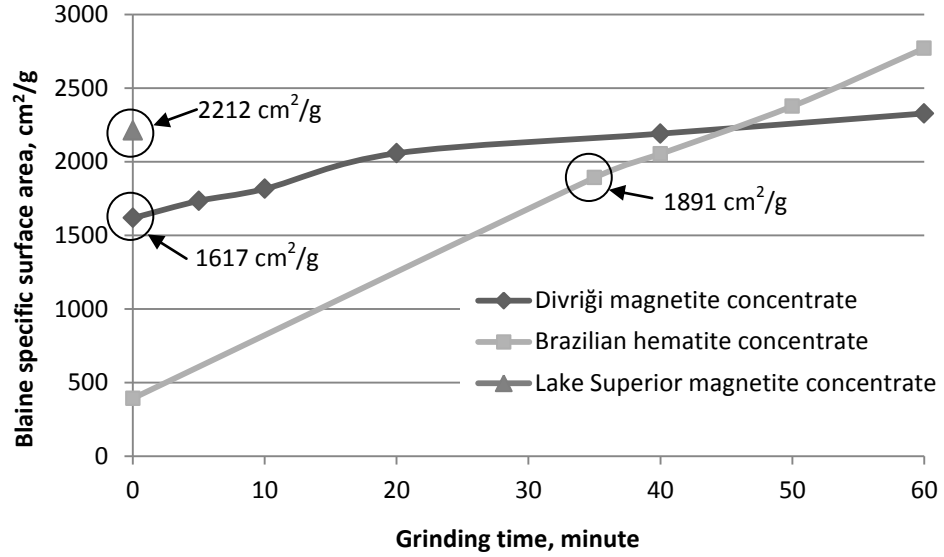
Figure 6. 1 Blaine specific surface areas of Divriği magnetite concentrate, Brazilian hematite ore and Lake Superior magnetite concentrate determined with Blaine air permeability apparatus

On the other hand, the as-received Brazilian hematite ore sample had only a Blaine surface area 392 cm^2/g. The Blaine surface area of hematite ore was increased sharply after grinding since the coarse particles produced new surfaces. The Blaine surface area of original size Brazilian hematite ore sample was increased from 392 cm^2/g to 2770 cm^2/g after 60 minutes grinding in ball mill.

The optimum grinding time for Brazilian hematite ore was determined as 35 minutes since this grinding time provides a Blaine surface area which almost equal to Blaine surface area of Divriği magnetite concentrate. The surface area of Brazilian hematite ore ground for 35 minutes was measured to be 1891 ±35 cm^2/g.

The surface areas of Divriği magnetite concentrate, Brazilian hematite ore and Lake Superior magnetite concentrate used in the pelletizing experiment were 1617 ±24 cm^2/g, 1891 ±35 cm^2/g and 2212 ±38 cm^2/g respectively.

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6.2 Pelletizing experiments with Divriği magnetite concentrate

The as-received size Divriği magnetite concentrate with 1617 ±24 cm^2/g Blaine specific surface area was used in pelletizing experiments. Particle size distribution of this sample is given in Figure 5.2 shows that P_{100}: 176.00 μm, P_{80}:61.98 μm and 63.68% of the particle is smaller than 44 μm (325 mesh).

6.2.1 Effect of heating time on compressive strength of pellets

Dry pellets are preheated and then fired to harden them. In order to determine an optimum preheating and firing time for pellet hardening in laboratory conditions by thermal treatment, effects of heating time on compressive strength of pellets were investigated. Pellets were produced by adding 0.10% CMC, 0.50% tincal, 0.50% calcined colemanite, 0.50% Reşadiye bentonite and 1.00% Reşadiye bentonite with Divriği magnetite concentrate. These pellets were dried at 105°C and then preheated at 1000°C and fired at 1300°C for 10, 20 and 30 minutes. Compressive strengths of thermally treated pellets were determined. The compressive strengths of these pellets are presented in Table 6.1. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 1 Effect of heating time on compressive strength of pellets produced with different binders and preheated at 1000°C and fired at 1300°C for 10, 20 and 30 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)					
				Heating at 1000°C for			Heating at 1300°C for		
				10 minutes	20 minutes	30 minutes	10 minutes	20 minutes	30 minutes
1	0.10% CMC	8.07	2.90 ±0.20	70.20 ±3.85	80.3 ±5.05	79.90 ±6.31	410.80 ±27.08	424.30 ±25.26	492.70 ±44.21
2	0.50% Tincal	7.55	2.00 ±0.00	77.90 ±7.76	88.20 ±3.53	90.50 ±5.64	337.90 ±36.16	358.30 ±24.96	377.80 ±38.33
3	0.50% Cal. Col.	7.46	2.10 ±0.20	129.80 ±10.30	151.90 ±11.82	161.70 ±10.81	413.80 ±33.73	484.00 ±40.46	554.20 ±53.99
4	0.50% Bentonite	8.50	3.00 ±0.22	146.80 ±12.73	150.10 ±7.08	158.70 ±6.19	396.30 ±31.22	494.40 ±43.66	569.50 ±35.45
5	1.00% Bentonite	9.00	4.50 ±0.36	193.50 ±15.26	196.40 ±10.23	202.90 ±7.95	580.80 ±34.80	604.20 ±40.98	697.20 ±30.51

The results of compressive strengths are shown graphically in Figure 6.2 for pellets preheated at 1000°C and in Figure 6.3 for pellets fired at 1300°C for 10, 20 and 30 minutes.

Compressive strengths of pellets produced with any of the binders and preheated at 1000°C increased with increasing heating time. The maximum compressive strengths belong to the bentonite bonded pellets with 0.50% and 1.00% addition levels. CMC and tincal addition resulted in lower compressive strength when compared to bentonite addition. However, 0.50% calcined colemanite addition also provided almost equal compressive strengths to the pellets produced with bentonite which is used in same addition level. The compressive strengths of these pellets were found to be 150.10 kg/p and 151.90 kg/p for 0.50% bentonite and 0.50% calcined colemanite added pellets, respectively, for 20 minutes preheating. 30 minutes preheating time did not increase these strengths significantly, therefore 20 minutes heating was accepted as optimum preheating time for pellets will be produced in the further experiments.
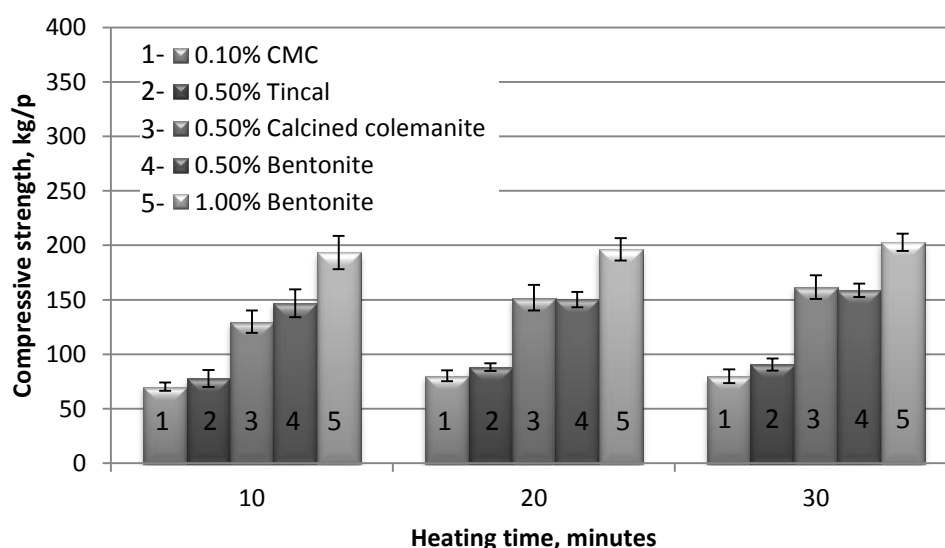
Figure 6. 2 Effect of heating time on compressive strength of pellets produced with different binders and preheated at 1000°C for 10, 20 and 30 minutes. The error bars show the 95% confidence level (P95)
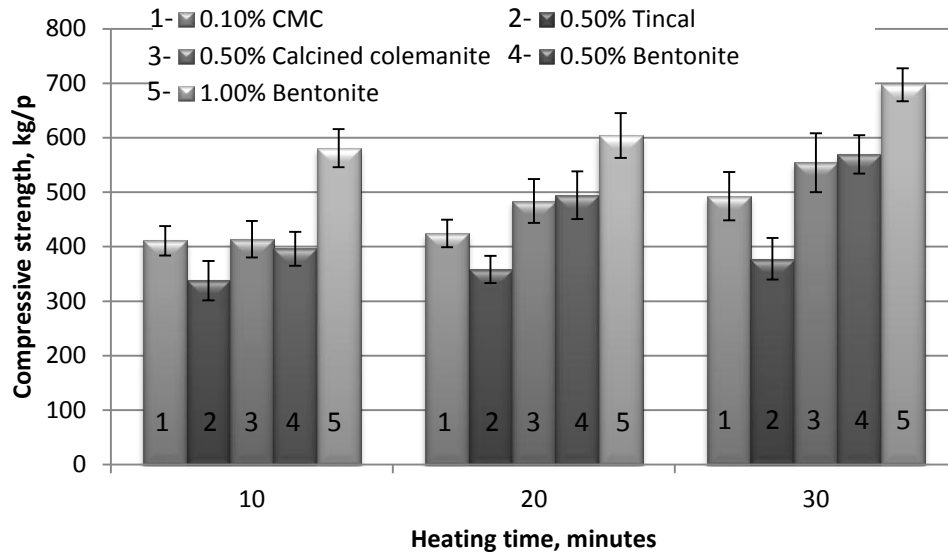
Figure 6. 3 Effect of heating time on compressive strength of pellets produced with different binders and fired at 1300°C for 10, 20 and 30 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of fired pellets were increased with the increasing heating time. In the industry, acceptable minimum compressive strength for fired pellets is 250 kg/p. All pellets had a greater compressive strength than this minimum value after firing for 10, 20 and 30 minutes, due to the relatively high firing temperature (1300°C). At this temperature magnetite pellets could get sufficient strength through oxidation and recrystallization. However, as the 20 minutes was accepted optimum preheating time, the optimum firing time has also been selected as 20 minutes for the future firing duration.

6.2.2 Effect of different binders on compressive strength of pellets

6.2.2.1 Effect of bentonite dosage on compressive strength of pellets

To compare the performance of the alternative organic binders and boron compounds added organic binders to bentonite binders, the pelletization experiments were started with 0.00%, 0.50% and 1.00% Reşadiye bentonite additions, to set up baseline values with bentonite binder. In these pelletizing experiments 1000 g dry Divriği magnetite

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concentrate, predetermined amount of distilled water and bentonite binder are used.

Wet pellets were first dried at 105°C, then were thermally treated at 400, 600, 800, 1000 and 1300°C for 20 minutes in muffle furnace in the laboratory. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.2. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 2 Effect of bentonite binder dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)					
				Dry @ 105°C	Dry @ 400°C	Preheat @ 600°C	Preheat @ 800°C	Preheat @ 1000°C	Fired @ 1300°C
1	Without binder	8.30	1.90 ±0.20	---	7.50 ±1.44	44.30 ±3.68	46.00 ±3.16	53.60 ±4.84	303.00 ±23.90
2	0.50% Bentonite	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	71.60 ±6.75	108.00 ±10.26	150.10 ±7.08	494.40 ±43.66
3	1.00% Bentonite	9.00	4.50 ±0.36	4.30 ±0.30	31.60 ±2.17	76.70 ±5.87	143.60 ±10.72	196.40 ±10.23	604.20 ±40.98

It can be seen from the Table 6.2, moisture content and drop number increased with increasing bentonite dosage. The pellets produced without binder has only 8.3% moisture content and 1.9 drop numbers. However, these values increased to 8.50% and 9.00% moisture content and 3.0 and 4.50 drop numbers with 0.50% and 1.00% bentonite addition, respectively.

Because of bentonite water adsorption capacity pellet moisture content was found greater for high bentonite dosage than ones with less bentonite dosage. Bentonite also provides mechanical strength and high drop numbers to the wet pellets. This phenomenon is explained in literature due to high moisture content by means high bentonite dosage or capillary, adhesional and cohesional bonding properties of bentonite.

The compressive strengths results are shown graphically in Figure 6.4 for pellets produced with bentonite and thermally treated at 400, 600, 800, 1000 and 1300°C for 20 minutes.
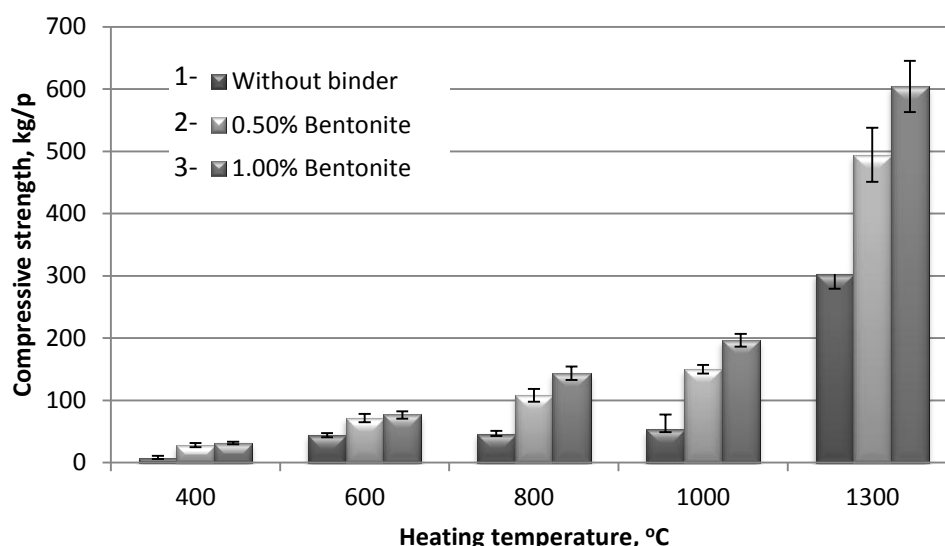
Figure 6. 4 Effect of bentonite binder dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

It is a well known fact that the increasing bentonite dosage can increase pellet quality in wet, dry and fired condition. Here, this fact has been shown one more time; the pellets with 1.00% bentonite has higher compressive strength than those produced with 0.50% bentonite for all temperatures at which pellets were heated. 0.50% bentonite addition level was determined as sufficient and the values for these pellets were accepted as baseline against alternative binders.

From the Figure 6.4, it can be seen again compressive strengths of all pellets increased with increasing temperature. $400^{o}C$, $1000^{o}C$ and $1300^{o}C$ were selected as heating temperatures and pellets were heated at these temperatures for the following experiments.

6.2.2.2 Effect of organic binders on compressive strength of pellets

Since the organic binders are most appropriate alternative binders to bentonite binder, some organic binders tested in this study. Technical grade CMC (Carboxy methyl cellulose), food grade corn starch, dextrin, an organic based polymer coded

DPEP06-0007 by Ciba Company, two organic based flocculants coded Superfloc[®] A-150LMW (low molecular weight) and Superfloc[®] A-150HMW (high molecular weight) manufactured by Cytec company were tested as organic binders.

Organic binders were added to the dry Divriği magnetite concentrate at different addition levels which are industrially acceptable dosages. Some of the organic binders were used as powder and others were used after dissolving in distilled water, according to their physical and chemical properties.

The performances of these organic binders on pellet quality were determined and compared to the baselines with bentonite binder. The results are given in the following subtitles, respectively.

6.2.2.2.1 Effect of CMC dosage on compressive strength of pellets

CMC is one of the important organic binders used as agglomeration aid material in many industries including iron ore pelletizing. Hence, first organic binder tested in this study was technical grade CMC. In order to see the performance of CMC as organic binder on compressive strength of pellets, four different addition levels ranging from 0.05% to 0.20% CMC were tested.

Wet pellets were first dried at $105^{o}C$, then were thermally treated at 400, 1000 and $1300^{o}C$ for 20 minutes in muffle furnace in the laboratory. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.3. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Organic binders are known for their ability to give good wet and dry quality to the pellets. The moisture contents of the pellets with CMC binders were found to be lower than the bentonite bonded pellets. The drop number of the bentonite bonded pellets was found 3.00 which was accepted as drop number baseline. Although the moisture contents of CMC bonded pellets are lower than the baseline, they were

found to have almost same drop numbers as bentonite bonded wet pellets.

Table 6. 3 Effect of CMC binder dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20± 0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.05% Technical CMC	7.93	2.50 ±0.33	---	12.30 ±1.21	77.70 ±4.98	419.60 ±26.48
3	0.10% Technical CMC	8.07	2.90 ±0.20	---	16.00 ±2.11	80.30 ±5.05	424.30 ±25.26
4	0.15% Technical CMC	7.75	3.00 ±0.29	---	16.50 ±2.36	83.10 ±6.09	517.10 ±43.39
5	0.20% Technical CMC	8.05	4.10 ±0.35	---	23.30 ±1.70	105.80 ±4.39	528.10 ±23.09

The compressive strengths results are shown graphically in Figure 6.5 for pellets produced with CMC binder and thermally treated at 400, 1000 and 1300ºC for 20 minutes.
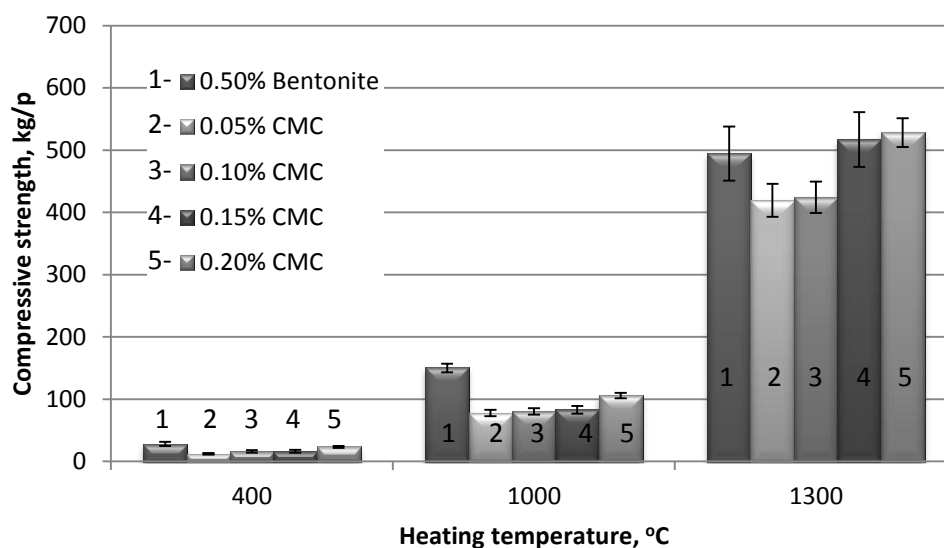
Figure 6. 5 Effect of CMC binder dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of pellets dried at $400^{o}C$ are slightly lower; 16.00-23.30 kg/p, than the bentonite bonded pellets' baseline value; 28.10 kg/p. At this temperature CMC completed its burning, so the effective binding features of CMC decreased at relatively higher temperatures.

At $1000^{o}C$, compressive strengths for CMC bonded pellets are significantly lower; 80.30 kg/p, about 50% less than the bentonite baselines (150.10 kg/p). The significant reduction of preheated pellet strength is most likely from the burning out of CMC binders at this temperature. Therefore, the use of organic binders such as CMC causes low preheated pellet strength in pelletizing industry.

However, fired pellet compressive strengths with CMC were found between 419.60-528.10 kg/p which are almost equal to that, 494.40 kg/p, obtained with bentonite. The reasons of the sufficient fired compressive strengths at $1300^{o}C$ are the mechanical strength created by oxidation of magnetite to hematite, recrystallization and crystal growth of ore grains in the structure. Therefore, the most important role for an additive to organic binders should be to recover the low preheated compressive strengths of magnetite pellets produced with organic binders alone.

6.2.2.2.2 Effect of corn starch dosage on compressive strength of pellets

The second organic binder tested in the thesis was food grade corn starch, since it is also used in some industrial applications as binders. In order to see the performance of corn starch on compressive strength of pellets, four different addition levels ranging from 0.10% to 0.40% corn starch by weight of the dry magnetite concentrate were tested.

Predetermined amount of corn starch was put in sufficient amount of distilled water, and boiled in a pressurized autoclave at $140^{o}C$ for 30 minutes. After dissolution of corn starch, this solution was stirred in a mixer to get uniform slurry. The required amount of starch solution was mixed with dry magnetite concentrate and wet pellets were formed.

Drying and thermal treatment were carried out in the same way and test conditions explained for CMC. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.4. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Moisture contents of pellets are almost equal to each other with all addition levels of corn starch and range from 8.48% to 8.80% which are very near to 8.50% moisture content of baseline pellets with bentonite. Drop numbers of pellets were found to be increased by increasing amount of corn starch additions from 2.80 to 3.30 drops. The drop numbers are also about same the baseline drop number value which is 3.00 with bentonite. Therefore corn starch can be considered suitable binder to provide sufficient drop number to the wet pellets.

Table 6. 4 Effect of corn starch dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.10% Corn starch	8.48	2.80 ±0.26	1.70 ±0.30	13.90 ±1.97	80.80 ±4.71	455.00 ±34.31
3	0.20% Corn starch	8.56	3.00 ±0.29	3.30 ±0.51	16.70 ±2.03	78.40 ±4.72	451.30 ±30.56
4	0.30% Corn starch	8.73	3.10 ±0.35	6.60 ±0.73	17.90 ±2.91	81.70 ±4.24	430.10 ±57.25
5	0.40% Corn starch	8.80	3.30 ±0.42	8.20 ±0.57	19.70 ±2.28	77.20 ±4.29	524.50 ±19.33

Corn starch yielded sufficient dry compressive strengths to pellets ranging from 1.70 kg/p to 8.20 kg/p with 0.10% and 0.40% corn starch addition level, respectively. The value of 1.70 is slightly lower than the baseline, 2.20 kg/p with bentonite, and the others are greater than baseline value and greater than the industrially required minimum value of 2 kg/p. Hence, corn starch may be a good option to get both sufficient wet and dry pellet qualities.

The results of compressive strengths are shown in Figure 6.6 for pellets produced with corn starch and thermally treated at 400, 1000 and 1300ºC for 20 minutes.

Figure 6. 6 Effect of corn starch dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of these pellets preheated at 400°C are lower; 13.90-19.70 kg/p, than the bentonite baseline; 28.10 kg/p. At this temperature corn starch is not effective binder due to burning without residue. Since the TGA analyses showed that a big portion of corn starch burnt at 300°C and completely burnt-out at about 500°C.

Similarly, compressive strengths of pellets preheated at 1000°C were found to be significantly lower than the baseline value with bentonite; the compressive strengths are about only 50% of the baseline value. These lower preheated compressive strengths are as a result of burning out of corn starch like CMC binders at 1000°C temperature. So, corn starch is also not capable of giving sufficient compressive strength to the preheated pellets.

On the other hand, fired pellet compressive strengths with different addition levels of corn starch were found to be almost equal to one obtained with bentonite. These result showed that after burning out of organic binders (in this case corn starch) they do not have any adverse effect on the strengthening mechanism by oxidation, recrystallization and crystal growth for fired magnetite pellets.

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6.2.2.2.3 Effect of dextrin dosage on compressive strength of pellets

Dextrin was also tested as organic binder for Divriği magnetite concentrate. Two different dosages, namely 0.50% and 1.00% were tested both as powder and after dissolving in distilled water, as the dextrin is a water soluble organic substance. No difference was observed between the usage of as powder or dissolved dextrin; both additions yielded virtually the same results in terms of balling and pellet quality.

Pelletizing and testing of pellet qualities were carried out using the same methods as explained before for other experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.5. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 5 Effect of dextrin on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.50% Dextrin	7.81	2.00±0.00	2.30 ±0.42	23.40 ±1.73	70.50 ±4.04	439.70 ±58.17
3	1.00% Dextrin	7.77	2.00±0.00	4.00 ±0.58	15.90 ±2.36	46.40 ±4.44	270.30 ±30.70

Moisture contents of pellets were measures about 7.81% and 7.77% which are almost identical as the previous two organic binders; CMC and corn starch. However, dextrin did not yield sufficient drop numbers for wet pellets. Drop numbers of wet pellets produced with dextrin were found to be only 2.00 for both dosages and off course lower than the baseline 3.00 obtained with bentonite.

The results of compressive strengths are shown graphically in Figure 6.7 for pellets produced with dextrin and thermally treated at 400, 1000 and 1300ºC for 20 minutes.
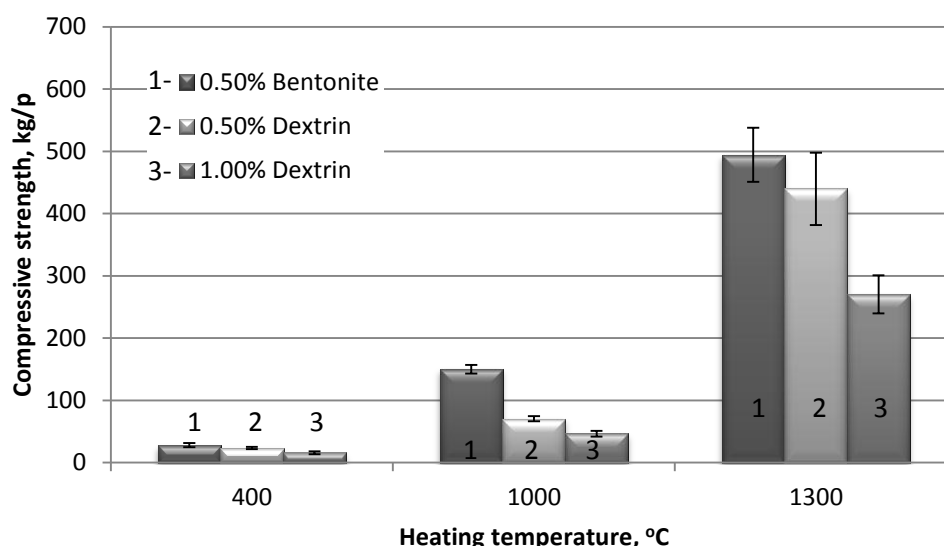
Figure 6. 7 Effect of corn starch dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

Dextrin also yielded sufficient dry compressive strengths to dry pellets, which are 2.30 kg/p and 4.00 kg/p with 0.50% and 1.00% dextrin addition, respectively. These values are considered to be sufficient since they are greater than the baseline value by bentonite and industrial minimum requirement. Dextrin also can be a good option for producing sufficient dry pellet qualities.

The compressive strengths of pellets preheated at 400°C were measured to be 23.40 and 15.90 kg/p for 0.50% and 1.00% dextrin addition, respectively. These values are lower than the bentonite baseline; 28.10 kg/p; however, the former is comparable to the baseline. It should be noted that, increasing dextrin dosage decreased the pellet strength heated at this temperature, so the dosage should be around 0.50% to provide strength to the pellets at this temperatures.

On the other hand, the compressive strengths of pellets preheated at 1000°C were found to be significantly lower than the baseline with bentonite. While addition level of dextrin is increased the preheated compressive strength is decreased. The compressive strength decrease is about 53.0% for pellets produced with 0.50%

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dextrin and 69.1% for pellets produced with 1.00% dextrin.

While compressive strength of fired pellets with 0.50% dextrin was found to be 439.70 kg/p which is slightly lower than bentonite baseline; 494.40 kg/ pellet. The dextrin addition of 1.00% decreased the fired compressive strength significantly from 494.40 kg/p to 270.30 kg/p.

The dextrin pellets resulted in with much lower compressive strength for preheated and fired pellets. Moreover, these strengths are not only lower than the baselines with bentonite but also lower than the values obtained with pellets without binder.

6.2.2.2.4 Effect of DPEP06-0007 polymer dosage on compressive strength of pellets

A polymer coded DPEP06-0007 by manufactured Ciba® Specialty Chemicals was used as organic based polymer binder. Four different dosages, ranging from 0.05% to 0.20% were tested after dissolving in distilled water, as the original powder size of polymer is not suitable to direct use.

Pelletizing and testing of pellet qualities were carried out using the same methods as explained for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.6. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Moisture contents of pellets were measured between 7.94% and 8.89% which are slightly higher than that of bentonite bonded pellets. Results showed that increasing polymer dosage resulted in progressively higher drop numbers; ranging from 2.20 to 5.30 which are sufficient.

Table 6. 6 Effect of DPEP06-0007 polymer on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105°C	Dry @ 400°C	Preheat @ 1000°C	Fired @ 1300°C
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20± 0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.05% DPEP06-0007 Polymer	7.94	2.20 ±0.26	---	13.40 ±1.83	89.40 ±7.05	506.20 ±28.19
3	0.10% DPEP06-0007 Polymer	8.32	2.70 ±0.30	---	14.20 ±1.89	88.40 ±5.35	483.30 ±32.72
4	0.15% DPEP06-0007 Polymer	8.89	3.60 ±0.32	---	14.00 ±1.57	80.20 ±7.86	475.90 ±23.72
5	0.20% DPEP06-0007 Polymer	8.83	5.30 ±0.59	---	15.00 ±1.89	78.90 ±4.20	416.40 ±26.65

The balling/agglomeration of the wet pellets with 0.05% and 0.10% DPEP06-0007 polymer was normal. Moreover, smother surface of wet pellets were observed after wet pellet formation with use of these addition levels. However, balling for the pellets with higher addition level than 0.10% was not easy; the formation of seeds and wet pellets was difficult and took more time to complete the balling. It was difficult to get properly sized wet pellets with use of those high addition levels. Therefore, the addition level of this polymer should be lower than 0.10% addition level. Otherwise, it is possible to have problem in balling equipment of plant; such as too small or too big pellet size or agglomerates with irregular shapes.

The compressive strengths results are shown graphically in Figure 6.8 for pellets produced with DPEP06-0007 polymer and thermally treated at 400, 1000 and 1300°C for 20 minutes.

The compressive strengths of pellets preheated at 400°C were determined to be 13.40-15.00 kg/p which are about 50% of the baseline value with bentonite; 28.10 kg/p. At 400°C the compressive strengths with DPEP06-0007 polymer additions are not comparable to pellets made with bentonite binder.

Similarly, the compressive strengths of pellets preheated at 1000°C were determined to be about 50% of the baseline value with bentonite. Moreover, the decrease in compressive strengths is increasing with the increasing addition level of DPEP06-0007 polymer. It is most likely due to burning out of this organic based chemical at

relatively higher temperatures and it cannot contribute any strength to the preheated pellets.
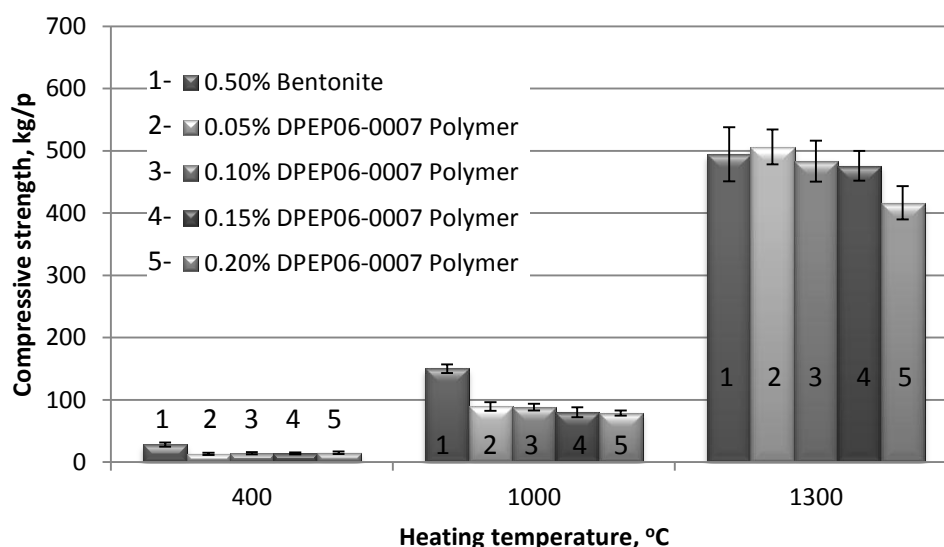
Figure 6. 8 Effect of DPEP06-0007 polymer dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

In contrast, fired pellet compressive strengths with different addition levels of DPEP06-0007 polymer were found to be roughly equal to one obtained with bentonite. The same results were observed in compressive strength decrease; decrease of compressive strength is increasing with the increasing addition level. This polymer also does not have a pronounced adverse effect on the strengthening mechanism of the fired pellets through oxidation of magnetite pellets.

6.2.2.2.5 Effect of Superfloc[®] A-150LMW and HMW dosages on compressive strength of pellets

Two flocculants coded Superfloc[®] A-150LMW and Superfloc[®] A-150HMW (low and high molecular weight, respectively) by manufactured by Cytec[®] Industries Inc. were used as organic based binder. In view of molecular weights of flocculants, two different dosages for both flocculants were tested. Addition levels were 0.05% and

0.10% for LMW flocculant and were 0.005% and 0.010% for HMW flocculant. Since the original powder size of these flocculants is not suitable to direct use as binder, they were used as water slurry after dissolving in distilled water.

The same methods were applied for pelletizing and testing of pellet qualities as explained for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.7. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 7 Effect of Superfloc® A-150LMW and Superfloc® A-150HMW on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.05% Superfloc A-150LMW	8.86	3.40±0.32	---	11.30 ±1.06	62.40 ±6.10	471.20 ±32.32
3	0.10% Superfloc A-150LMW	8.71	5.00±0.77	---	9.00 ±1.13	61.10 ±3.30	405.30 ±26.95
4	0.005% Superfloc A-150HMW	8.47	2.20±0.26	---	11.90 ±1.56	50.80 ±6.62	369.80 ±18.24
5	0.010% Superfloc A-150HMW	8.00	2.00±0.00	---	7.40 ±1.21	56.30 ±2.34	352.40 ±33.12

Moisture contents of pellets were measured between 8.00% and 8.86% which are almost equal to moisture content 8.50% of bentonite bonded pellets. Results showed that increasing flocculant dosage resulted in progressively higher drop numbers for pellets made with LMW flocculant. Drop numbers were found to be 3.40 and 5.00 for those pellets made with 0.05% and 0.10% Superfloc® A-150LMW addition, respectively.

On the contrary, the drop numbers of pellets with HMW flocculant were found only 2.00 and 2.20 which are insufficient when compared with the drop number baseline of 3.00 of wet pellets with bentonite. It is thought that these addition levels of HMW flocculant are not appropriate level; it should be used higher addition level than those levels to produce sufficient wet drop numbers.

The balling/agglomeration of the wet pellets with the addition levels preferred for the flocculants were normal, no difficulty were faced during seed and wet pellet formation. Besides, smother surface of wet pellets were observed after wet pellt production with the use of these flocculants as binder.

The compressive strengths results are shown graphically in Figure 6.9 for pellets produced with Superfloc[®] A-150LMW and Superfloc[®] A-150HMW and thermally treated at 400, 1000 and 1300°C for 20 minutes.

The compressive strengths of pellets preheated at 400°C were determined between 7.40 and 11.90kg/p which are drastically lower than the baseline value with bentonite; 28.10 kg/p. The reduction of strength is more pronounced with increasing addition level of flocculants for both LMW and HMW. Therefore, compressive strengths of pellets preheated at 400°C are not comparable to pellets made with bentonite binder.
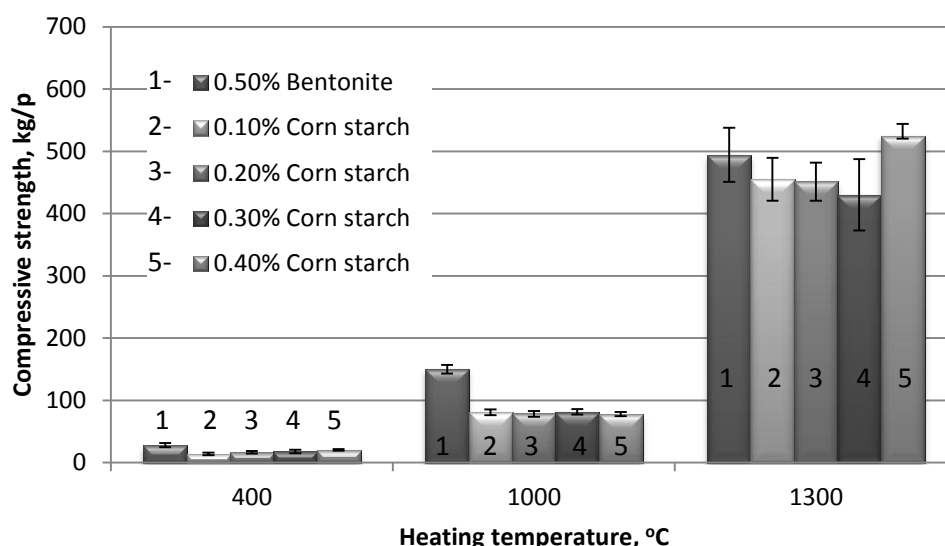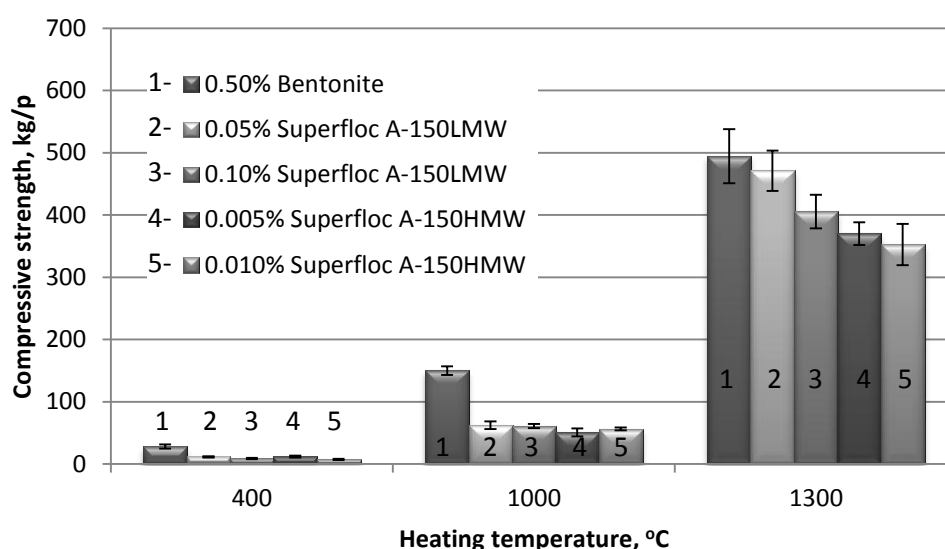

Figure 6. 9 Effect of Superfloc[®] A-150LMW and Superfloc[®] A-150HMW dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of pellets preheated at 1000°C were determined to be about average values of 62 kg/p and 53 kg/p for LMW and HMW flocculants, respectively. These strengths cannot be compared to the baseline value 150.1 kg/p of bentonite bonded pellets since they are too low. It can be said that these flocculants are not suitable binder to provide sufficient preheated pellet strength.

Fired pellet compressive strengths with LMW flocculants were found to be a little lower than that of obtained with bentonite. Decrease of compressive strength is increasing with the increasing addition levels of flocculants. It was decreased from a baseline level of 494.40 to 471.20 and further 405.30 kg/p when addition level was increased. Furthermore, the compressive strength decrease is markedly low for HMW flocculants. They were found to be 369.80 kg/p and 352.40 kg/p when HMW flocculant was used. That means adverse effects of these flocculants on strengthening mechanism of magnetite pellets are becoming important when the addition levels are increased.

6.2.2.3   Effect of boron compounds on compressive strength of pellets

Organic binders and organic based chemicals were found to give sufficient wet and dry pellet properties, however they failed to provide sufficient preheated compressive strength to the pellets. Therefore, in order to get comparable or improved preheated pellet strength, some boron compounds were tested as binder or strength improving additives for Divriği magnetite concentrate in the study. Borax pentahydrate, boric acid, tincal and colemanite were used as boron containing compounds.

Boron compounds were added to the dry Divriği magnetite concentrate at different addition levels to determine the most appropriate dosage. Boron compounds were used after grinding in mill or mortar to get suitable particle size distribution for balling. Colemanite was used after calcination in order to avoid decrepitation of colemanite during thermal treatment.

The performances of these boron compounds on pellet quality were determined and compared to the baselines with bentonite binder. The results are given in the following subtitles.

6.2.2.3.1 Effect of colemanite, tincal, borax pentahydrate and boric acid addition on compressive strength

Calcined colemanite, tincal, borax pentahydrate and boric acid were tested as strength improving additives in this study. To see the effect of these boron compounds as binder on pellet strength they were used alone and trial addition level like 0.50% at first. Calcined colemanite, tincal, and boric acid were used at 0.50% and borax pentahydrate was tested for two different addition levels; 0.50% and 1.00% by weight of dry Divriği magnetite concentrate.

Wet pellets were first dried at 105°C, then were thermally treated at 400, 1000 and 1300°C for 20 minutes in muffle furnace in the laboratory. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.8. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 8 Effect of calcined colemanite, tincal, borax pentahydrate and boric acid addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105°C	Dry @ 400°C	Preheat @ 1000°C	Fired @ 1300°C
1	0.50% Bentonite (Baseline)	8.50	3.00± 0.22	2.20± 0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.50% Calcined colemanite	7.46	2.10± 0.20	---	12.40 ±0.78	151.90 ±11.82	554.20 ±53.99
3	0.50% Boric acid	8.15	2.80± 0.30	---	19.30 ±2.15	121.70 ±8.81	515.20 ±33.07
4	0.50% Tincal	7.86	2.00± 0.00	---	21.20 ±2.24	88.20 ±3.53	358.30 ±24.96
5	0.50% Borax pentahydrate	8.15	2.00± 0.00	---	12.60 ±1.44	81.40 ±8.98	375.90 ±38.69
6	1.00% Borax pentahydrate	8.00	2.00± 0.00	---	10.40 ±1.99	76.70 ±6.81	400.20 ±28.75

The moisture content tests of the pellets produced with any boron compound resulted in lower moisture content than the bentonite bonded pellets. All pellets produced with any boron compounds had about 2.00 drop numbers which is lower than baseline value of 3.00 with bentonite. After the second drop, all wet pellets made

with calcined colemanite, tincal or borax pentahydrate addition were cracked. Only wet pellets made with boric acid addition had 2.80 drop number which is slightly lower than 3.00, and may be considered comparable.

The compressive strengths results are shown graphically in Figure 6.10 for pellets produced with calcined colemanite, tincal, borax pentahydrate and boric acid addition and thermally treated at 400, 1000 and 1300°C for 20 minutes.
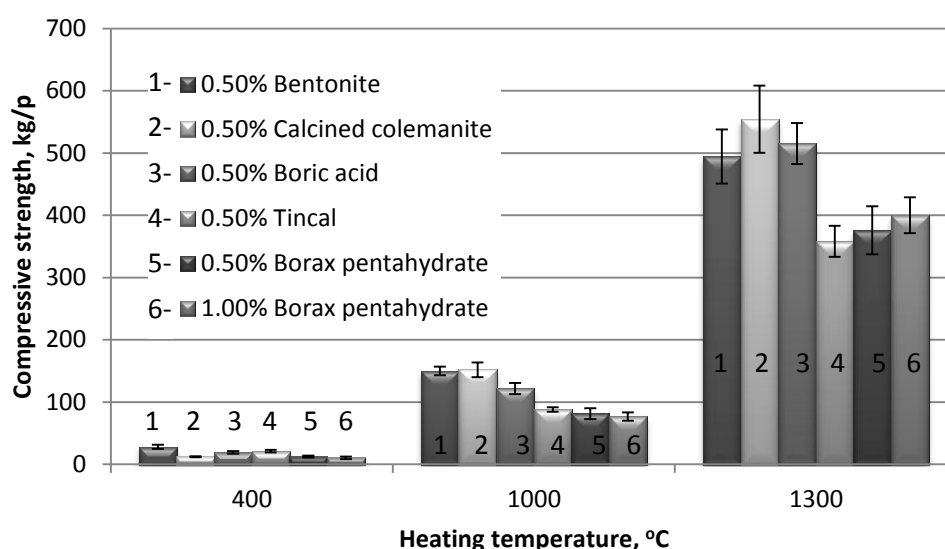
Figure 6. 10 Effect of calcined colemanite, tincal, borax pentahydrate and boric acid addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of pellets preheated at 400°C were determined to be various; ranging between 10.40 and 21.20 kg/p which are lower than baseline of bentonite bonded pellet; 28.10 kg/p. Compressive strength of pellets made with 0.50% tincal addition was 21.20 kg/p which are higher than those of obtained by using other boron compounds. This is most likely due to lower melting point of tincal mineral, since tincal has the lowest melting point among all boron compounds. It is expected that after melting of any additive, here it is tincal, it spreads over the magnetite grains and bind them together. However, if the melting point of additive is higher than the heating temperature, it will not melt and not bind the particle

together; as a result no contributions on strength increase can be observed. For instance, the low compressive strengths were found for pellets produced with colemanite addition and. heated at a temperature lower than colemanite melting point. The compressive strength of pellets was found to be only 12.40 kg/p with 0.50% calcined colemanite addition. Calcined colemanite addition did not contribute to the strength increase at $400^{o}C$ heating temperature which is lower than the melting point ($986^{o}C$) of colemanite.

The contribution of calcined colemanite addition on strength increase for pellets preheated at $1000^{o}C$ was found more pronounced. Since this temperature is slightly over than its melting point. Compressive strength of pellets contain 0.50% calcined colemanite was found to be 151.90 kg/p which is almost equal to baseline value of 150.10 kg/p with 0.50% bentonite binder. Boric acid also provided a reasonable strength increase, which is 121.70 kg/p; however it is lower than baseline. The other boron compounds borax pentahydrate and tincal were found to be incapable to increase strength, since pellets contain those compounds had only an average strength of 80 kg/p which is not comparable to baseline.

Fired pellet compressive strengths with addition of calcined colemanite and boric acid were found to be 554.20 and 515.20 kg/p respectively, a little higher than that of obtained with baseline with bentonite, 494.40 kg/p. The other boron compounds borax pentahydrate and tincal were found to decrease the strength. For example it was decreased from 494.40 kg/p to 358.30 kg/p and 375.90 kg/p when 0.50% borax pentahydrate and 0.50% tincal were used respectively.

As the calcined colemanite provided sufficient strength for both preheated and fired pellets, effect of calcined colemanite dosage on compressive strength of pellets were investigated in detail and the results are given following.

6.2.2.3.2 Effect of calcined colemanite dosage on compressive strength of pellets

In view of the fact that better results in respect to preheated and fired pellet compressive strengths were obtained by addition of calcined colemanite, further

experiments were done to determine an optimum calcined colemanite dosage. The second reason to prefer to use colemanite is because of availability of natural colemanite in Turkey. Four addition dosages ranging from 0.25% to 1.00% were tested as binder to see the effect of dosage on compressive strength of pellets.

Pelletizing and pellet quality tests were carried out with the methods as explained for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.9. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 9 Effect of calcined colemanite on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20± 0.39	28.10 ±3.31	150.10 ±7.08	494.40± 43.66
2	0.25% Calcined colemanite	7.33	2.10 ±0.20	---	13.10 ±1.66	123.60 ±10.81	446.60 ±27.21
3	0.50% Calcined colemanite	7.46	2.10 ±0.20	---	12.40 ±0.78	151.90 ±11.82	554.20 ±53.99
4	0.75% Calcined colemanite	7.52	2.30 ±0.30	---	9.80 ±1.30	181.00 ±19.09	542.80 ±53.42
5	1.00% Calcined colemanite	7.73	2.20 ±0.26	---	9.20 ±1.48	183.60 ±16.10	653.80 ±7.96

Moisture contents of pellets were measured between 7.33% and 7.73% which are markedly lower than the moisture content 8.50% of bentonite bonded pellets. Results showed that increasing calcined colemanite dosage does not have positive effect on wet pellet drop number, since all pellets with different dosage resulted in with only a drop number about 2.20. Drop number test results showed that calcined colemanite is not suitable to be used as binder alone.

The compressive strengths results are shown graphically in Figure 6.11 for pellets produced with different dosages of calcined colemanite and thermally treated at 400, 1000 and 1300ºC for 20 minutes.

The compressive strengths of pellets preheated at 400°C were determined between 9.20 and 13.10kg/p which are lower than the baseline value with bentonite; 28.10 kg/p. The reduction of strength is more pronounced with increasing addition level from 0.25% to 1.00% of calcined colemanite. Therefore, compressive strengths of pellets preheated at 400°C are not comparable with the pellets made with bentonite binder. However, these compressive strengths can be considered sufficient since the pellets, at this temperature, are not subjected to dynamic force. They have to only withstand the static load from pellet bed mass on the travelling grate and from air pressure created by drying/preheating fans. Therefore the important preheating compressive strength should be reinstated when the preheated pellets are cascading from travelling grate to the firing kiln.

Figure 6. 11 Effect of calcined colemanite dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

Results presented in Figure 6.11 indicated that increasing calcined colemanite addition levels increased the compressive strengths pellets of preheated at 1000°C. The compressive strengths of preheated pellets ranged from 123.60 kg/p with 0.25% calcined colemanite to 183.60 kg/p with 1.00% calcined colemanite additions. These values are substantially higher than the ones obtained with organic binders alone and equal or better than the baseline, 150.10 kg/p, with 0.50% bentonite.

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The compressive strengths of pellets fired at $1300^{o}C$ were determined between 446.60 - 653.80 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. Gradually increase of compressive strength of pellets is valid for fired pellet, as well. Only compressive strength of pellets made with 0.25% calcined colemanite addition has lower fired strength than the baseline by bentonite bonded pellets. All the compressive strengths of fired pellets, produced with 0.50% or higher addition level of calcined colemanite, were notably higher than that of baseline with bentonite.

As the compressive strengths of preheated pellets produced with 0.50% bentonite and 0.50% calcined colemanite were nearly equal, 150.10 kg/p for the former and 151.9 kg/p for the latter, and the compressive strength of fired pellets of 0.50% CC were higher than baseline, it was decided that the addition level of calcined colemanite at 0.5% would be sufficient.

6.2.2.4 Effect of calcined colemanite added organic binders on compressive strength of pellets

In the light of the results given above, neither organic binders nor calcined colemanite can be used alone as binders in the pelletizing of Divriği magnetite concentrate. While calcined colemanite falls short of the wet pellet quality, organic binders fail to meet the preheated pellet strengths. Therefore, the combination of organic binders and calcined colemanite; CMC plus calcined colemanite, corn starch plus calcined colemanite and DPEP06-0007 polymer plus calcined colemanite were tested for the production of pellets with sufficient wet, preheated and fired pellet quality. The addition levels of CMC, corn starch and DPEP06-0007 polymer were kept constant at 0.10% for the former two and 0.05% for the latter. Calcined colemanite addition levels to organic binders were ranged from 0.25% to 1.00%.

The performances of these organic binders together with calcined colemanite on the pellet quality were determined and compared with the baselines with bentonite binder. The results are given in the following subtitles.

6.2.2.4.1 Effect of CMC plus calcined colemanite on compressive strength of pellets

CMC and calcined colemanite were used together as combined binder to get sufficient wet, dry and preheated pellet strengths. While the addition level of CMC was constant at 0.10%, four different calcined colemanite addition levels ranging from 0.25% to 1.00% were tested.

Pelletizing experiments were carried out in the same way as explained before for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.10. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 10 Effect of CMC plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.10% CMC + 0.25% Cal.col.	8.52	2.70± 0.30	---	6.70± 0.78	91.70 ±5.14	464.40 ±27.14
3	0.10% CMC + 0.50% Cal.col.	8.63	2.90± 0.26	---	9.10± 0.94	121.50 ±8.00	465.00 ±34.00
4	0.10% CMC + 0.75% Cal.col.	8.72	2.90± 0.26	---	5.90± 0.74	132.90 ±9.35	507.30 ±23.87
5	0.10% CMC + 1.00% Cal.col.	8.91	3.00± 0.41	---	6.10± 0.85	144.50 ±11.55	510.40 ±44.11

Moisture contents of pellets were measured between 8.52% and 8.91% which are slightly greater than the moisture content of baseline which is 8.50% with bentonite. All combined binders yielded drop numbers near to 3.00 which are considered to be sufficient drop numbers for wet pellets in this study. The addition of CMC improved the low drop numbers obtained with only calcined colemanite.

The compressive strengths results are shown graphically in Figure 6.12 for pellets produced with CMC plus calcined colemanite addition and thermally treated at 400, 1000 and 1300ºC for 20 minutes.

The compressive strengths of pellets preheated at 400°C were found to be much lower (5.90-9.10 kg/p) than the bentonite baseline; 28.10 kg/p. Moreover, these strengths are also lower than the strengths obtained by only CMC or calcined colemanite addition alone. However these strengths can be considered sufficient, since they are higher than the acceptable minimum dry compressive strength (2.2 kg/p).
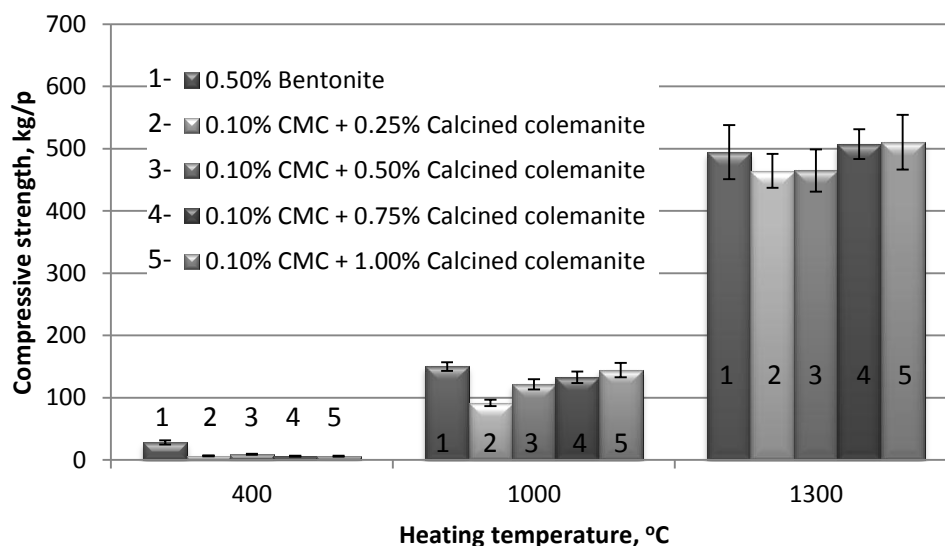
Figure 6. 12 Effect of CMC plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

It can be seen in Figure 6.12 that increasing calcined colemanite addition levels increased the compressive strengths of pellets preheated at 1000°C. The compressive strengths of preheated pellets ranged from 91.70 kg/p with 0.25% calcined colemanite to 144.50 kg/p with 1.00% calcined colemanite additions. These values are slightly lower than the ones obtained by only same addition level of calcined colemanite. However, they are substantially higher than the ones obtained with CMC alone and near to the baseline value which is 150.10 kg/p obtained with 0.50% bentonite.

The compressive strengths of pellets fired at 1300°C were determined between

464.40-510.40 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. All these fired pellet compressive strengths are near to the baseline value, 494.40 kg/p.

These results showed that CMC and calcined colemanite combination provided sufficient strengths to the pellet at all conditions; wet, dry, preheated and fired.

6.2.2.4.2 Effect of corn starch plus calcined colemanite on compressive strength of pellets

Corn starch and calcined colemanite were used together as combined binder to get sufficient wet, dry and preheated pellet strengths. While the addition level of corn starch was constant at 0.10%, four different calcined colemanite addition levels ranging from 0.25% to 1.00% were tested.

Pelletizing experiments were carried out in the same way as explained before for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.11. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 11 Effect of corn starch plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.10% Corn S.+ 0.25% Cal.col.	8.34	2.90 ±0.20	2.10 ±0.20	11.60 ±1.06	104.20 ±7.77	450.00 ±33.62
3	0.10% Corn S + 0.50% Cal.col.	8.46	3.00 ±0.29	2.10 ±0.20	12.50 ±1.38	141.70 ±12.55	521.80 ±39.13
4	0.10% Corn S + 0.75% Cal.col.	8.59	3.10 ±0.20	2.00 ±0.00	5.90 ±0.94	154.40 ±11.95	544.00 ±35.31
5	0.10% Corn S + 1.00% Cal.col.	8.60	3.20 ±0.26	2.00 ±0.00	9.30 ±0.88	178.60 ±15.85	581.60 ±36.64

Moisture contents of pellets were measured between 8.34% and 8.60% which are slightly greater than the moisture content of baseline which is 8.50%. The drop

numbers obtained with all addition levels differ from 2.90 to 3.20 which are about same baseline drop number. Corn starch recovered the lower drop numbers obtained around 2.00 with only calcined colemanite addition.

The compressive strengths results are shown graphically in Figure 6.13 for pellets produced with corn starch plus calcined colemanite addition and thermally treated at 400, 1000 and 1300°C for 20 minutes.
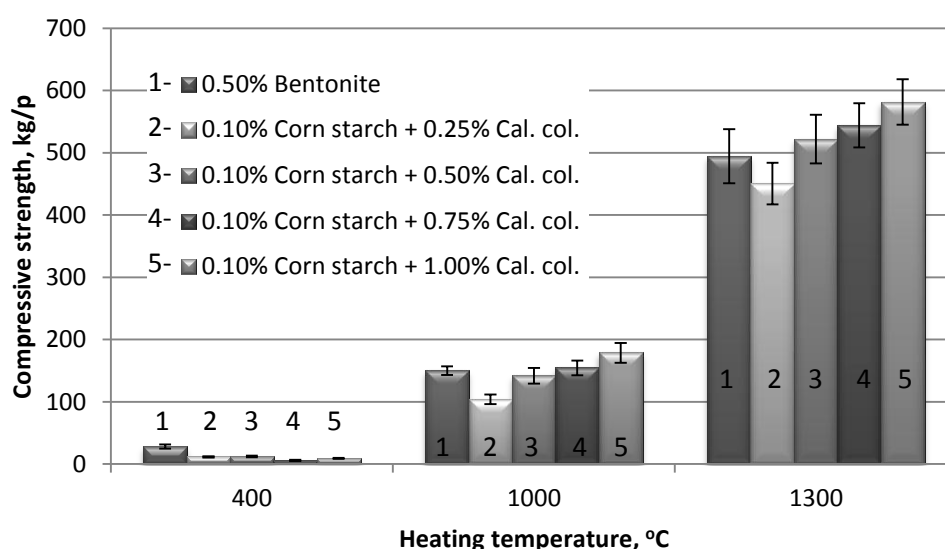
Figure 6. 13 Effect of corn starch plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

Corn starch yielded sufficient compressive strengths to pellets dried at 105°C.The values are 2.00 and 2.10 kg/p which are almost same to the baseline value of 2.20 kg/p. Corn starch seems to be a good option to get both sufficient wet and dry pellet strengths.

The compressive strengths of pellets dried at 400°C were found to be much lower (5.90 - 12.50 kg/p) than the bentonite bonded pellet baseline; 28.10 kg/p. However these strengths can be considered sufficient, since they are higher than the acceptable minimum industrial dry compressive strength which is 2.2 kg/p.

It can be seen in Figure 6.13 that increasing calcined colemanite addition levels increased the compressive strengths of pellets preheated at 1000°C. The compressive strengths of preheated pellets ranged from 104.200 kg/p with 0.25% calcined colemanite to 178.60 kg/p with 1.00% calcined colemanite additions. These values are slightly lower than the ones obtained by only same addition level of calcined colemanite. However, they are significantly higher than the ones obtained with CMC alone and near to the baseline value which is 150.10 kg/p obtained with 0.50% bentonite.

The compressive strengths of pellets fired at 1300°C were determined between 450.00 - 581.60 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. All these fired pellet compressive strengths are near to the baseline value, 494.40 kg/p.

These results showed that when corn starch and calcined colemanite used together as binder, they can provide sufficient strength to the pellet at all conditions; wet, dry, preheated and fired.

6.2.2.4.3 Effect of DPEP06-0007 polymer plus calcined colemanite on compressive strength of pellets

DPEP06-0007 polymer and calcined colemanite were used together as combined binder to get sufficient wet, dry and preheated pellet strengths. While the addition level of DPEP06-0007 polymer was constant at 0.05%, four different calcined colemanite addition levels ranging from 0.25% to 1.00% were tested.

Pelletizing experiments were carried out using the same methods as explained before for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.12. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.
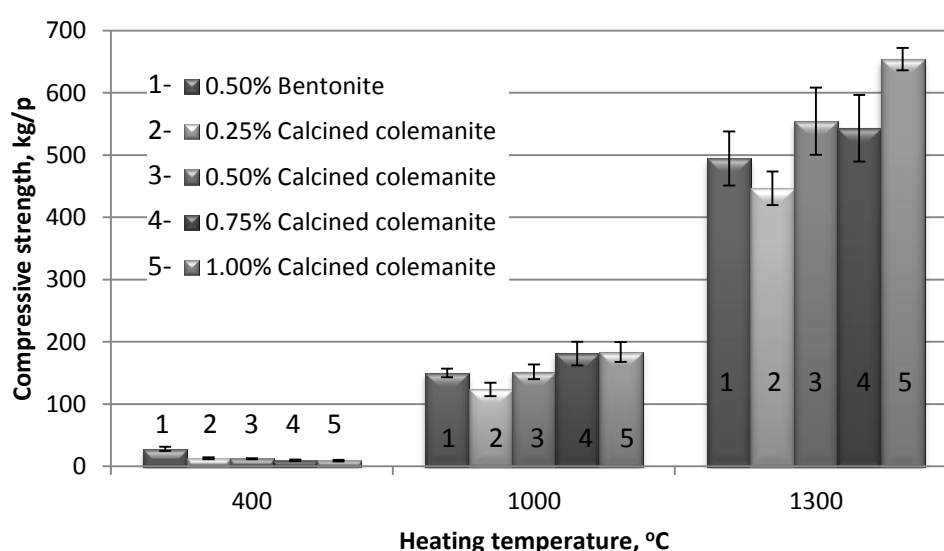
Table 6. 12 Effect of DPEP06-0007 polymer plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105°C	Dry @ 400°C	Preheat @ 1000°C	Fired @ 1300°C
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	2.20 ±0.39	28.10 ±3.31	150.10 ±7.08	494.40 ±43.66
2	0.05% DPEP + 0.25% Cal.col.	9.00	3.10 ±0.35	---	5.20 ±0.64	70.90 ±3.90	381.80 ±26.44
3	0.05% DPEP + 0.50% Cal.col.	9.02	3.30 ±0.30	---	5.20 ±0.64	85.20 ±5.21	398.70 ±23.92
4	0.05% DPEP + 0.75% Cal.col.	9.21	2.50 ±0.32	---	7.40 ±1.10	122.60 ±9.77	492.50 ±51.92
5	0.05% DPEP + 1.00% Cal.col.	9.22	2.60 ±0.32	---	8.50 ±0.73	168.80 ±11.77	562.20 ±49.33

Moisture contents of pellets were measured between 9.00% and 9.22% which are a little greater than the moisture content of baseline pellets which is 8.50%. The drop numbers obtained with all addition levels differ from 2.50 to 3.30 which can be considered acceptable drop numbers. When the calcined colemanite additions are 0.25/ and 0.50%, the drop numbers were found to be 3.10 and 3.30 which are greater than the baseline drop number of bentonite bonded pellets.

The compressive strengths results are shown graphically in Figure 6.14 for pellets produced with DPEP06-0007 polymer plus calcined colemanite addition and thermally treated at 400, 1000 and 1300°C for 20 minutes.

The compressive strengths of pellets dried at 400°C were found between 5.20 - 8.50 kg/p, they are lower than 28.10 kg/p which is baseline value belongs to pellets bonded with bentonite. However these strengths are considered sufficient, since they are higher than the minimum acceptable dry compressive strength (2.2 kg/p).

When the strength of pellets preheated at 1000°C is examined, the strength increase can be seen with increasing calcined colemanite addition. The first two preheated strengths were found to be much lower than baseline preheated strength value. However it is increased to a comparable level by addition of 0.75% calcined colemanite. Moreover, when the addition level of calcined colemanite is increased to 1.00%, the strength became 168.80 kg/p which is greater than baseline strength.
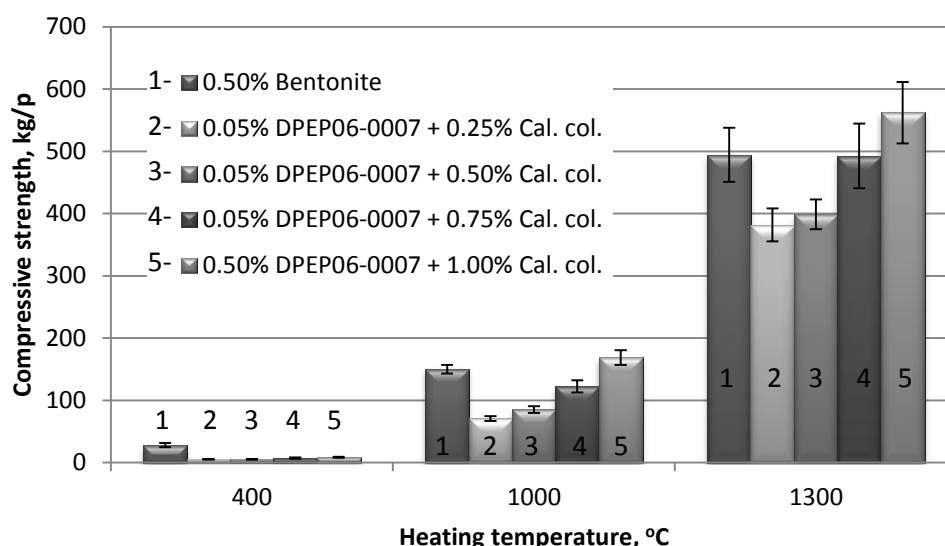
Figure 6. 14 Effect of DPEP06-0007 polymer plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of pellets fired at 1300°C were determined between 381.80-562.20 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. The first two fired pellet compressive strengths are lower than baseline value but they are still acceptable since they are greater than the minimum required the latter two values are near to and greater than the baseline value 494.40 kg/p.

These results showed that when DPEP06-0007 polymer and calcined colemanite are used together as binder, they can produce sufficient strength to the pellet at all conditions; wet, dry, preheated and fired. However this combination is not as good as the CMC plus calcined colemanite or corn starch plus calcined colemanite combination.

6.2.2.5 Effect of lower firing temperature and reduced bentonite plus calcined colemanite binder dosage on compressive strength of pellets

In the light of the results obtained for pelletizing of Divriği magnetite concentrate the lower firing temperature may be tested, since the fired pellet compressive strengths

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were found much higher than the industrially required minimum strength limit which is 250 kg/p for fired pellet. Therefore, lower firing temperatures; 1000, 1100, 1200 and 1300°C were tested on the pellets added boric acid and calcined colemanite. In these pelletizing experiments, besides lower firing temperature, the combinations of bentonite and calcined colemanite were tested. However, bentonite and calcined colemanite addition levels were reduced at this time to see also the effect of reduced dosages of binders.

Boric acid was tested at 0.50% alone and two reduced addition levels of bentonite plus calcined colemanite; namely 0.15% bentonite plus 0.15% calcined colemanite, and 0.25% bentonite plus 0.25% calcined colemanite were tested.

The compressive strengths of thermally treated pellets at lower firing temperatures were determined and the results are given in the Table 6.13. The results of compressive strength for these pellets were compared with the baselines obtained with bentonite binder. Besides bentonite baselines, experiments results previously acquired with the lowest addition levels of calcined colemanite also were given in the table to compare the new performances. Table also shows the moisture content and drop numbers of wet pellets so produced.

Table 6. 13 Effect of lower firing temperatures on compressive strength of pellets thermally treated at 1000, 1100, 1200 and 1300°C for 20 minutes. Boric acid and reduced rate of bentonite plus calcined colemanite were used as binder

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Heated @ 1000°C	Heated @ 1100°C	Heated @ 1200°C	Heated @ 1300°C
1	0.50% Bentonite (Baseline)	8.50	3.00 ±0.22	150.10 ±7.08	---	---	494.40± 43.66
2	0.25% Calcined colemanite	7.33	2.10 ±0.20	123.60 ±10.81	---	---	446.60 ±27.21
3	0.50% Boric acid	8.15	2.80± 0.30	121.70 ±8.81	215.20 ±20.20	408.20 ±24.57	515.20 ±33.07
4	0.15% Ben. + 0.15% Cal. col.	8.31	2.60 ±0.32	118.80 ±8.96	156.90 ±12.40	342.20 ±17.00	468.20 ±32.32
5	0.25% Ben. + 0.25% Cal. col.	8.39	2.80 ±0.26	122.20 ±15.54	191.40 ±20.79	351.30 ±22.02	489.40 ±32.94

The moisture contents of wet pellets are low for pellets produced with only calcined colemanite addition. However they are almost same to that of bentonite bonded

baseline pellets when only 0.15% or 0.25% bentonite is used together with same amount of calcined colemanite.

The addition of such amount of bentonites improved the insufficient drop numbers obtained when only calcined colemanite is used. Drop numbers of combined binders are practically reached to the baseline drop numbers with bentonite. This result shows that the reduced amount of bentonite may recover the inadequate wet pellet drop numbers of only calcined colemanite containing pellets.

The compressive strengths results are shown graphically in Figure 6.15 for pellets produced with reduced rate of bentonite plus calcined colemanite addition and thermally treated at 1000, 1100, 1200 and 1300°C for 20 minutes.
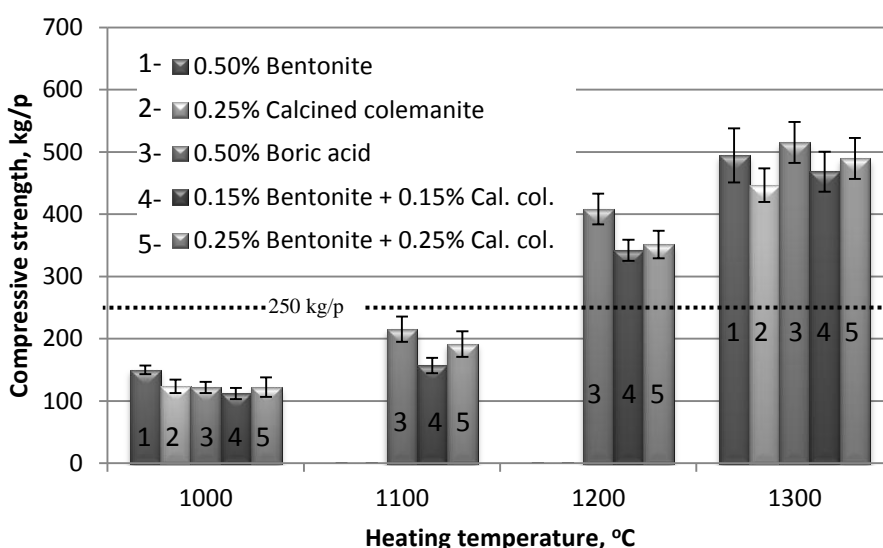
Figure 6. 15 Effect of lower firing temperatures on compressive strength of pellets thermally treated at 1000, 1100, 1200 and 1300°C for 20 minutes. Boric acid and reduced rate of bentonite plus calcined colemanite were used as binder. The error bars show the 95% confidence level (P95). Dashed line shows 250 kg/p which is the industrially required minimum strength limit for fired pellet compressive strength

The compressive strengths of pellets heated at different temperatures can be seen in Figure 6.15. They progressively increased when the heating temperature or addition

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level of binders are increased. The pellets produced with 0.50% boric acid has 121.70 kg/p and pellets with lower addition levels of bentonite and calcined colemanite have 118.80 and 122.20 kg/p which are slightly lower than 150.10 kg/p belongs to bentonite bonded baseline pellets at 1000°C. However, they are much higher than the strengths obtained without binder or organic binders alone.

When the temperature was increased to 1100°C, strengths of boric acid containing pellets were increased to 215.20 kg/p and the others to 156.90 and 191.40 kg/p which are insufficient considering the required limit which is 250 kg/p. A dashed line indicating that limit was drawn in Figure 6.15 to compare the results easily.

On the other hand, when the temperature was increased to 1200°C, strengths became 408.20 for boric acid containing pellets and 342.20 and 351.30 kg/p for the others, respectively. Now these pellets are strong enough since they meet the minimum strength limit. These results indicate that the low temperature i.e. 1200°C can be employed to get sufficient fired pellet strength. Moreover, it can be concluded that the minimum temperature to provide the minimum required strength limit for fired pellet is somewhere between 1100°C and 1200°C. This results are so significant because lowering of firing unit of pelletizing plant will lead to energy saving.

The compressive strengths of all pellets fired at 1200°C and 1300°C are higher than the limit and almost same values to the baseline pellets.

6.3 Pelletizing experiments with Brazilian hematite ore

The as-received size Brazilian hematite ore was ground in a ball mill for optimum grinding time to get a suitable size distribution. Ground hematite ore used in pelletizing experiments had a Blaine surface area of 1891 ±35 cm^2/g. Particle size distribution of this sample is given in Figure 5.7 shows that P_{100}: 248.90 μm, P_{80}: 76.95 μm and 61.07% of the particles is smaller than 44 μm (325 mesh).

6.3.1 Effect of different organic binders on compressive strength of pellets

Organic binders tested for Divriği magnetite concentrate were also used for Brazilian hematite ore. In the view of the results for use of organic binders obtained with using Divriği magnetite concentrate, the most appropriate addition level of organic binders were used for hematite ore.

Technical grade CMC (Carboxyl methyl cellulose), food grade corn starch, dextrin, an organic based polymer coded DPEP06-0007 by Ciba Company, two organic based flocculants coded Superfloc® A-150LMW (low molecular weight) and Superfloc® A-150HMW (high molecular weight) manufactured by Cytec company were tested as organic binders.

Organic binders were added to the dry Brazilian hematite ore at suitable addition levels which were found suitable dosages. Some of the organic binders were used as powder and others were used after dissolving in distilled water, according to their physical and chemical properties.

The performances of these organic binders on pellet quality were determined and compared to the baselines with bentonite binder. For the hematite ore, preheated pellet compressive strength is so important due to lack of the strengthening mechanism by oxidation as in the case of magnetite pellets. The other strengthening mechanism through recrystallization takes place at relatively high temperature such as $1200^{o}C$-$1350^{o}C$ for hematite pellets according to genesis of ore used in pellet production (Meyer, 1980). Therefore, the low strength of hematite pellets in industry would be a problem especially when the travelling grate and rotary kiln furnace system is used. Hence, the focus of this study is on the preheated and fried compressive strength of hematite pellets. The results are given in the following subtitles, respectively.

6.3.1.1 Effect of CMC, corn starch and dextrin addition on compressive strength of pellets

CMC, corn starch and dextrin organic binders were tested at several different dosages for Divriği magnetite concentrate. In order to see the performances of these organic binders on a hematite ore, hematite pellets were also produced using these organic binders at addition levels of 0.10%, 0.20% and 0.50%, respectively.

Wet pellets were first dried at 105°C, then were thermally treated at 400, 1000 and 1300°C for 20 minutes in muffle furnace in the laboratory. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.14. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

The moisture content of wet pellets was found to be 7.50% using bentonite binder. CMC and corn starch bonded pellets were found to have higher moisture contents than 8.00%. However, only dextrin bonded pellets resulted in a lower moisture content that is 7.30%.

Table 6. 14 Effect of addition of CMC, corn starch and dextrin organic binders on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
2	0.10% CMC	8.44	4.70 ±0.30	---	---	19.80 ±2.18	330.90±22.87±
3	0.20% CMC	8.73	9.00 ±0.51	3.20 ±0.26	3.00 ±0.29	35.00 ±2.48	378.50 ±29.37
4	0.20% Corn starch	8.00	4.00 ±0.41	---	---	14.00 ±0.83	280.10 ±27.05
5	0.50% Dextrin	7.30	2.00 ±0.00	---	---	11.90 ±1.19	189.30 ±26.55

The baseline drop number of pellets produced with bentonite was found to be 3.40. Higher drop numbers were obtained by using CMC and corn starch; these drop

numbers are 4.00 for 0.20% corn starch added pellets, and 4.70 and 9.00 for 0.10% and 0.20% CMC added pellets, respectively.

The compressive strengths results are shown graphically in Figure 6.16 for pellets produced with CMC binder and preheated at1000°C and 1300°C for 20 minutes.
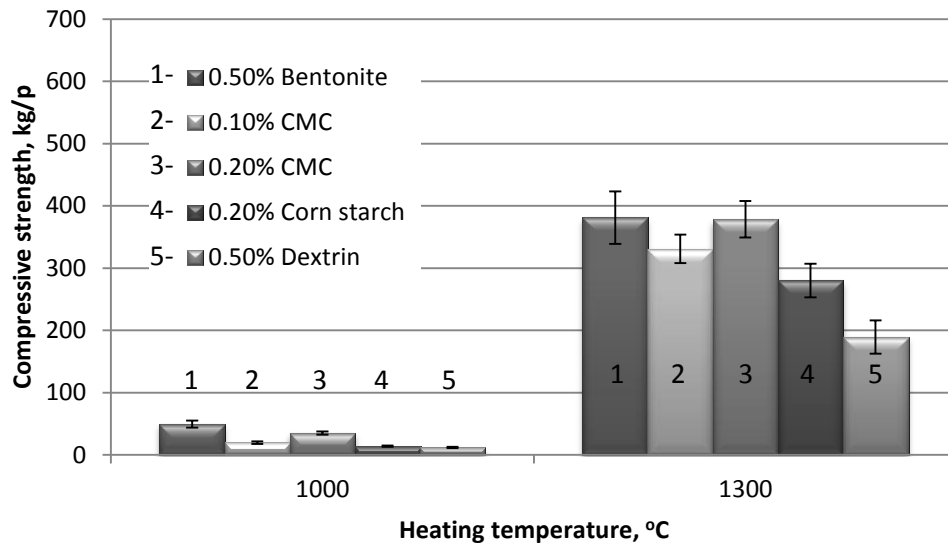
Figure 6. 16 Effect of addition of CMC, corn starch and dextrin organic binders on compressive strength of pellets preheated at 1000°C and fired at 1300°C for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strength of pellets produced with bentonite binder and preheated at 1000°C was found 49.60 kg/p and accepted as baseline value. The compressive strengths of pellets produced with organic binders are significantly lower than the baseline value of bentonite bonded pellets. They were determined between 11.90-35.00 kg/p which are not comparable to baseline compressive strength. These organic binders were found to not contribute to the preheated strength of hematite pellets. Therefore, the use of these organic binders causes much lower preheated pellet strength in hematite ore pelletizing.

When the fired compressive strengths of pellets observed, it can be seen that the baseline strength of fired pellets with bentonite addition is 381.10 kg/p and the others

produced with organic binders are between 189.30 - 378.50 kg/p. Only CMC bonded pellets resulted in with comparable strengths (330.90 - 378.50 kg/p) to the baseline value. Corn starch and dextrin were found to decrease fired pellets' strength significantly. Moreover, the pellets contain 0.50% dextrin has merely 189.30 kg/p which is also lower than the industrially required fired pellet strength which is 250 kg/p.

6.3.1.2 Effect of DPEP06-0007 polymer, Superfloc® A-150LMW and HMW addition on compressive strength of pellets

DPEP06-0007 polymer, Superfloc® A-150LMW and HMW organic based chemicals were tested as agglomeration aid binders for hematite ore using at addition levels of 0.10%, 0.05% and 0.005%, respectively. In order to see the performances of these chemicals as binder on quality of hematite pellets, baseline values were set up with bentonite binder on hematite pellets. The pelletizing and test methods to form and to determine the quality of pellets are same as explained previously.

The results obtained by using the organic based chemicals were compared with the baselines obtained with bentonite binder. The compressive strengths of thermally treated pellets are given in the Table 6.15. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 15 Effect of addition of DPEP06-0007 polymer, Superfloc® A-150LMW and HMW organic binders on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
2	0.10% DPEP06-0007 Polymer	9.61	10.00±0.33	---	---	20.50 ±2.27	287.50 ±29.60±
3	0.05% Superfloc A-150LMW	9.43	3.00 ±0.00	---	---	5.90 ±0.68	191.30 ±18.09
4	0.005% Superfloc A-150HMW	7.40	2.00 ±0.00	---	---	13.30 ±1.43	210.50 ±27.24

The moisture contents of wet pellets were found to be 9.61% and 9.43% by DPEP06-0007 polymer and Superfloc® A-150LMW, respectively. The wet pellets had only 7.40% moisture when Superfloc® A-150HMW was used. The former two addition levels are considered sufficient when the moisture contents compared with the moisture content of bentonite bonded pellets. On the other hand, the latter can be said insufficient and the addition level should be increased to increase moisture content.

Sufficient drop number was obtained by using DPEP06-0007 polymer. This drop number was found to be 10.00 which is about triple the baseline drop number which is 3.40. However, both Superfloc® additions did not yield enough drop number with these addition levels. In order to get a sufficient drop number, the addition level of these binders should be increased.

The compressive strengths results are shown graphically in Figure 6.17 for pellets produced with DPEP06-0007 polymer, Superfloc® A-150LMW and HMW binders and preheated at 1000°C and 1300°C for 20 minutes.
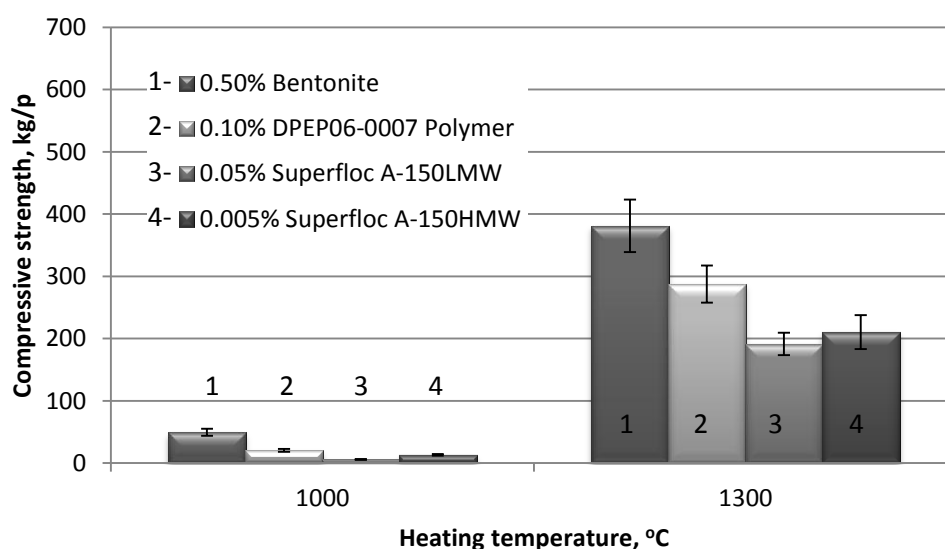
Figure 6. 17 Effect of addition of DPEP06-0007 polymer, Superfloc® A-150LMW and HMW organic binders on compressive strength of pellets preheated at 1000°C and fired at 1300°C for 20 minutes. The error bars show the 95% confidence level (P95)

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The compressive strengths of pellets produced with organic based chemicals were found to be drastically lower than the bentonite bonded pellets' baseline value. They were determined between 5.90-20.50 kg/p which are not comparable to baseline compressive strength which is 49.60 kg/p. These organic based chemicals were found to decrease the preheated strength of hematite pellets. Therefore, in the case of using these organic based chemicals will be harmful in respect to preheated strength.

As seen from the Figure 6.17, the fired compressive strengths of pellets produced with organic based chemicals are much lower than the fired baseline strength. Only DPEP06-0007 polymer bonded pellets resulted in with 287.50 kg/p which is lower than the baseline, however it is about the industrially required value, 250 kg/p. The other two strengths (191.30 and 210.50 kg/p) cannot be compared to the baseline value and much lower than the industrial fired compressive strength.

6.3.2 Effect of boron compounds on compressive strength of pellets

Organic binders; CMC, corn starch and organic based polymer; DPEP06-0007 are found to give sufficient drop number to wet pellets, however they failed to provide sufficient compressive strength to the preheated and fired pellets. Therefore, in order to get adequate or improved preheated and fired pellet strengths, the same boron compounds (boric acid, borax pentahydrate and colemanite) excluding tincal tested for Divriği magnetite concentrate were also tested as binder or strength improving additives in hematite ore pelletizing. Tincal is eliminated since it did not perform as good as other boron compounds.

Boron compounds were added to the dry Brazilian hematite ore at proper addition levels which are found to be the most appropriate dosage for Divriği magnetite concentrate. Boron compounds were used after a grinding process in mill or mortar to get suitable particle size distribution for balling. Colemanite mineral was used after a process of calcination in order to prevent from decrepitation of colemanite during thermal treatment, since it has chemically bonded water in its structure.

The performances of these boron compounds on pellet quality were determined and compared to the baselines obtained with bentonite binder. The results are given in the following subtitles.

6.3.2.1 Effect of boric acid, borax pentahydrate and calcined colemanite addition on compressive strength of pellets

Boric acid, borax pentahydrate and calcined colemanite were tested as strength improving additives in hematite ore pellets. To see the effect of these boron compounds as strength improving additives on pellet strength they were used alone at addition level of 0.50% which is found suitable dosage for magnetite pellets. The pelletizing and test methods to form and to determine the quality of pellets are same as explained previously.

The results obtained by using the boron compounds were compared with the baselines obtained with bentonite binder. A pelletizing experiment was also carried out without binder to show the effect of bentonite binder and boron compounds on pellet quality. The compressive strengths of thermally treated pellets are given in the Table 6.16. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 16 Effect of boric acid, borax pentahydrate and calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	Without binder	6.90	2.20 ±0.26	---	---	19.00 ±1.27	253.50 ±30.01
2	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
3	0.50% Boric acid	8.00	2.60 ±0.32	---	---	113.70 ±8.93	460.90 ±29.67
4	0.50% Borax pentahydrate	7.22	2.50 ±0.33	2.00 ±0.00	2.00 ±0.00	119.40 ±13.18	536.50 ±56.27
5	0.50% Calcined colemanite	7.34	2.50 ±0.33	---	---	116.10 ±5.71	602.00 ±54.80

The moisture contents of pellets with borax pentahydrate and calcined colemanite addition are 7.22% and 7.34% which are between the moisture content 6.90% of

pellets without binder and moisture content of 7.50 with bentonite binder. Only boric acid containing pellets have a little higher moisture content that is 8.00%.

However, none of the boron compounds addition can yield sufficient drop number to the wet pellets. All pellets produced with any boron compounds had about 2.50 drop numbers which is than the baseline value of 3.40 with bentonite.

The results of compressive strengths are shown graphically in Figure 6.18 for pellets produced with boric acid, borax pentahydrate and calcined colemanite addition and preheated at1000°C and 1300°C for 20 minutes.
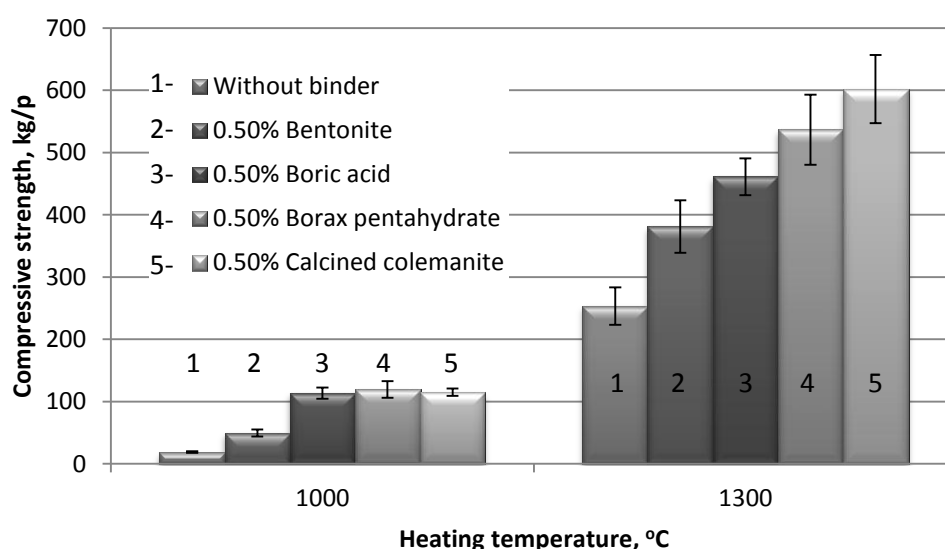
Figure 6. 18 Effect of boric acid, borax pentahydrate and calcined colemanite addition on compressive strength of pellets preheated at 1000°C and fired at 1300°C for 20 minutes. The error bars show the 95% confidence level (P95)

The compressive strengths of preheated pellets at 1000°C produced without binder was merely 19.00 kg/p, showing that hematite pellets cannot become strong enough without a good binder. On the other hand, bentonite binder can increase the preheated compressive strength to 49.60 kg/p. Furthermore, this strength was improved by the addition of boron compounds. Preheated compressive strengths were found to be 113.70, 119.40 and 116.10 kg/p with the addition of 0.50% boric

acid, borax pentahydrate and calcined colemanite, respectively. They are significantly higher than 49.60 kg/p of baseline strength for bentonite bonded pellet. It is believed that boron compounds make the preheated pellets stronger through physical melting and binding the iron oxide grains at the surface.

The fired pellet strength was found to be 253.50 kg/p without binder and 381.10 kg/p with 0.50% bentonite added pellets. The contributions of boron compounds addition on strength increase for fired pellets at $1300^{o}C$ were found more pronounced. Since the strengths were increased to 460.90, 536.50 and 602.00 kg/p with the addition of 0.50% boric acid, borax pentahydrate and calcined colemanite, respectively. They are notably higher than that of 381.10 kg/p which is accepted as baseline with bentonite addition. The higher compressive strengths of fires pellets at $1300^{o}C$ contain any boron compounds are due to complete melting of the boron compounds at this elevated firing temperature. Since the boron compounds melted completely, they could bind the iron oxide grains well (see title 6.5.3 for micro image of fired pellets)

6.3.2.2   Effect of calcined colemanite dosage on compressive strength of pellets

Although all boron compounds provided sufficient and improved strength for both preheated and fired hematite pellets, colemanite was selected for further pelletizing experiments, since it is a natural and abundant mineral in Turkey. The effects of calcined colemanite dosage on compressive strength of pellets were investigated in detail and the results are given below.

Since the remarkable preheated and fired pellet compressive strength increase was obtained with addition of boron compounds, an optimum addition level should be determined. As all boron compounds were found to give about same strength increase to hematite pellets, it is advantageous to use a natural mineral than other processed compounds. Therefore, colemanite was selected to specify an optimum dosage since it is a natural mineral and moreover it is abundant in Turkey. Further experiments were carried out to determine an optimum calcined colemanite dosage. Four addition levels ranging from 0.25% to 1.00% were tested to see the effect of dosage on compressive strength of pellets.

Pelletizing and pellet quality tests were carried out with the methods as explained for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.17. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 17 Effect of calcined colemanite dosage on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
2	0.25% Calcined colemanite	7.24	2.30 ±0.30	---	---	83.90±7.49	478.90±44.70
3	0.50% Calcined colemanite	7.34	2.50 ±0.33	---	---	116.10±5.71	602.00±54.80
4	0.75% Calcined colemanite	7.39	2.50 ±0.33	---	---	151.40±22.80	772.00±95.37
5	1.00% Calcined colemanite	7.74	2.50 ±0.33	---	---	219.30±18.11	893.60±76.80

Moisture contents of pellets were measured between 7.24% and 7.74% which three of them a little lower than the moisture content 7.50% of bentonite bonded baseline pellets.

However, results showed that increasing calcined colemanite dosage does not have positive effect on wet pellet drop number, since all pellets with increasing dosage resulted in with only a drop number about 2.50. This test results shows that calcined colemanite is not suitable to be used as binder alone due to insufficient drop number

The results of compressive strengths are shown graphically in Figure 6.19 for pellets produced with different dosages of calcined colemanite addition and preheated at1000ºC and 1300ºC for 20 minutes.

The compressive strengths of pellets preheated at 1000ºC were determined between 83.90 and 219.30kg/p which are markedly higher than the baseline value with bentonite; 49.60 kg/p. Furthermore, these values are also substantially higher than the ones obtained with organic binders alone. The strength increase is more

pronounced with increasing addition level of calcined colemanite from 0.25% to 1.00%. Therefore, compressive strengths of pellets preheated at 1000°C can be improved with addition of calcined colemanite. Since the 83.90 kg/p preheating strength is not high enough, 0.50% or higher dosage would be optimum rate for calcined colemanite addition into hematite pellets to produce sufficient strength.
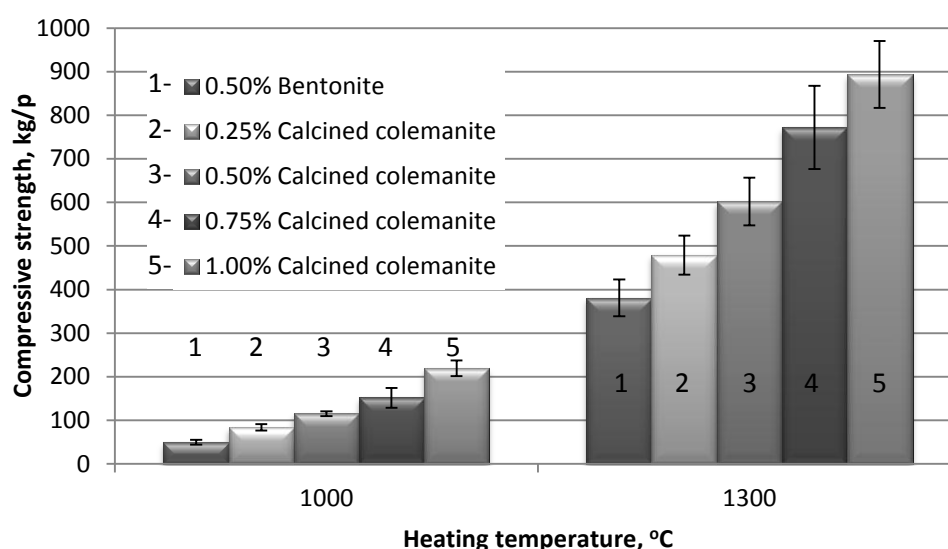
Figure 6. 19 Effect of calcined colemanite dosage on compressive strength of pellets preheated at 1000°C and fired at 1300°C for 20 minutes. The error bars show the 95% confidence level (P95).

The compressive strengths of pellets fired at 1300°C were determined between 478.90 - 893.60 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. All the compressive strengths of fired pellets, produced with 0.50% or higher addition level of calcined colemanite, were notably higher than that of baseline with bentonite which is 381.10 kg/p. At this temperature gradually strength increase observed for preheated pellets gives place to a sharply strength increase for fired pellets. Such that, these fired pellets strengths are unnecessarily higher than the industrially minimum required strength which is 250 kg/p. Therefore, it can be suggested either to lower the dosage of calcined colemanite or to lower the firing temperature of hematite pellets to get reasonable high fired pellet strength. The first offer is not plausible; since the lower calcined colemanite dosage would not increase

the preheating strength to a sufficient value. So the second offer is the only way to implement the target. Lower firing temperature can also decrease energy consumption of firing unit of pelletizing plant.

6.3.3 Effect of calcined colemanite added organic binders on compressive strength of pellets

The findings showed that neither organic binders nor calcined colemanite can be used alone as binders in the pelletizing of Brazilian hematite ore. Whilst calcined colemanite falls short of the wet pellet quality, organic binders fail to meet the preheated and fired pellet strengths. Therefore, combination of an organic binder and calcined colemanite; CMC plus calcined colemanite, corn starch plus calcined colemanite and DPEP06-0007 polymer plus calcined colemanite were tested to produce pellets with sufficient wet, preheated and fired pellet strength. The addition levels of CMC, corn starch and DPEP06-0007 polymer were kept constant at 0.10% by weight of dry hematite ore. Calcined colemanite addition levels mixed to organic binders were ranged from 0.25% to 1.00% by weight of dry hematite ore.

The performances of these organic binders together with calcined colemanite on pellet quality were determined and compared with the baselines with bentonite binder. The results are given in the following subtitles, respectively.

6.3.3.1 Effect of CMC plus calcined colemanite on compressive strength of pellets

CMC and calcined colemanite were used together as combined binder to get sufficient wet, preheated and fired hematite pellet strengths. While the addition level of CMC was constant at 0.10%, four different calcined colemanite addition levels ranging from 0.25% to 1.00% were tested.

Pelletizing experiments were carried out in the same way as explained before for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.18. The results of compressive

strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 18 Effect of CMC plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
2	0.10% CMC + 0.25% Cal.col.	8.57	4.20 ±0.44	---	---	81.60 ±4.56	448.80 ±37.49
3	0.10% CMC + 0.50% Cal.col.	8.53	4.00 ±0.41	---	---	121.00 ±10.37	535.10 ±48.68
4	0.10% CMC + 0.75% Cal.col.	8.78	4.10 ±0.39	---	---	156.20 ±14.27	664.70 ±62.84
5	0.10% CMC + 1.00% Cal.col.	8.66	4.00 ±0.41	---	---	199.80 ±21.27	841.10 ±77.10

Moisture contents of pellets were measured between 8.53% and 8.78% which are almost 1.00% greater than the moisture content of baseline pellets which is 7.50%.

All combined binders yielded drop numbers about 4.00 which are higher than the 3.40 and they are surely considered to be sufficient drop numbers for wet hematite pellets in this study. The CMC addition recovered the low drop numbers (only 2.50) with addition of calcined colemanite alone.

The results of compressive strengths are shown graphically in Figure 6.20 for pellets produced with 0.10% CMC plus different dosages of calcined colemanite addition and preheated at1000ºC and 1300ºC for 20 minutes.

When the preheated pellet strengths are examined, the contribution of calcined colemanite addition on compressive strength increase can easily be seen from the Figure 6.20. The presence of calcined colemanite seems definitely to impart strength to the hematite pellet by developing slag bonds. The preheated pellet strengths were steadily increased from 81.60 kg/p to 199.80 kg/p by addition of calcined colemanite of 0.25% and 1.00%, respectively. These strengths are higher than the baseline preheating strength and almost same to those of obtained with only calcined colemanite addition. Therefore, it can be said that the addition of CMC together with

calcined colemanite does not have an adverse effect on preheating strength of hematite pellets which improved by calcined colemanite addition.
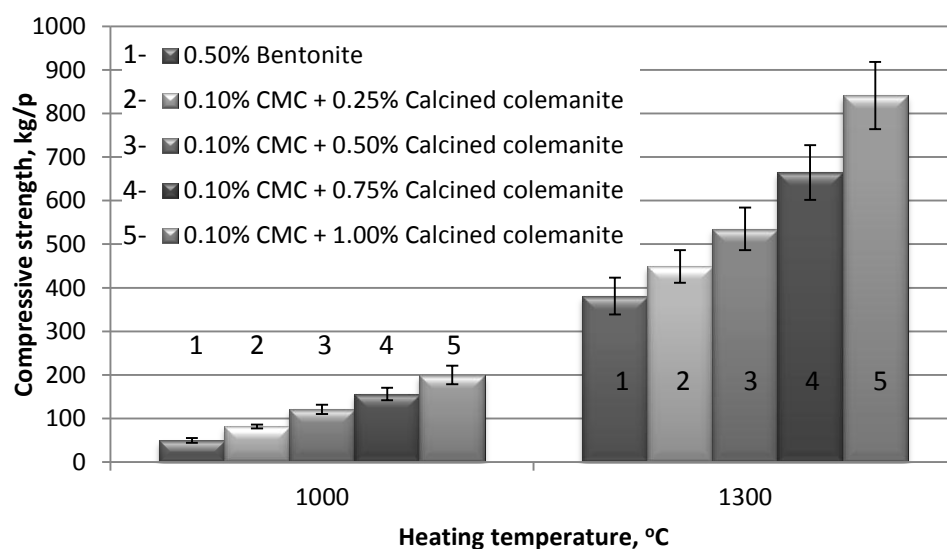
Figure 6. 20 Effect of CMC plus calcined colemanite addition on compressive strength of pellets preheated at 1000°C and fired at 1300°C for 20 minutes. The error bars show the 95% confidence level (P95)

The same sharp increase in fired pellet compressive strength is valid for also CMC and calcined colemanite combination. The compressive strengths of pellets fired at 1300°C were ranged between 448.80 - 841.10 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. All these fired pellet compressive strengths are much greater than the baseline fired strength value; 381.10 kg/p.

These results showed that CMC and calcined colemanite provide sufficient strength to the pellet at all conditions; wet, preheated and fired. Moreover, quite high fired pellet strengths encourage testing lower firing temperature for hematite pelletizing.

6.3.3.2 Effect of corn starch plus calcined colemanite on compressive strength of pellets

Corn starch and calcined colemanite were used together as combined binder to get

sufficient wet, preheated and fired hematite pellet strengths. While the addition level of corn starch was constant at 0.10%, four different calcined colemanite addition levels ranging from 0.25% to 1.00% were tested.

Pelletizing experiments were carried out in the same way as explained before for previous experiments. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.19. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 19 Effect of corn starch plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
2	0.10% Corn S.+ 0.25% Cal.col.	8.86	3.60 ±0.29	---	---	92.30 ±6.21	446.30 ±43.98
3	0.10% Corn S.+ 0.50% Cal.col.	8.64	3.20 ±0.26	---	---	118.20 ±5.61	512.20 ±68.03
4	0.10% Corn S.+ 0.75% Cal.col.	8.88	3.80 ±0.28	---	---	150.20 ±12.67	611.80 ±69.74
5	0.10% Corn S + 0.50% Cal.col.	8.78	4.00 ±0.00	---	---	217.80 ±16.71	736.90 ±86.57

Moisture contents of pellets were measured between 8.64% and 8.88% which are more than 1.00% higher than the 7.50% moisture content of baseline pellets produced with bentonite binder.

In the presence of corn starch the relatively low drop numbers previously obtained with wet pellets produced with only calcined colemanite addition was improved. Corn starch and calcined colemanite combination yielded drop numbers about the same or greater than the 3.40 and they are sufficient when compared with this baseline drop number value. Corn starch addition improved the drop numbers this why the wet bonding properties of corn starch. Hence, it can be said that the use of corn starch together with calcined colemanite is possible to increase wet pellet drop numbers.

The results of compressive strengths are shown graphically in Figure 6.21 for pellets produced with 0.10% corn starch plus different dosages of calcined colemanite addition and preheated at $1000^{o}C$ and $1300^{o}C$ for 20 minutes.
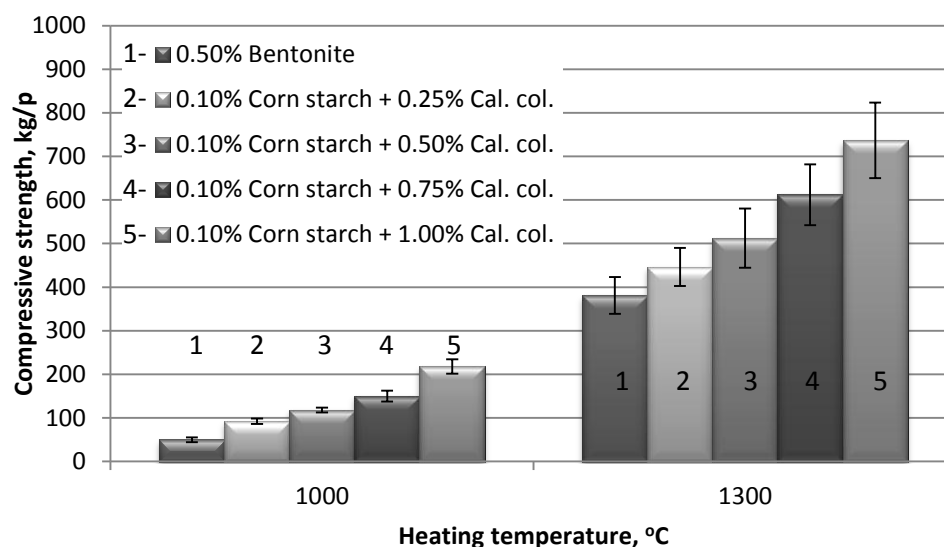
Figure 6. 21 Effect of corn starch plus calcined colemanite addition on compressive strength of pellets preheated at $1000^{o}C$ and fired at $1300^{o}C$ for 20 minutes. The error bars show the 95% confidence level (P95)

A similar progressively strength increase for preheated pellets can be seen from the Figure 6.21. The strength was increased from 49.60 kg/p to 92.30 kg/p with 0.25% calcined colemanite addition and reached to 217.80 kg/p with 1.00% calcined colemanite addition. No adverse effect of corn starch addition was detected on improved preheating pellet strength with addition of calcined colemanite.

When the pellets are fired at $1300^{o}C$ the compressive strengths of pellets produced with corn starch and calcined colemanite combination became significantly high. They were measured between 446.30kg/p and 736.90 kg/p which are greater than the baseline value with bentonite bonded pellets.

These results showed that corn starch can be used together with calcined colemanite to provide sufficient strength to the wet pellets. The results of preheated and fired

pellets strengths indicated that the addition of corn starch does not have undesirable effect on strength increase.

6.3.3.3 Effect of DPEP06-0007 polymer plus calcined colemanite on compressive strength of pellets

The last combination binder tested to get sufficient wet, preheated and fired hematite pellet strengths is DPEP06-0007 polymer and calcined colemanite. Since DPEP06-0007 polymer yielded significantly high drop numbers to wet hematite pellets when used at 0.10% by weight of the dry hematite ore. This addition level of DPEP06-0007 polymer was kept constant at 0.10% and four different calcined colemanite additions ranging from 0.25% to 1.00% were added to prepare combined binder.

Pelletizing experiments were carried out using the same methods as explained before for previous tests. The compressive strengths of thermally treated pellets were determined and the results are given in the Table 6.20. The results of compressive strength for these pellets were compared with the baseline obtained with bentonite binder. Table also shows the moisture content and drop numbers of wet pellets.

Table 6. 20 Effect of DPEP06-0007 polymer plus calcined colemanite addition on compressive strength of pellets thermally treated at different temperatures for 20 minutes

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Dry @ 105ºC	Dry @ 400ºC	Preheat @ 1000ºC	Fired @ 1300ºC
1	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	2.80 ±0.26	2.70 ±0.30	49.60 ±5.63	381.10 ±42.25
2	0.10% DPEP + 0.25% Cal.col.	8.47	8.00±0.67	---	---	85.70 ±6.90	414.80 ±40.55
3	0.10% DPEP + 0.50% Cal.col.	8.86	8.50±0.73	---	---	127.50 ±11.98	457.70 ±51.86
4	0.10% DPEP + 0.75% Cal.col.	9.10	8.20±0.58	---	---	144.70 ±12.95	652.40 ±65.46
5	0.10% DPEP + 0.50% Cal.col.	9.47	9.00±0.51	---	---	173.80 ±14.25	789.70 ±86.88

Moisture contents of pellets were measured between 8.47% and 9.10% which are considerably greater than the moisture content of baseline which is 7.50% of bentonite bonded pellets.

All combined binders yielded drop numbers about 8.00 which are more than double the baseline drop number and they are the highest drop numbers obtained with using combination binders for wet hematite pellets in this study.

The compressive strengths' results are shown graphically in Figure 6.22 for pellets produced with 0.10% DPEP06-0007 polymer plus different dosages of calcined colemanite addition and preheated at1000^{o}C and 1300°C for 20 minutes.
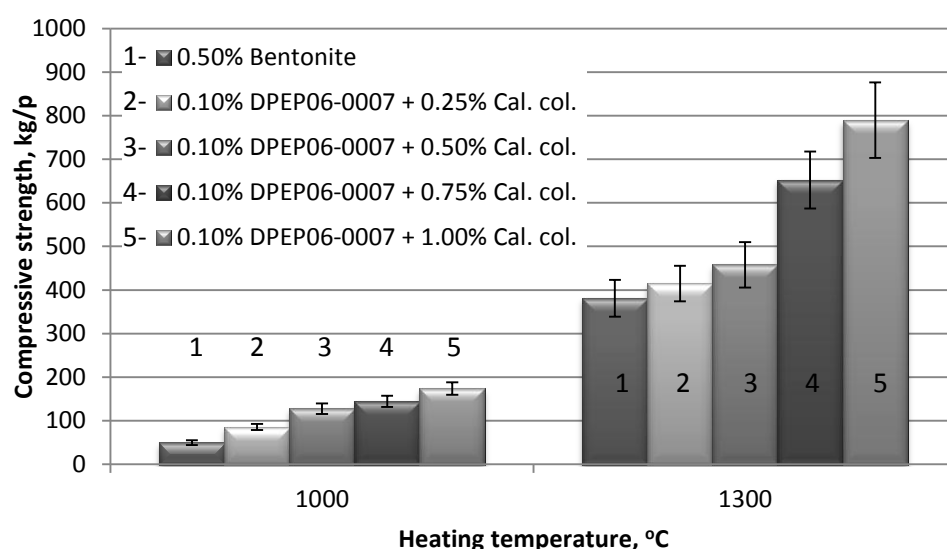
Figure 6. 22 Effect of DPEP06-0007 polymer plus calcined colemanite addition on compressive strength of pellets preheated at 1000°C and fired at 1300°C for 20 minutes. The error bars show the 95% confidence level (P95).

Figure 6.22 shows that the contribution of calcined colemanite addition on preheated pellet strength is increasing when the addition level is increased. The presence of calcined colemanite seems definitely to impart strength to the hematite pellet by developing slag bonds. Since the preheating compressive strength was only 49.60 kg/p for bentonite bonded pellet, however this is increased to 127.50 and 173.80 kg/p with addition of 0.50% and 1.00% calcined colemanite addition, respectively. These strengths are not only higher than the baseline preheating strength but also almost same to those of obtained with only calcined colemanite addition and much greater than the strengths obtained through only organic binders addition. Hence, it obvious

that the addition of DPEP06-0007 polymer to recover the wet pellet properties does not decrease preheating strength of hematite pellets when used together with calcined colemanite.

When the fired pellet strengths are examined for this combined binder, it can be seen that the sharp increase on fired pellets strength is similar to those obtained for the former combined binders. The compressive strengths of pellets fired at 1300°C were ranged between 414.80-789.70 kg/p with 0.25% and 1.00% calcined colemanite addition, respectively. All these fired pellet compressive strengths are much greater than the baseline fired strength value; 381.10 kg/p.

These results showed that DPEP06-0007 polymer plus calcined colemanite provide sufficient strength to the pellet at all conditions; wet, preheated and fired. Moreover, quite high fired pellet strengths encourage testing lower firing temperature for hematite pelletizing.

6.3.4 Effect of lower firing temperature and reduced bentonite plus calcined colemanite binder dosage on compressive strength of pellets

In the light of the results obtained for pelletizing of Brazilian hematite ore, the lower firing temperature may be tested, since the fired pellet compressive strengths were found much higher than the industrially required minimum strength limit which is 250 kg/p for fired pellet. Especially the fired pellet strengths were found to reach 900 kg/p with addition of calcined colemanite.

Therefore, lower firing temperatures; 1000, 1100, 1200 and 1300°C were tested by using boric acid addition and calcined colemanite addition on fired pellet compressive strength increase. In these pelletizing experiments, besides lower firing temperature, the combinations of bentonite and calcined colemanite were tested. However, bentonite addition levels were reduced at this time to see also the effect of reduced bentonite addition levels. Boric acid was tested at 0.50% alone and combinations of bentonite and calcined colemanite were tested; 0.25% bentonite was mixed with 0.50% and 1.00% calcined colemanite separately.

The compressive strengths of thermally treated pellets at lower firing temperatures were determined and the results are given in the Table 6.21. The results of compressive strength for these pellets were compared with the baselines obtained with bentonite binder. Besides bentonite baselines, previous experiments results acquired with the lowest addition levels of calcined colemanite are also given in the table for comparison. Table also shows the moisture content and drop numbers of wet pellets so produced.

The moisture content of wet pellets is low for pellets produced with only calcined colemanite addition. However the moisture contents of others are almost higher than that of bentonite bonded baseline pellets when only 0.25% bentonite is used together with 0.50% or 1.00% calcined colemanite.

Table 6. 21 Effect of lower firing temperatures on compressive strength of pellets thermally treated at 1000, 1100, 1200 and 1300°C for 20 minutes. Boric acid and reduced rate of bentonite plus calcined colemanite were used as binder

Binder codes	Binder and dosages	Moisture content %	Wet drop number	Mean compressive strengths (kg/p with ±P95)			
				Heated @ 1000°C	Heated @ 1100°C	Heated @ 1200°C	Heated @ 1300°C
1	0.50% Bentonite (Baseline)	7.50	3.40 ±0.32	49.60 ±5.63	---	---	381.10 ±42.25
2	0.25% Calcined colemanite	7.24	2.30 ±0.30	83.90 ±7.49	---	---	478.90 ±44.70
3	0.50% Boric acid	8.00	2.60 ±0.32	113.70 ±8.93	207.60 ±18.37	330.90 ±22.28	460.90 ±29.67
4	0.25% Ben. + 0.50% Cal. col.	8.58	3.50 ±0.32	141.40 ±13.95	234.50 ±26.19	420.00 ±33.35	589.00 ±49.20
5	0.25% Ben. + 1.00% Cal. col.	8.18	3.40 ±0.32	179.40 ±13.61	240.40 ±23.55	445.50 ±42.35	634.80 ±43.94

The drop numbers of pellets produced with calcined colemanite or boric acid alone are insufficient. The addition of 0.25% bentonite improved the drop numbers obtained with only calcined colemanite addition. Drop numbers of combined binders are exactly the same as the baseline drop numbers with bentonite. This result shows that the reduced amount of bentonite may recover the inadequate wet pellet drop numbers of only calcined colemanite containing pellets.
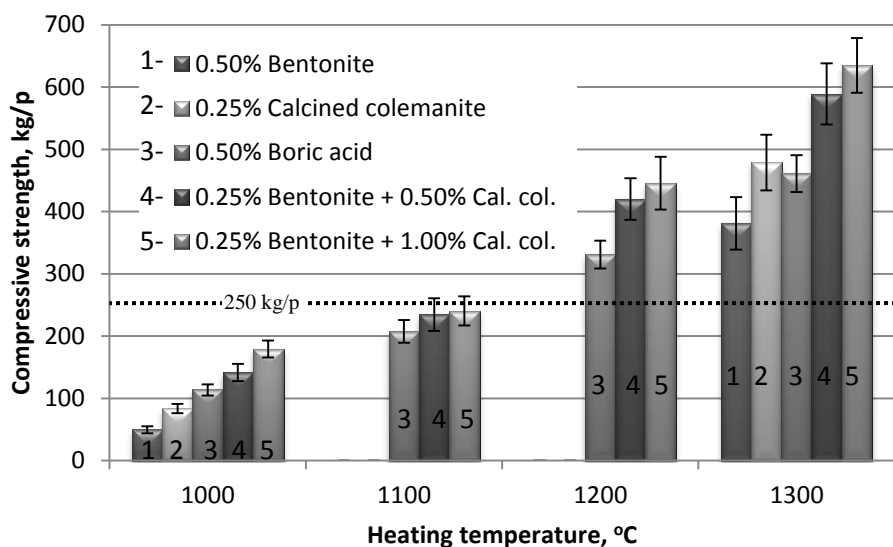
Figure 6. 23 Effect of lower firing temperatures on compressive strength of pellets thermally treated at 1000, 1100, 1200 and 1300°C for 20 minutes. Boric acid and reduced rate of bentonite plus calcined colemanite were used as binder. The error bars show the 95% confidence level (P95). Dashed line shows 250 kg/p which is the industrially required minimum compressive strength limit for fired pellets

The compressive strengths of pellets heated at different temperatures lower than 1300°C can be seen in Figure 6.23. They progressively increased when the heating temperature or addition level of binders are increased. The pellets heated at 1000°C and produced with 0.50% boric acid has 113.70 kg/p and pellets with lessened addition levels of bentonite and calcined colemanite have 141.40 and 179 40 kg/p which are significantly higher than 49.60 kg/p belongs to bentonite bonded baseline pellets at 1000°C. These strengths are of course much higher than the strengths obtained without binder or organic binders alone.

When the temperature was increased to 1100°C, strengths of boric acid containing pellets were increased to 207.60 kg/p and the others to 234.50 and 240.40 kg/p which are almost sufficient in point of industrially required limit which is 250 kg/p. A dashed line indicating that limit was drawn in Figure 6.23 to compare the results easily.

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On the other hand, when the temperature was increased to 1200°C, strengths became 330.90 for boric acid containing pellets and 420.00 and 445.50 kg/p for the others, respectively. Now these pellets are unquestionably strong enough since they meet the minimum strength limit. These results indicate that the low temperature i.e. 1200°C can be employed to get sufficient fired hematite pellet strength. Moreover, it can be concluded that the minimum temperature to provide the minimum required strength limit for fired pellet is at somewhere a little over 1100°C. This results are so significant because lowering of firing unit of pelletizing plant will lead to energy saving.

The compressive strengths of all hematite pellets fired at 1300°C are without doubt higher than the limit and much greater than the strength value of the baseline pellets.

6.4 Pelletizing experiment with Lake Superior District magnetite concentrate

This part of the experimental study of the thesis was carried out in the Michigan Technological University Chemical Engineering department Laboratories (MTUCEL).

The original size magnetite concentrate from a pelletizing plant located at the Lake Superior district, Michigan, USA was used in pelletizing experiments. The Blaine surface area of this iron oxide was 2212 ±38 cm^2/g and specific gravity was determined to be 4.64. Particle size distribution of this sample is given in Figure 5.6 shows that P$_{100}$: 62.23 μm, P$_{80}$:27.60 μm and 96.53% of the particles is smaller than 44 μm (325 mesh).

All pelletizing experiments were carried out separately at least three times to ensure reproducibility of experiments. In each pellet batch, 20 randomly selected pellets were tested to determine pellet quality, indicated by the mean value and calculated 95% confidence interval (P95). Results of the pelletizing experiment tests (moisture contents and drop numbers of wet pellets, dry and thermally treated pellet compressive strengths) are given in the following sections.

6.4.1 Effect of different binders on moisture contents and drop numbers of wet pellet

To compare the performance of the alternative organic binders and boron compounds added organic binders to bentonite binders, the pelletization experiments were started without binder, with 0.66% Lake Superior bentonite (from a pelletizing plant located at Lake Superior district) and 0.66% Reşadiye bentonite additions, to set up baseline values with bentonite binder. In these pelletizing experiments about 2500 g moist Lake Superior magnetite concentrate was used as iron oxide.

Calcined colemanite 0.66%, technical grade CMC 0.10%, DPEP06-0007 Polymer 0.10% and Superfloc$^{®}$ A150-LMW 0.10% were tested alone as alternative binder. These organic binders, 0.10% addition level, were also tested together with 0.66% calcined colemanite to see the combined effect of binders on pellet quality.

Wet pellets are produced in pelletizing drum and then dried at 105°C to determine moisture content and to get dry pellets. Wet pellet drop numbers and compressive strengths were determined before wet pellet moisture content determination.

Wet pellet moisture content (WPMC) values obtained with alternative binders alone and in combination are shown in Table 6.22 and graphically presented in Figure 6.24. The tested binders are coded in the first column of Table 6.22 and these codes are used to refer the binder names and dosages in the following Figures 26-27.

WPMCs varied from 8.38 to 10.22%. The smallest WPMC was found to be 8.38% for the pellets produced without binder (code 1). The WPMCs of pellets made with bentonite samples are 8.53% and 8.44% (codes 2 and 3). The WPMC produced with only calcined colemanite is 8.52 (code 4) -about the same as bentonite bonded pellets. However, the WPMCs are greater for the pellets contain organic binders (codes 5-10). The value increased up to 10.22% for the pellets produced with CMC plus calcined colemanite addition. The water absorption capacity of the organic based binders can be shown to be the reason of relatively high WPMCs obtained with organic binder use.

Table 6. 22 Results of the pelletizing experiments with Lake Superior district magnetite concentrate

Binder Codes	Binder Name and Dosages	Moisture Content %	Wet Drop Number from 46 cm	Mean compressive strengths (kg/p with ±P95)						
				Wet	Dry @ 105ºC	Heated @ 800ºC	Heated @ 1000ºC	Heated @ 1100ºC	Heated @ 1200ºC	Heated @ 1300ºC
1	No binder	8.38	3.17 ±0.23	1.92 ±0.14	1.35 ±0.07	30.08 ±1.54	48.28 ±2.93	77.45 ±5.76	402.60 ±23.90	643.25 ±32.79
2	Lake Superior bentonite, 0.66%	8.53	4.40 ±0.32	2.36 ±0.12	5.51 ±0.33	40.61 ±2.00	72.94 ±4.76	109.65 ±6.44	468.45 ±17.60	842.25 ±38.56
3	Reşadiye bentonite, 0.66%	8.44	4.27 ±0.33	2.52 ±0.13	6.37 ±0.38	55.05 ±3.65	98.77 ±5.45	138.94 ±10.46	558.00 ±19.59	854.65 ±41.72
4	Calcined colemanite, 0.66%	8.52	3.21 ±0.22	1.92 ±0.15	1.90 ±0.14	23.84 ±1.65	123.89 ±10.18	280.80±14.55	699.00 ±28.74	1072.10 ±42.16
5	Technical CMC, 0.10%	10.06	27.25 ±0.81	1.87 ±0.11	5.94 ±0.49	18.48 ±1.09	29.88 ±1.94	49.40 ±3.35	301.60 ±20.66	670.45 ±27.97
6	DPEP06-0007 polymer, 0.10%	8.78	10.53 ±0.77	2.29 ±0.15	3.38 ±0.25	31.30 ±1.78	47.45 ±3.12	80.24 ±6.53	402.55 ±17.35	741.50 ±35.11
7	Superfloc A150-LMW, 0.10%	9.43	18.88 ±0.87	2.20 ±0.15	4.51 ±0.31	30.24 ±2.53	43.50 ±2.36	69.10 ±4.35	368.40 ±21.75	770.55 ±37.16
8	Technical CMC, 0.10% + Calcined colemanite, 0.66%	10.22	22.33 ±0.93	1.89 ±0.09	2.89 ±0.22	16.90 ±1.01	94.95 ±7.34	254.40 ±11.47	440.50 ±23.17	903.15 ±32.70
9	DPEP06-0007 Polymer, 0.10% + Calcined colemanite, 0.66%	9.44	15.53 ±0.76	2.26 ±0.12	2.53 ±0.16	22.02 ±1.17	125.24 ±9.13	278.85 ±19.25	561.30 ±21.73	968.40 ±35.60
10	Superfloc A150-LMW, 0.10% + Calcined colemanite, 0.66%	10.14	13.18 ±0.70	1.74 ±0.11	1.99 ±0.11	20.49 ±0.98	119.82 ±8.25	275.00 ±16.03	525.15 ±23.46	958.25 ±32.49
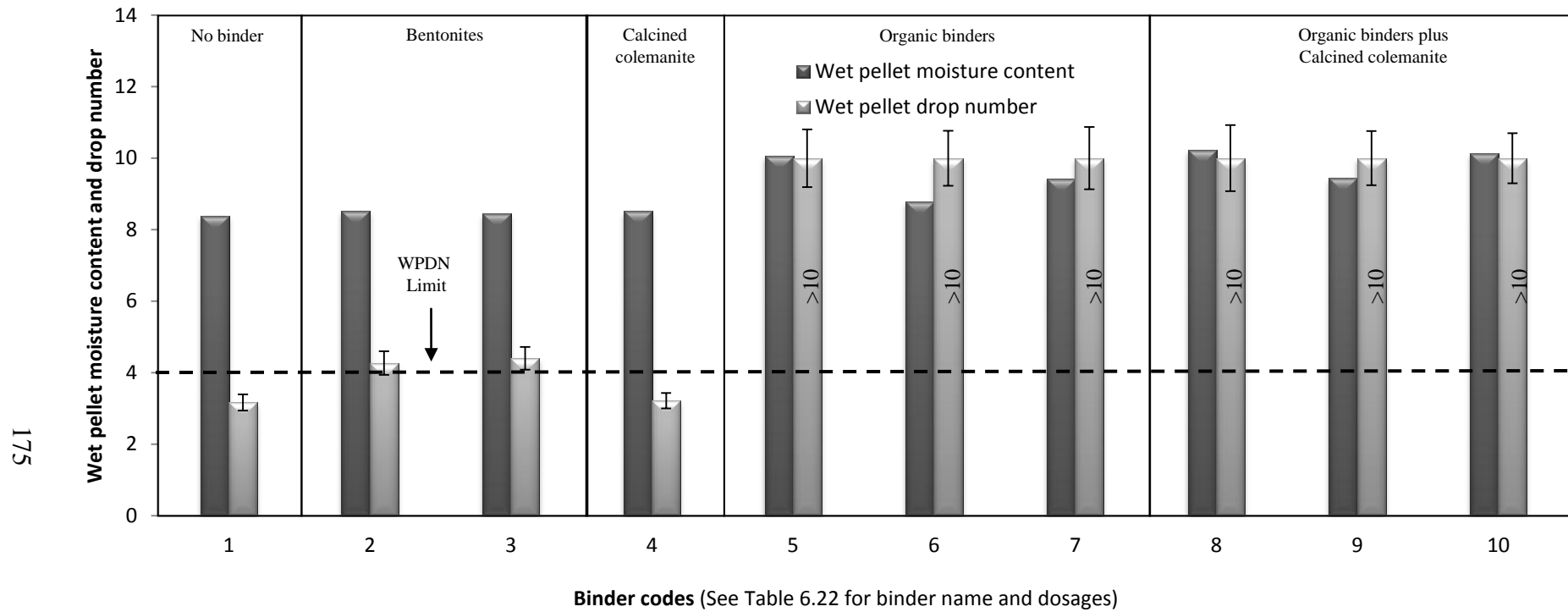
Figure 6. 24 Wet pellet moisture content (WPMC) and wet pellet drop numbers (WPDN) obtained with different binders. The error bars show the 95% confidence level (P95). Dashed line shows 4 which is the industrially accepted minimum drop number limit for wet pellets

Wet pellet drop numbers (WPDN) of the pellets can be seen in Table 6.22 and graphically drawn in Figure 6.24. According to experience, the industrially required minimum value should be at least 4 (Meyer, 1980) from a height of 45 cm (18 in.). The WPDNs obtained by using reference bentonite binders was found to be 4.27 and 4.40, which are slightly over the limit so they are sufficient. However, WPDN values for pellets made with no binder and with only calcined colemanite addition were determined to be 3.17 and 3.21, respectively, which are a little lower than the required value. Therefore, they can be considered insufficient and the production of pellets without binder or only with calcined colemanite addition seems impossible in terms of sufficient WPDN. The WPDNs produced with organic binders were found to be much greater (>10.00). It was concluded that these organic binders and tested dosages have increased the degree of plasticity of wet pellets with such a fine particle size (96.53% is smaller than 44μm) of magnetite concentrate. The wet pellets with high degree of plasticity are shown in Figure 6.25. These pellets were not fragile as much as other pellets produced with other binders since they were smashed after drop number test and wet compressive strength measurement.

If the plasticity of wet pellets is higher than normal range, the permeability of pellet bed in drying zone on travelling grate will be affected adversely. If they are not plastic enough, they will become fragile or will not have sufficient wet pellet strength to survive on travelling grate. Therefore optimum wet strength and plasticity is important and can be controlled by changing the addition dosage of binder during wet pellet formation. Hence, lower addition levels of these organic binders should be tested for this type of finely ground magnetite concentrates.

Figure 6. 25 Wet pellets with high degree of plasticity after drop number test and wet compressive strength measurement

6.4.2 Effect of different binders on wet and dry pellet compressive strengths

Wet and dry pellet compressive strengths of the pellets produced with different binder additions were determined.

Wet pellet compressive strengths (WPCS) values obtained with alternative organic binders alone and in combination with calcined colemanite are given in Table 6.22 and graphically shown in Figure 6.26. The compressive strength of wet pellets produced in industry usually lies between 1.0 and 2.0 kg (2.2 and 4.4 lbf) (Ball, *et al.,* 1973). Therefore, WPCS should be greater than 1 kg/p or 2.2 lbf to meet this specification. All WPCS of pellets were found to be greater than this required limit value. The sufficient WPCS is due to controlling of the wet strength mainly by the viscous forces of moisture/liquid.

Dry pellet compressive strengths (DPCS) are given in Table 6.22 and graphically shown in Figure 6.26 as well. In the induration process, a minimum dry strength of 2.2 kg or 5.0 lbf is essential in the critical phase of drying when the weight of bed of pellets is supported by the-just dry pellets (Ball, *et al.,* 1973). Hence, DPCS should be, at minimum, 2.2 kg/p or 5.0 lbf to withstand weight of the pellet bed. The DPCSs were found vary from 1.35 kg/p to 6.37 kg/p. The lowest value, determined as insufficient was for the pellets made with no binder (code 1). The second lowest, and insufficient, value was 1.90 kg/p for pellets bonded with only calcined colemanite (code 4). These results together with the insufficient WPDN of these pellets show that the production of pellets with sufficient wet and dry quality is impossible without binder or with only calcined colemanite addition. However, the DPCSs of pellets bonded with bentonite were found to be 5.51 kg/p and 6.37 kg/p (code 2 and 3). On the other hand, the DPCSs of pellets by organic binders found to be lower than those obtained by bentonite pellet but they are still greater than the minimum required limit. The DPCSs of pellets produced with combination binders (codes 8, 9 and 10) were found to be sufficient as well. However, the calcined colemanite addition decreased the DPCSs of these pellets when compared to values obtained using organic binders alone (codes 5, 6 and 7).

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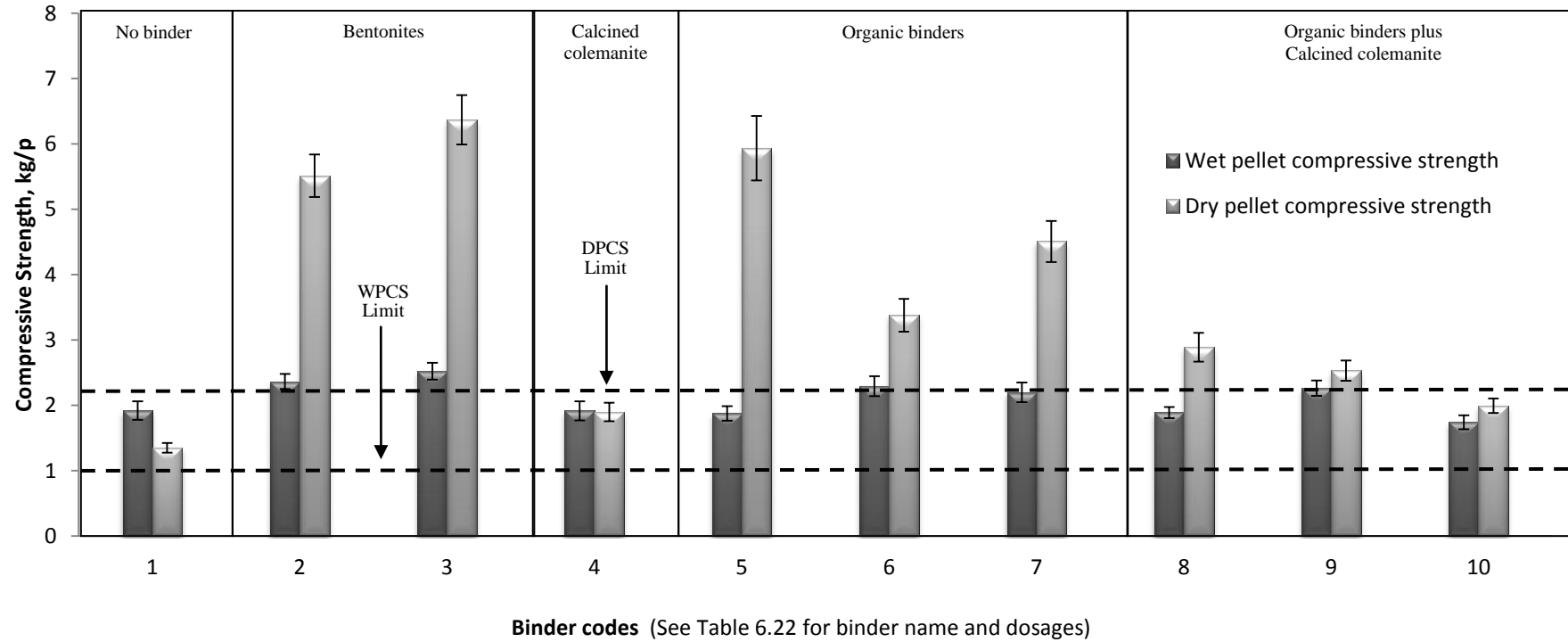
Figure 6. 26 Wet pellet compressive strengths (WPCS) and dry pellet compressive strengths (DPCS) obtained with different binders. The error bars show the 95% confidence level (P95). Dashed lines show 1 kg/p and 2.2 kg/p which are industrially required minimum compressive strength limit for wet and dry pellets, respectively.

6.4.3 Effect of different binders on preheated and fired pellet compressive strengths

Thermally treated pellet compressive strength can be divided in two parts: preheated and fired pellet strengths, since firing is accomplished by two stages: preheating and firing of pellets. Preheated pellet strength is particularly important for the thermal treatment of pellets with the travelling grate and rotary kiln induration system. The pellets must have a sufficient strength while cascading from the travelling grate to the rotary kiln. If the strength is insufficient, pellet chip and dust will form and both pellet quality and operation efficiency will be affected adversely. To show the effect of the different binders on the thermally treated pellet strength, dry pellets were heated at different temperatures namely, 800-1000-1100-1200 and 1300°C for 30 minutes in a box furnace. The compressive strengths of thermally treated pellets were determined.

The compressive strength values obtained with alternative binders alone and in combination are tabulated in Table 6.22 and graphically shown in Figure 6.27. The compressive strengths of pellets are increasing with the increasing temperatures.

When the compressive strength of pellets heated at 800°C are examined we can see that the compressive strengths of pellets made without binder is 30.08 kg/p (code 1) and with organic binders 18.48, 31.30 and 30.24 kg/p (codes 5, 6 and 7, respectively). They are lower than the 40.61 and 55.05 kg/p obtained with reference pellets with bentonite binders (codes 2 and 3, respectively). The reason of the lower compressive strength of pellets produced with organic binders is the burning out of organic binders virtually without any or little residue (see part 5.1.7) at such temperatures. The compressive strength of pellets heated at 800°C with calcined colemanite is 23.84 kg/p (code 4) or combination of an organic binder and calcined colemanite are 16.90 22.02 and 20.49 kg/p (codes 8, 9 and 10, respectively). They are also lesser than those obtained with bentonite bonded pellets (codes 2 and 3). The reason of the lower strength of these pellets with calcined colemanite addition is the relatively low heating temperature (800°C) since the colemanite has a melting point of 986°C. At 800°C colemanite did not start to melt and did not effectively bind the magnetite ore grains (see title 6.5.3).
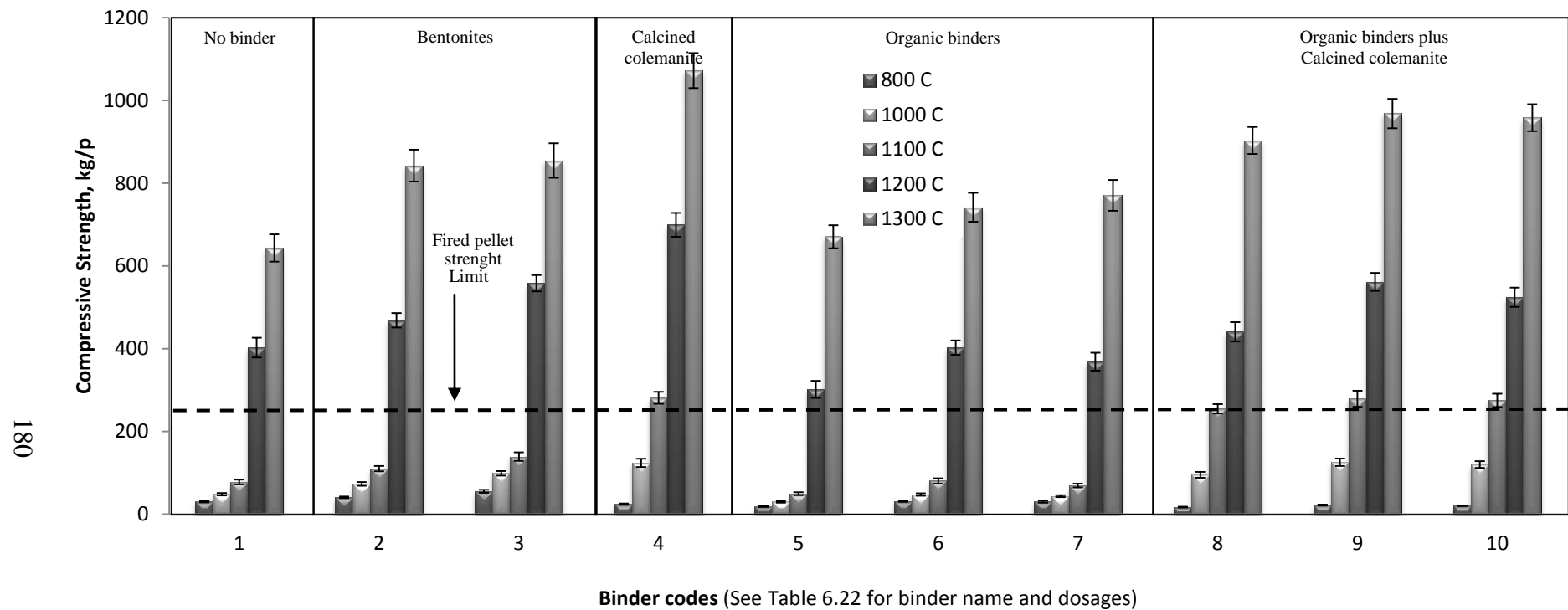
Figure 6. 27 Compressive strengths of pellets produced with different binders and thermally treated at 800°C, 1000°C, 1100°C, 1200°C and 1300°C for 30 minutes. The error bars show the 95% confidence level (P95). Dashed line shows 250 kg/p which is the industrially required minimum compressive strength limit for fired pellets

However, when the temperature increased to 1000°C, the compressive strengths of pellets made with only calcined colemanite (code 4), or combination of calcined colemanite and an organic binder (codes 8, 9 and 10), were found greater than the reference values obtained with bentonites (codes 2 and 3). Since this temperature (1000°C) is about the melting point (986°C) of colemanite and colemanite started to melt and bond the magnetite grains together.

When the temperature is increased to 1100°C, the compressive strengths are increased for all pellets. Compressive strengths were determined to be 77.45 kg/p for pellets without binder (code 1) and 109.65 and 138.94 kg/p (codes 2 and 3) for pellets bonded with two bentonite binders. Since these values are smaller than the required limit they are not sufficient for product pellet compressive strength. It can be concluded that, at 1100°C the compressive strength increase by bentonite addition is not sufficient.

However, the effect of colemanite addition on the pellet strength increase is more pronounced at this temperature. The strengths of pellets with calcined colemanite addition (codes 4, 8, 9 and 10) are significantly greater than the bentonite bonded reference pellets (codes 2 and 3). These values were determined to be 280.80 kg/p for pellets produced with only calcined colemanite addition and 254.40, 278.40 and 275.00 kg/p for pellets produced with calcined colemanite and an organic binder combination. All these values are greater than the values obtained by pellets bonded with reference bentonite binders. These strengths are without doubt considered to be sufficient since the minimum industrially required strength for product pellets is 250 kg/p (550 lbf) (Ball, et al., 1973). Firing temperature of iron oxides is generally 1250-1350°C depending on the genesis of iron oxides. The industrially sufficient compressive strength was obtained for the pellets hardened at 1100°C with the addition of 0.66% calcined colemanite. This result shows that in the presence of calcined colemanite in pellet feed, the lower firing temperature is enough to get industrially sufficient compressive strength. This means if calcined colemanite is added during iron ore pellet production, the energy consumption can be lowered by lowering firing temperature.

On the other hand, the compressive strength of pellets produced with organic based binders (codes 5, 6 and 7) are much smaller than both reference pellets with bentonite and than industrially required limit. These values were determined to be only 49.40, 80.24 and 69.10 kg/p for pellets with addition of organic based binders (codes 5, 6 and 7) respectively.

The compressive strengths of pellets fired at 1200°C were determined to be much increased by heat increase for all pellets. A value jump was observed in compressive strengths of all pellets fired at 1200°C. The reason for this sudden increase is believed due to the completion of oxidation and commences of recrystallization of magnetite grains at this temperature.

The compressive strength of pellets without binder was 402.60 kg/p (code 1) and were 468.45 and 558.00 kg/p (code 2 and 3) for bentonite bonded reference pellets. However, the presence of 0.66% calcined colemanite in pellet mix increased the strength significantly and the strength reached to 699.00 kg/p (code 4). The compressive strength of pellets produced with organic based binders (codes 5, 6 and 7) were resulted in a little lower; 301.60, 402.55 and 368.40 kg/p, respectively, than bentonite bonded pellets. But these values are still sufficient enough to meet required strength limit. When calcined colemanite was added to pellet mix together with an organic based binders (codes 8, 9 and 10), the compressive strengths were found to be 440.50, 561.30 and 525.15 kg/p, respectively.

The compressive strengths of pellets fired at 1300°C were also determined and found to be much higher for all pellets. The compressive strength of pellets without binder was determined to be 643.25 kg/p (code 1). The reference bentonite bonded pellets' compressive strengths were found to be 842.25 and 854.65 kg/p (code 2 and 3). The addition of 0.66% calcined colemanite in pellet mix increased the strength extensively and the strength reached to a maximum value; 1072.10 kg/p (code 4). The compressive strength of pellets produced with organic based binders (codes 5, 6 and 7) were determined to be lower; 670.45 and 741.50 and 770.55 kg/p, respectively, than reference pellets bonded with bentonite. When calcined colemanite was added to pellet mix together with an organic based binders (codes 8, 9 and 10),

the compressive strengths were found to be 903.15, 968.40 and 958.25 kg/p, respectively.

The compressive strengths of all pellets produced without binder or with any binder and fired at a temperature higher than 1200^oC are strong enough even much higher than the required limit (250 kg/p). This results show that the strength increases by binder is secondary at higher temperatures than 1200^oC. Therefore, the strengthening mechanism of pellets at 1200^oC and 1300^oC is most probably due to mainly two reasons:

   a) the oxidation of magnetite to hematite,
   b) the crystal growth and recrystallization of magnetite grains

The strengths of pellets made with bentonite or calcined colemanite and fired over 1200^oC are higher than those of obtained by without binder or with only organic binders. The reason of higher strength by addition of bentonite or calcined colemanite is due to melting of these binders and bonding the particle grains together. The partial melting and grain growth of the pellets contain either material are shown on SEM micro images under the following title.

6.5   Bonding mechanisms of colemanite : SEM studies of pellets

Pellets attain their mechanical strength during thermal treatment, namely preheating and firing cycles. Strengthening and bonding mechanism of preheated and fired pellets are discussed under title of 2.1.5.

Two major thermal bonding systems which impart strength to the pellets are summarized by Ball, *et al.,* 1973 and Meyer, 1980 in literature

   a) Change of the crystalline structure during firing either by crystal transformation and growth upon oxidation of magnetite to hematite or by crystal growth when hematite is used as iron oxide only. Mineral grain growth, essentially a physical process in which the smaller particles consolidate into

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larger ones with resulting loss in surface energy - this process may take place in solid state or through a liquid melt medium, and

b) The reaction of slag-forming constituents which are either present as gangue in natural ores or concentrates or added before the pelletizing, such as binder, acid oxides, basic additives such as limestone or dolomite. Basic components react with acid components and under certain conditions also with iron oxides. Thus, slag or crystal bonding is achieved as a result of the melt formation.

In order to understand the reason for compressive strength increase of calcined colemanite added pellets, the morphology and microstructure of these pellets were examined under scanning electron microscope (SEM). The strength increase and bonding mechanism of calcined colemanite addition to magnetite and hematite pellets was tried to be explained by the physical changes of grains. The physical changes can be partial melting of grain surface, grain shape changing, crystal structure changing and crystal growth of mineral grains forming pellets. The effects of bentonite and calcined colemanite were visually observed on the pellets thermally treated at different temperatures.

JEOL JSM-6400 scanning electron microscopy (SEM) was used to take micro photo of fired (at 1300°C) Divriği magnetite and Brazilian hematite pellets in Metallurgical and Materials Department at METU to ascertain the crystal structure changing. Same equipment was used for Lake Superior magnetite pellets in Applied Chemical and Morphological Analysis Laboratory at MTU for pellets heated at 800-1000-1100-1200 and 1300°C to see the effect of heating temperature on crystal structure changing.

6.5.1 SEM studies of Divriği magnetite pellets

JEOL JSM-6400 scanning electron microscopy (SEM) was used to take micro image of Divriği magnetite pellets fired at 1300°C for 20 minutes to see the effect of binders on microstructure (grain/crystal change). The half pellets broken during compression strength tests were used in the SEM image taking. The broken pellets

with practically even surface were selected and coated with gold. The micro images of fired Divriği magnetite pellets produced with **A)** 0.50% bentonite **B)** 0.50% calcined colemanite **C)** 0.10% CMC plus 0.50% calcined colemanite **D)** 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite **E)** 0.10% corn starch plus 0.50% calcined colemanite were taken at x500 magnification level with 20 kV beam energy and given in Figure 6.28. Since the compressive strengths of pellets are affected by microstructure of pellets and bonding mechanism of binders, average compressive strength of pellets are shown on micro images.

During heating under oxidizing atmosphere, the magnetite mineral grains oxidize to hematite with simultaneous conversion of the cubic magnetite into the hexagonal hematite lattice. According to the genesis of magnetite, the oxidation starts at about 300-600°C and is to be terminated at a temperature of 1100°C. It begins on the crystal and grain surfaces (Meyer, 1980). This is confirmed on the Divriği magnetite pellets (see title 6.7.1 for mineralogy of these pellets) fired at 1300°C produced with 0.50% bentonite, 0.50% calcined colemanite and with combined binders.

The grain growth is a little larger in bentonite bonded magnetite pellet (Figure 6.28-A) than colemanite bonded magnetite pellet (Figure 6.28-B). The grain size is roughly 40-50 µm in bentonite bonded pellets, 30-40 µm in calcined colemanite bonded pellets. Although, the micro image views (grain size) of these two pellets are a little different than each other, there is no more difference in their compressive strengths (494.40 and 554.20 kg/p, respectively). The other latter three micro image views of pellets produced with combination of calcined colemanite and an organic binder (Figure 6.28-C, D and E) are more or less similar to each other and that of bonded with calcined colemanite alone (Figure 6.28-B). The presence of organic binders did not adversely affect the grain growth and compressive strength of pellets fired at this temperature.

Figure 6. 28 SEM micro images of fired Divriği magnetite pellets at 1300°C for 20 minutes. Pellets were produced with **A)** 0.50% bentonite **B)** 0.50% calcined colemanite **C)** 0.10% CMC plus 0.50% calcined colemanite **D)** 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite **E)** 0.10% corn starch plus 0.50% calcined colemanite. Micro images were taken at x500 magnification level

6.5.2 SEM studies of Brazilian hematite pellets

JEOL JSM-6400 scanning electron microscopy (SEM) was used to take micro image of Brazilian hematite pellets fired at 1300°C for 20 minutes to see the effect of binders on microstructure (grain/crystal change). The half pellets broken during compression strength tests were used in the SEM image taking. The broken pellets with practically even surface were selected and coated with gold. The micro images of fired Brazilian hematite pellets produced with **A)** 0.50% bentonite **B)** 0.50% calcined colemanite **C)** 0.10% CMC plus 0.50% calcined colemanite **D)** 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite **E)** 0.10% corn starch plus 0.50% calcined colemanite were taken at x500 magnification level with 20 kV beam energy and given in Figure 6.29. Average compressive strengths of pellets are shown on micro images.

The grain growth is better in hematite pellets produced with calcined colemanite (Figure 6.29-B) than those of hematite pellets bonded with bentonite (Figure 6.29-A). While the grain size is roughly 20-30 μm in bentonite bonded pellets, 40-50 μm in calcined colemanite bonded pellets. The greater grain size is responsible for greater compressive strength of hematite pellets obtained upon calcined colemanite addition, as larger crystals or grains are formed as a result of a liquid melt medium of added calcined colemanite and lead to stronger pellets. Therefore, the compressive strength of pellets was found to be greater; 602.00±54.80 kg/p for pellets contained calcined colemanite than 381.10 ±42.25 kg/p for pellets contained bentonite.

Schmitt, 2005 have also explained this strength increase by the bonding mechanism that occurs when the boron compounds melt and fuse the iron ore grains together at contact points. These findings can explain the greater strength of hematite pellets obtained with calcined colemanite addition. Boron in colemanite and the constituents found in iron ore formed larger crystal complexes.
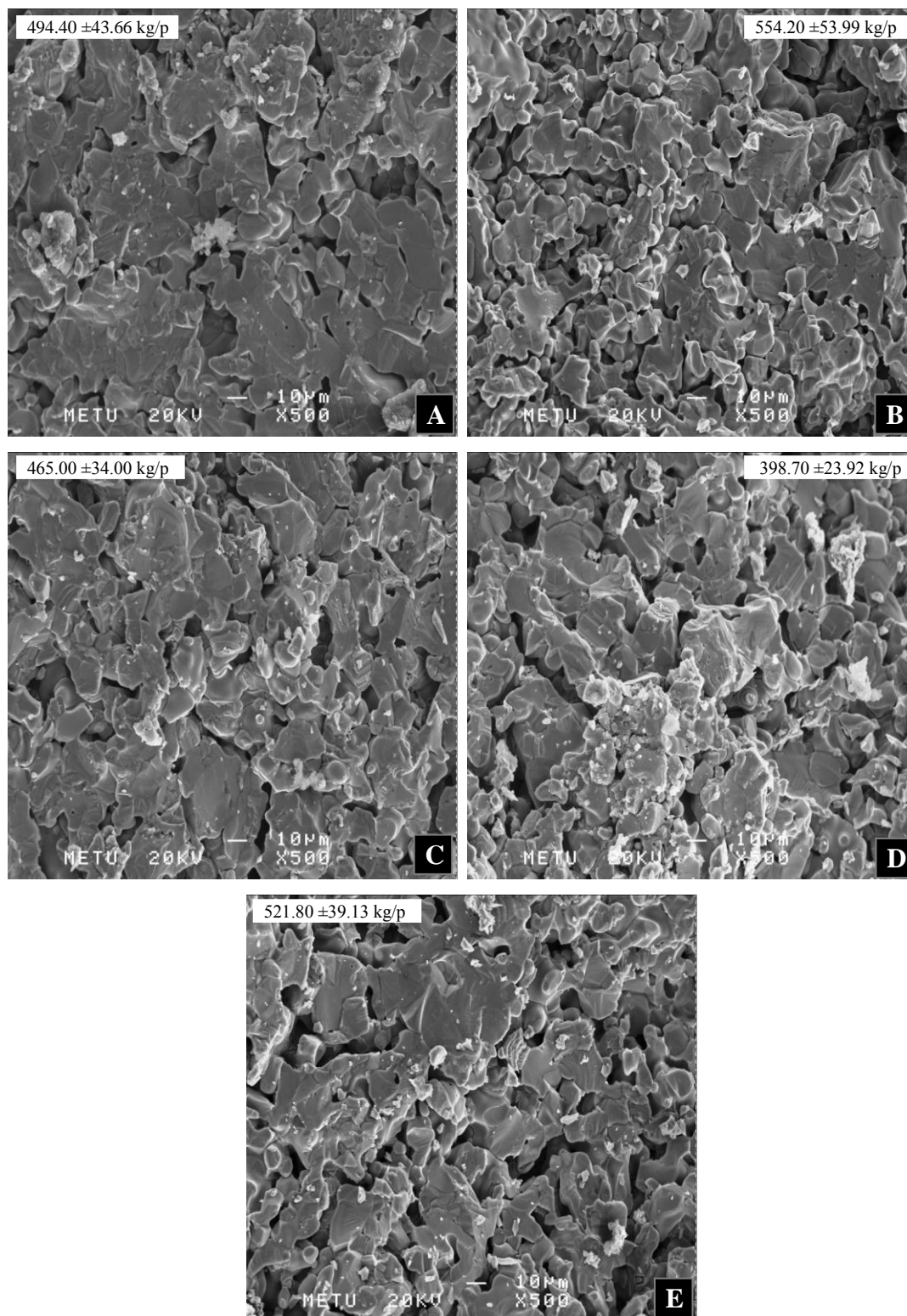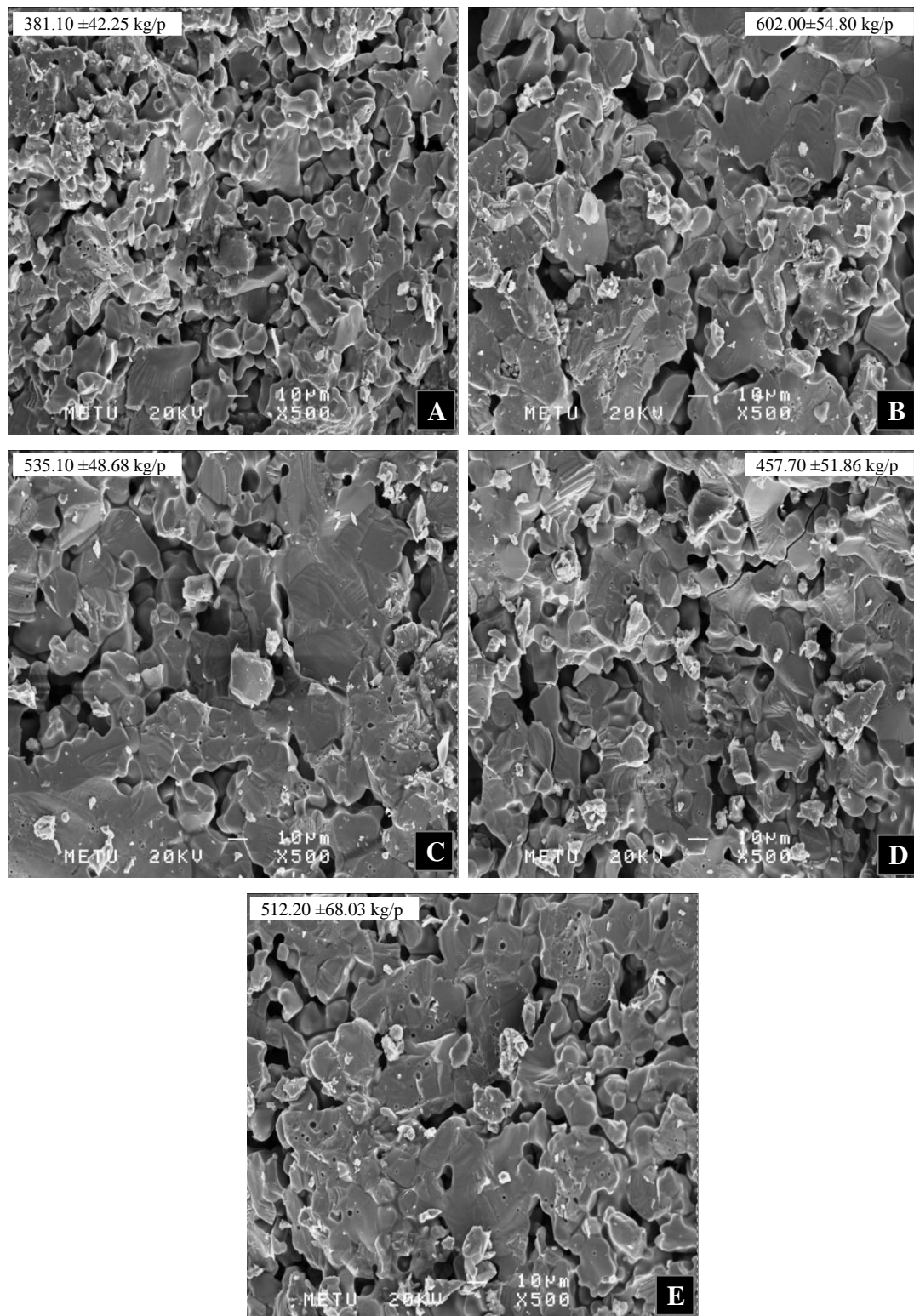
Figure 6. 29 SEM micro images of fired Brazilian hematite pellets at 1300°C for 20 minutes. Pellets were produced with **A)** 0.50% bentonite **B)** 0.50% calcined colemanite **C)** 0.10% CMC plus 0.50% calcined colemanite **D)** 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite **E)** 0.10% corn starch plus 0.50% calcined colemanite. Micro images were taken at x500 magnification level

The other pellets (Figure 6.29-C, D and E) produced with combination of calcined colemanite and an organic binder also have larger grain size as that of pellets made with only calcined colemanite addition. This result shows the presence of organic binder did not decrease the positive effect of calcined colemanite on grain growth. The compressive strengths of these pellets were determined ranged from 457.70 kg/p to 535.10 kg /p, which are greater than that of pellets bonded with bentonite and a little lower than pellets bonded with only calcined colemanite.

The appearance of surfaces and edges of hematite grain of pellets contain calcined colemanite looks like semi-melted and rounded (Figure 6.29-B). This can be seen on pellets contain bentonite (Figure 6.29-A); however, it is more obvious in calcined colemanite containing pellets. This is most probably due to formation of melted slag complexes since boron and SiO_2 are expected to melt and bond hematite grains.

6.5.3 SEM studies of Lake Superior magnetite pellets

JEOL JSM-6400 scanning electron microscopy (SEM) was used to take micro image of Lake Superior magnetite pellets heated at 800-1000-1100-1200 and 1300°C for 30 minutes to see the effect of heating temperature on microstructure (crystal change) depending on the binders used. The micro images of pellets producewith 0.66% Reşadiye bentonite and 0.66% calcined colemanite were taken. The half pellets broken during compression strength tests were used in the SEM images. The broken pellets with practically even surface were selected and coated with carbon. Micro images were taken at a working distance of 39 mm and with two magnification levels namely x500 and x3700 at 20 KV beam energy.

The first scanning electron microscopy images are shown in Figure 6.30 taken at x500 magnification level to examine a bigger portion of the surface of pellets. In order to compare the effects of same addition level of both bentonite and calcined colemanite, micro images of pellets are given together in the same row. In the left column of the Figure 6.30, micro images of bentonite bonded pellets, in the right column, micro images of calcined colemanite bonded pellets can be seen. The temperatures which pellets were heated for 30 minutes are shown on both micro images.

In these scanning electron microscopy images, relatively a bigger portion of cross section of pellets can be seen. Therefore, some relief can be seen since the self-broken pellets with as smooth as possible surface were selected to prepare sample for scanning electron microscopy.

During taking the micro images, the whole cross section was scanned and different images were taken from outer shell or from inner core of the pellets. However, no duplex or triplex microstructure has been observed between outer shell and inner core of the pellets. These findings showed that the pellets with pretty same size (12.7-11.5 mm in diameter) were indurated uniformly during thermal treatment.
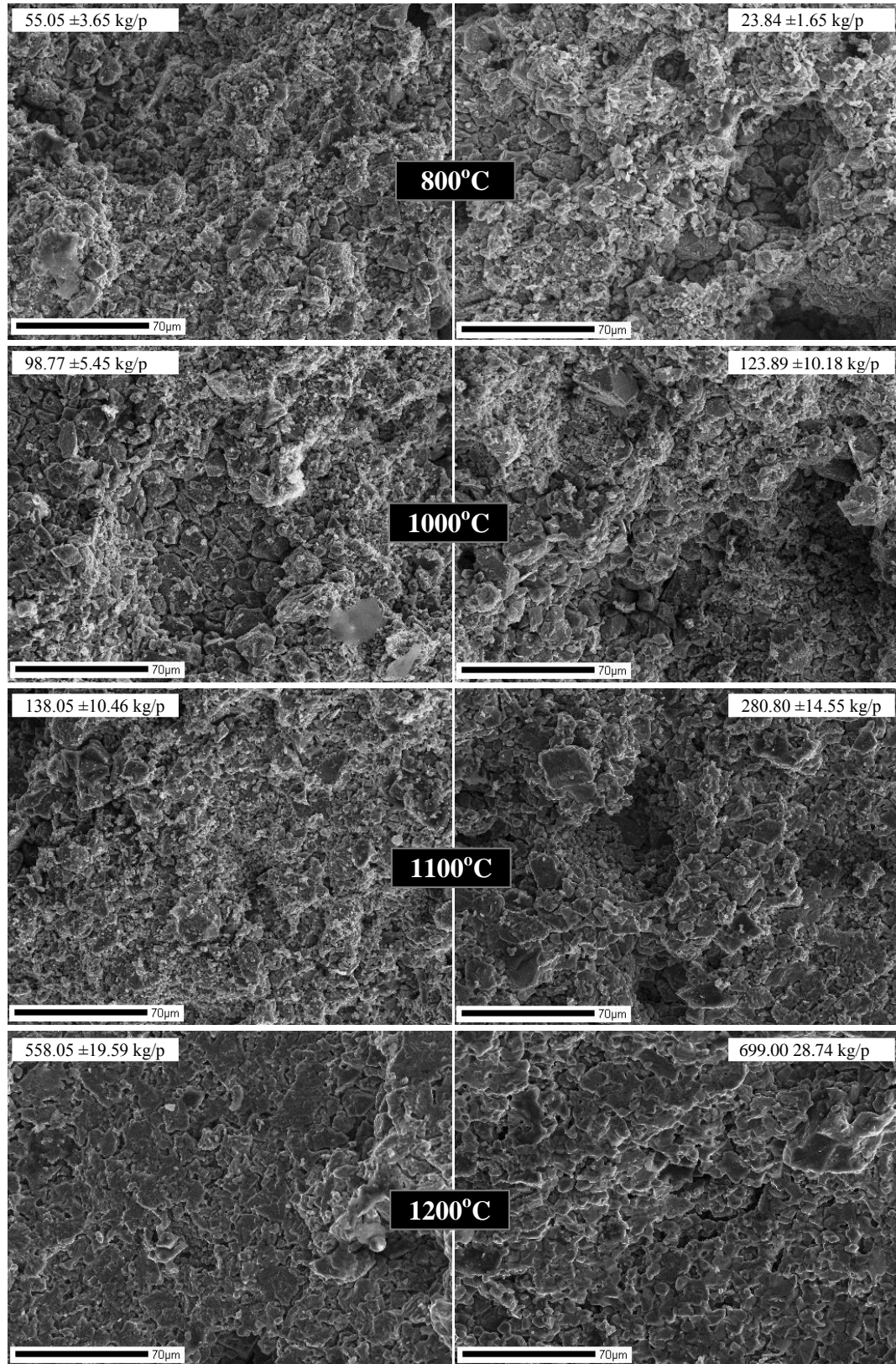
Figure 6. 30 SEM micro images of Lake Superior District magnetite pellets produced with 0.66% Reşadiye bentonite (left column) and 0.66% calcined colemanite (right column). The temperatures which pellets were heated for 30 minutes were shown on the micro images. Micro images were taken at x500 magnification level
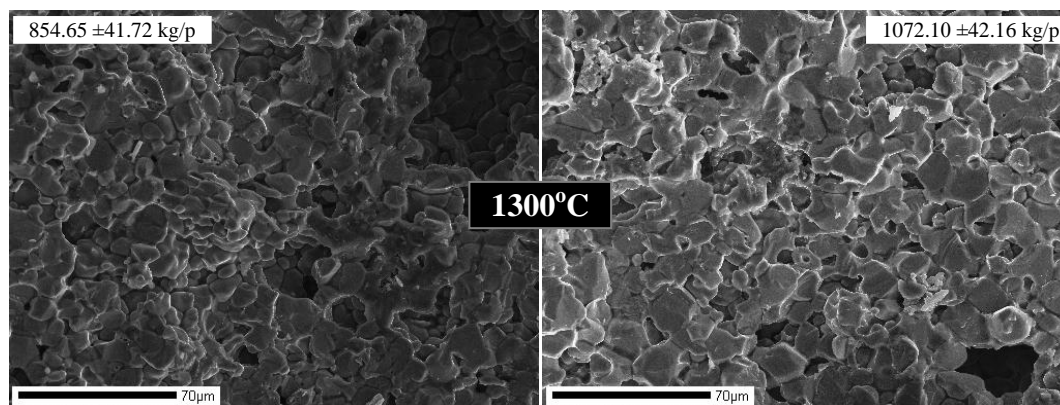
Figure 6. 31 Cont'd

Scanning electron microscopy images showed that the surfaces of pellets produced with either bentonite or calcined colemanite addition had about same microstructure. While the angled grains/microstructures stand out for pellets heated at 800 and $1000^{o}C$, the rounded ones are dominant for pellets heated at 1100, 1200 and $1300^{o}C$. The rounded grains show that bentonite and calcined colemanite give the grains solid state bonding by inter-diffusion of contacting grains at a temperature above $1100^{o}C$. In order to see detailed surface of grains and inter-diffusion of contact between grains, the closer images were taken.

The second scanning electron microscopy images are presented in Figure 6.31 were taken at x3700 magnification level to examine closer view of grain surface and interaction between them. In order to compare the effects of same addition level of both bentonite and calcined colemanite, micro images of pellets are given together in the same row. In the left column of the Figure 6.31, micro images of bentonite bonded pellets, in the right column, micro images of calcined colemanite bonded pellets can be seen. The temperatures which pellets were heated for 30 minutes are shown on both micro images.
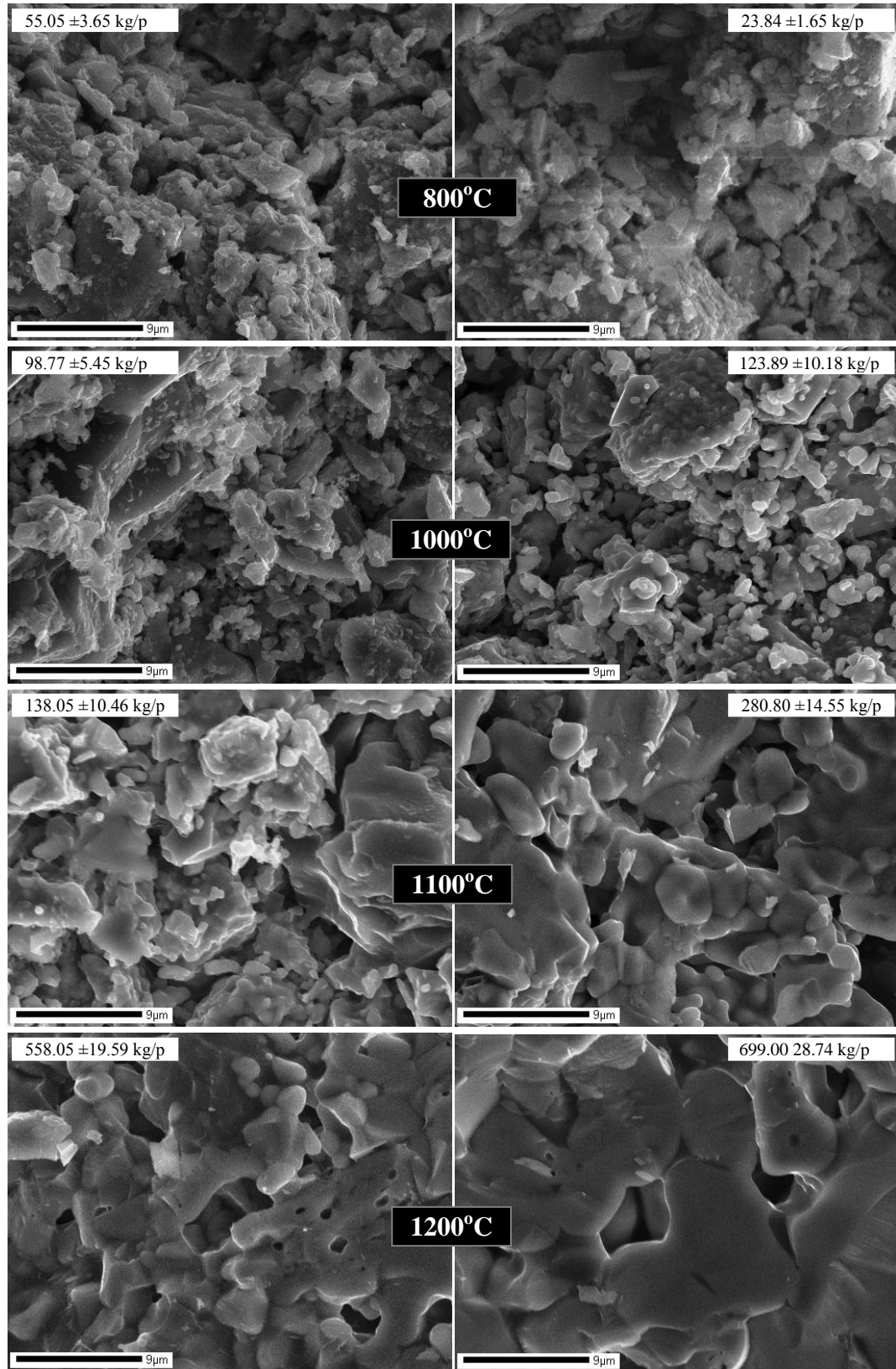
Figure 6. 32 SEM micro images of Lake Superior District magnetite pellets produced with 0.66% Reşadiye bentonite (left column) and 0.66% calcined colemanite (right column). The temperatures which pellets were heated for 30 minutes were shown on the micro images. Micro images were taken at x3700 magnification level
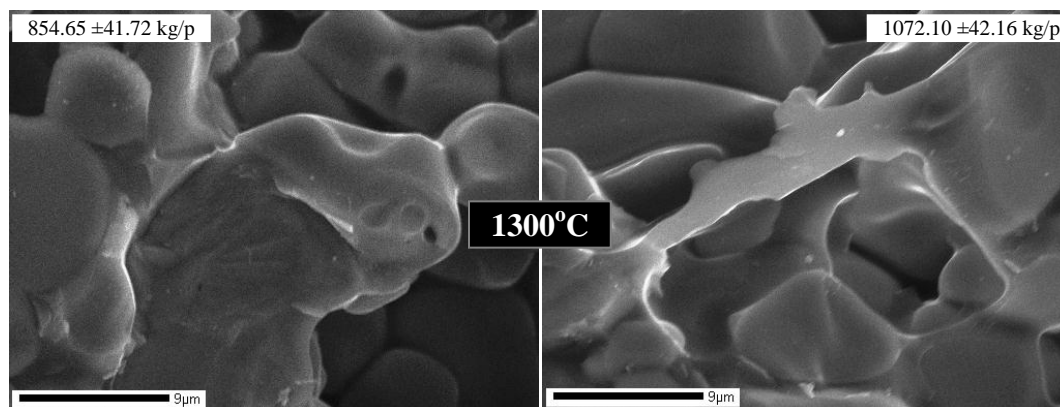
Figure 6. 33 Cont'd

In these scanning electron microscopy images, separate grains of pellets can be seen. The grains of pellets seem to be granular, sharp, cubic or angled (not rounded) for pellets heated at 800 and 1000°C. The grains start to be rounded for pellets contain 0.66% calcined colemanite and heated at 1100°C as a result of relatively high temperature. However, this rounded grain surface cannot be observed entirely for pellets bonded with 0.66% bentonite and heated at same temperature. The grain surface started to be rounded at 1200°C and completely rounded at 1300°C for bentonite bonded pellets.

For pellets fired at 1200 and 1300°C the shape of grains are more rounded due to complete melting of bentonite or calcined colemanite. Throughout the induration process bentonite or calcined colemanite used as binder provided solid state bonding by inter-diffusion of contacting grains. This bonding type can be shown as example for sinter bridges, partial melting or crystallization of soluble substances as explained by (Pietsch, 2005) and shown schematically in Figure 6.32. The presence of calcined colemanite at contact point of iron oxide grains causes the partial melting of grains and then grain growth via binding. Hence, compressive strength of pellets were gradually increased as a function of temperature and reached to maximum value for pellets fired at 1300°C since the higher temperature can increase the partial melting and made stronger binding. The desired strength (250kg/p) for fired pellets was obtained for pellets fired at low temperature. The pellets contain 0.66% calcined colemanite and fired at 1100°C had sufficient compressive strength. Therefore, the

presence of calcined colemanite is beneficial to provide sufficient compressive strength for pellets fired at only 1100°C.
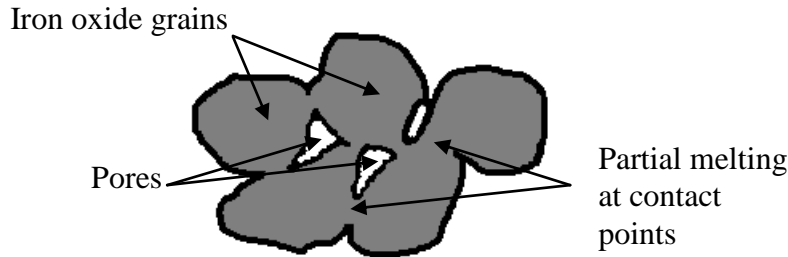
Figure 6. 34 Bonding mechanism of calcined colemanite: sinter bridges, partial melting or crystallization of soluble substances.

Boron compounds are known for their low melting temperatures as well as for their ability to also lower the melting temperatures of silicates in literature. The main reason of the increase of the preheated and fired pellet strength is due to physical melting of colemanite at temperatures above 1000°C since it has a melting point of 986°C (Tektaş, 2007). B-Fe-Si (Boron-Iron-Silicon) isothermal section at 1000°C was computed by Raghavan, 2007. Many different phases (FeB, FeSi, Fe$_2$B, Fe$_5$SiB$_2$, Fe$_{4.7}$ Si$_2$B, Fe$_2$Si$_{0.4}$B$_{0.6}$ and combinations) were depicted in this study (Raghavan, 2007). The presence of all there elements in the pellet feed forms, with a high degree of probability, at least one of these phases during and after thermal treatment of pellets (preheating or firing). The formation of such phases and effects in pellet structure should be investigated in detail in a separate research.

6.6   Porosity determination tests of pellets

Porosities of pellets were calculated using real and apparent volumes of pellets thermally treated at different temperatures. The real and apparent volumes of pellets were calculated using real and apparent densities of the pellets. The real and apparent densities of the pellets were found by pycnometer and wax immersing methods, respectively. Distilled water and acetone were used as liquid media in real density measurements. Apparent volume of pellets was determined according to ASTM C914-09. In this method the apparent volume of pellets was found by coating pellets with wax paraffin and immersing in distilled water.

Porosities of Lake Superior magnetite pellets produced with different binders and thermally treated at 105-800-1000-1100-1200 and 1300°C were determined to see the effects of both binders and heating temperatures on porosity of pellets.

The porosities of pellets were also observed visually on pellets produced with 0.66% calcined colemanite and heated at 1000°C for 30 minutes. Two different porosities were observed, namely macro and micro porosities, on these pellets. These porosities are shown on micro images of pellets in Figure 6.33.
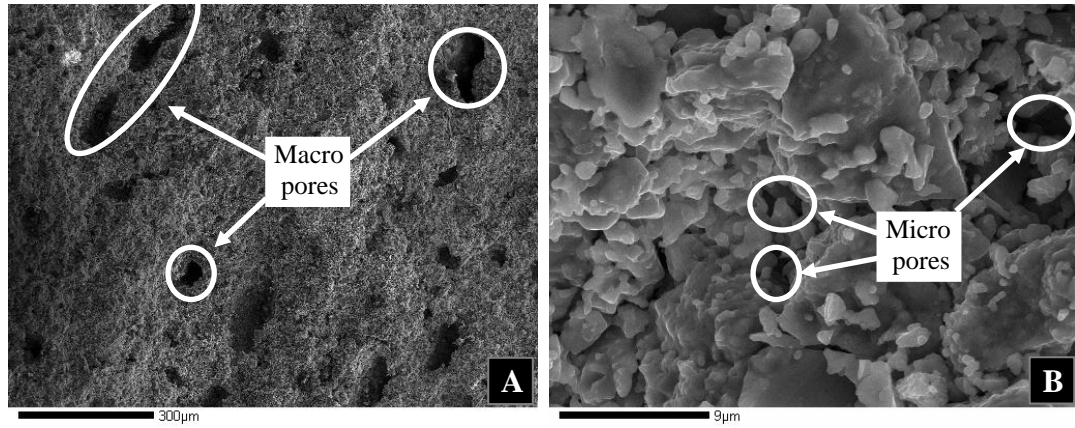
Figure 6. 35 Porosities of Lake Superior District magnetite pellets showing **A)** macro pores on micro photo taken at x100 magnification level and **B)** micro pores on micro photo taken at x3700 magnification level. Pellets produced with 0.66% calcined colemanite and heated at 1000°C for 30 minutes

Results of the porosity measurements are given in Table 6.23. In Table 6.23 the mean porosity of 5 pellets from each batch are given with the 95% confidence interval (P95). The porosity values are also shown in Figure 6.34 graphically.

The porosities of dry pellets are about 27-32% for all pellets. When the heating temperature was increased the porosities decreased gradually. However, porosity decrease is so slow up to 1000°C for all pellets. Above this temperature, porosities decreased rapidly with starting of melting of binders. When the temperature is increased to 1100°C the porosity decrease is more pronounced for pellets contain bentonite or calcined colemanite.

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Table 6. 23 Results of the porosities of Lake Superior District magnetite pellets produced with different binders and heated at different temperatures ranged from 105°C (dry pellets) to 1300°C (fired pellets).

Binder Codes	Binder Name and Dosages	Mean pellet porosity (% with ±P95)					
		Dry @ 105°C	Heated @ 800°C	Heated @ 1000°C	Heated @ 1100°C	Heated @ 1200°C	Heated @ 1300°C
1	No binder	27.83 ±0.11	26.38 ±0.63	26.21 ±0.26	25.92 ±0.18	22.85 ±0.83	19.55 ±0.50
2	Lake Superior bentonite, 0.66%	29.60 ±0.24	27.58 ±0.37	27.41 ±0.18	26.34 ±0.23	22.98 ±0.76	18.31 ±0.35
3	Reşadiye bentonite, 0.66%	28.07 ±0.22	25.65 ±0.35	25.57 ±0.16	24.57 ±0.19	21.81 ±0.85	19.53 ±0.20
4	Calcined colemanite, 0.66%	30.92 ±0.23	30.58 ±0.14	28.91 ±0.28	25.57 ±0.33	22.67 ±0.69	18.04 ±0.35
5	Technical CMC, 0.10%	29.12 ±0.66	28.68 ±0.63	28.10 ±0.17	27.78 ±0.41	25.21 ±0.92	23.35 ±0.60
6	DPEP06-0007 polymer, 0.10%	27.32 ±0.45	26.06 ±0.22	26.28 ±0.27	25.58 ±0.14	22.56 ±0.50	19.94 ±0.59
7	Superfloc A150-LMW, 0.10%	28.36 ±0.59	28.13 ±0.18	27.92 ±0.38	27.06 ±0.13	24.92 ±0.80	21.66 ±0.21
8	Technical CMC, 0.10% + Calcined colemanite, 0.66%	32.36 ±0.45	31.45 ±0.34	30.42 ±0.51	25.88 ±0.26	23.23 ±0.72	19.83 ±0.35
9	DPEP06-0007 polymer, 0.10% + Calcined colemanite, 0.66%	31.20 ±0.56	30.50 ±0.32	30.28 ±0.58	24.76 ±0.15	22.90 ±0.74	18.77 ±0.32
10	Superfloc A150-LMW, 0.10% + Calcined colemanite, 0.66%	31.81 ±0.59	31.38 ±0.42	29.43 ±0.40	25.74 ±0.10	23.46 ±0.36	19.22 ±0.36
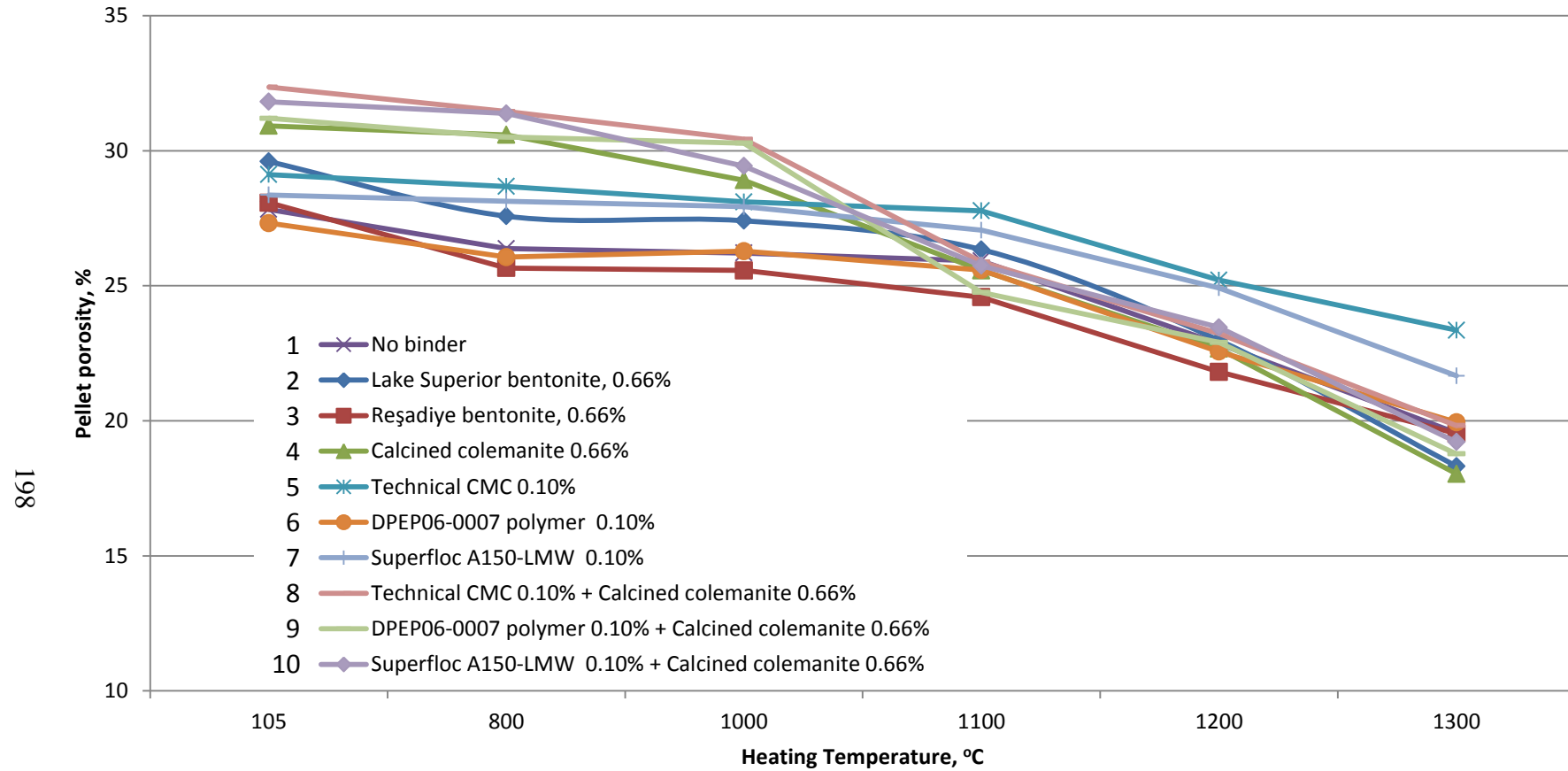
Figure 6. 36 Porosities of Lake Superior District magnetite pellets produced with different binders and heated at different temperatures ranged from 105°C (dry pellets) to 1300°C (fired pellets)

With increasing of temperature to 1200°C or 1300°C the porosity decrease is sharper for all pellets. The porosities were determined to be about 18-21% for pellets fired at 1300°C.

The porosity differences between pellets contain organic based binders and bentonite or calcined colemanite is only about 2-3%. If the pellets are accepted as product pellets fired at 1200°C, the highest porosity about 25% was obtained with pellets produced with organic binder addition. If pellets contain bentonite or calcined colemanite, this time porosity will be around 22-23% at the same temperature.

In literature, typical porosities for green and dry pellets from high grade iron oxide are mentioned in the range 31-36%, whilst a porosity of 22-30% for fired pellets is associated with good reducibility (Ball *et al.,* 1973).

The porosities found for pellets produced with different binder addition are about in the same range mentioned above for typical industrial pellets.

6.7 Dust generation tests of fired pellets

As mentioned under title 4.6.2, iron ore pellets should have sufficient mechanical strengths against degradation. Beside the mechanical strength, pellets should generate less dust during operation since the process efficiency and the equipments are affected adversely by dust. Dust is also problem for product pellets since they abrade during transportation to the reduction furnaces. Moreover, dust is considered as lost and a problem for environment since they are becoming airborne in plant or during transportation. Therefore, increasing the mechanical strength and decreasing the dust generation of pellets are necessary for better operation and handling of pellets.

The dust generations of fired pellets at 1200°C were determined with a novel apparatus. A diagram and photo of dust tower is given in Figure 4.5. This tower is unique in that it simulates material handling while allowing for direct measurement of airborne particulate percentage.

The procedure involved weighing the fired pellets in 500 to 1000 g and dropping them through a counter-current air stream through 11 inclined steel platforms. The air stream was passed through a filter to remove airborne particles. The weight of the particles collected on the filter paper was reported as the amount of airborne dust generated. During drop test some fines can also be generated depend on the pellet strength and shape due to dropping from 11 inclined steel platforms. Hence these fines can be collected in the bottom pan of the apparatus. However, the fine fragment generation was not more since the fired pellets are strong enough and no pellet breakdown observed.

Dust tower test was utilized to simulate the pellet breakdown and abrasion during handling by free fall of fired pellets through dust tower. After dropping of all pellets, fine fractions were collected and analyzed. Results of the dust tower - pellet breakdown tests of Lake Superior District magnetite pellets produced with different binders and heated at 1200°C (fired pellets) are given in the Table 6.24.

Table 6. 24 Results of the dust tower - pellet breakdown tests of Lake Superior District magnetite pellets produced with different binders and heated at 1200°C (fired pellets)

Binder Codes	Binder Name and Dosages	Coarse, %	Mean pellet fines (% with ±P95)		
		+6.35 mm (+3 mesh)	-6.35 mm +500 μm (-3 mesh +32	-500 μm (32 mesh)	
				Fines [1]	Airborne dust [2]
1	No binder	99.9297	No broken fragments were observed since no pellet breakdown was carried out with fired pellets by using dust tower	0.0373 ±0.0030	0.0331 ±0.0018
2	Lake Superior bentonite, 0.66%	99.9411		0.0320 ±0.0045	0.0269 ±0.0024
3	Reşadiye bentonite, 0.66%	99.9373		0.0321 ±0.0059	0.0306 ±0.0028
4	Calcined colemanite, 0.66%	99.9650		0.0182 ±0.0012	0.0168 ±0.0011
5	Technical CMC, 0.10%	99.9625		0.0166 ±0.0023	0.0209 ±0.0023
6	DPEP06-0007 polymer, 0.10%	99.9567		0.0180 ±0.0021	0.0252 ±0.0040
7	Superfloc A150-LMW, 0.10%	99.9561		0.0171 ±0.0013	0.0268 ±0.0026
8	Technical CMC, 0.10% + Calcined colemanite, 0.66%	99.9698		0.0139 ±0.0004	0.0162 ±0.0008
9	DPEP06-0007 polymer, 0.10% + Calcined colemanite, 0.66%	99.9663		0.0155 ±0.0021	0.0182 ±0.0012
10	Superfloc A150-LMW, 0.10% + Calcined colemanite, 0.66%	99.9643		0.0161 ±0.0003	0.0196 ±0.0016

[1] Fines show the fine fragments cannot be vacuumed by counter-current air stream and collected in the dust tower bottom drawer after dropping of all pellets excluding airborne dust
[2] Airborne dusts show the dust vacuumed by dust tower counter-current air stream and collected on filter paper

The mean values for fractions are given with the 95% confidence interval (P95) in Table 6.24. During the dust tower test coarse (+6.35 mm) and fine fractions (-6.35 mm +500 μm, -500 μm and airborne dust) can be generated after dropping of pellets in -12.7+11.5 mm diameter size. The fine fractions of -500 μm and airborne dust generation rates were presented graphically in Figure 6.35.
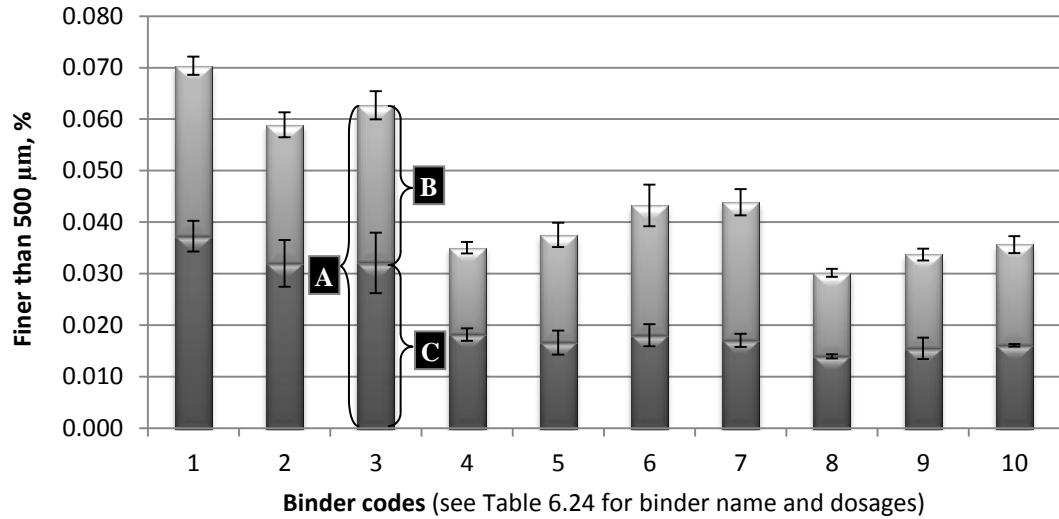
Figure 6. 37 Fine fraction of dropped pellets produced with different binders and fired at 1200°C. **A)** -500 μm fraction named as fine fraction and consist of two groups; **B)** airborne dust was collected on filter paper and **C)** fine part cannot be vacuumed by counter-current air stream was collected in the dust tower bottom drawer after dropping of all pellets. The error bars show the 95% confidence level (P95)

The fine fraction (-500μm containing airborne dust) were determined between 0.0302% and 0.0703% by weight of the drooped pellets. This values seem to be low, however if capacity of a pelletizing plant is considered this fine rates will become significant as loss. The fine fraction was divided into two groups; airborne dust and other. In Figure 6.35, it can be seen that the fine fragments (-500μm) consist of about 50% of airborne and about 50% of other fines. This means half of the fines generated due to pellet breakdown or abrasion during handling of pellets will become airborne and considered as loss or environment problem.

Since the dust tower was designed to measure the airborne dust directly under a certain counter-current air stream, the fines excluding airborne dust are considered as side issue. Main reason of testing of fired pellets in terms of dust generation rates was simulate their dust generation potential while they are dropping from one transportation site point to other. Therefore, airborne dust was here considered as main issue in terms of dust generation potential of fired pellets.

Airborne dusts of fired pellets produced with different binders were found between 0.0162% and 0.0331% by weight of fired pellets. This dust rates will become significant if capacity of a pelletizing plant is considered as loss and environment problem.

The highest airborne dust generation; 0.0331%, was found for pellets made without binder (code 1) and the lowest dust generation; 0.0162%, for pellets produced with CMC plus calcined colemanite (code 8).

The reference pellets produced with bentonites were found to be 0.0269% and 0.0306% for pellets contain 0.66% Reşadiye bentonite and Lake Superior bentonite, respectively (code 2 and 3). The pellets produced with 0.66% calcined colemanite generated 0.0168% airborne dust which is lower than dust rates generated from pellets bonded with reference bentonite binders.

The airborne dusts of pellets produced with organic or organic based manufactured binders were found 0.0209%, 0.0252% and 0.0268% for pellets produced with 0.10% Technical CMC, DPEP06-0007 Polymer and Superfloc® A150-LMW (codes 5, 6 and 7), respectively. These dust generation rates are also lower than those of bentonite bonded pellets (codes 2 and 3). The reason of the lower dust generation is most probably due to the smoothness of pellet surfaces. The airborne dust generation arose from the surface of pellets since no pellet breakdown was observed. Therefore, the photos of pellets were taken and surfaces of pellets were compared. The smoothest pellet surfaces were observed for pellets contain organic or organic based manufactured binders. The pellet surfaces were seen to be rough for pellets produced without binder (Figure 36-A). The bentonite bonded pellet surfaces were found to be

a little smother (Figure 36-B) than surface of pellets without binder, however they are not as smooth as organic binder containing pellets (Figure 36-C).

The dusts of pellets produced with an organic binder plus calcined colemanite were determined to be 0.0162%, 0.0182% and 0.0196%, respectively (codes 8, 9 and 10). The surfaces of these pellets (Figure 36-D) were also smoother than those of pellets without binder or with bentonite binder due to the presence of organic binders.
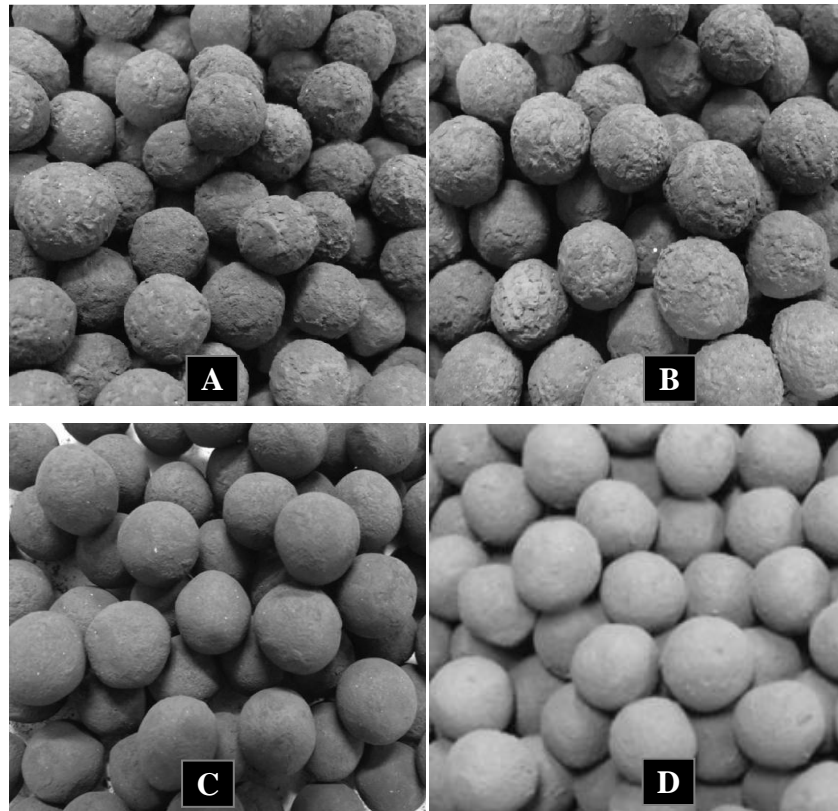
Figure 6. 38 Surfaces of the Lake Superior magnetite pellets produced **A)** without binder, with **B)** 0.66% Reşadiye bentonite **C)** 0.10% technical CMC and **D)** 0.10% technical CMC plus 0.66% calcined colemanite

The airborne dusts collected on filter paper were also analyzed to determine their particle size distribution. The particle size distribution of airborne dust generated from selected pellets produced without binder, with 0.66% Reşadiye bentonite and with 0.10% CMC and with 0.10% CMC plus 0.66% calcined colemanite can be seen in Figure 6.37.

The airborne dust particle size distribution curves showed that the percentage of particulate matter (PM_{10} which is particles with 10 μm diameter and smaller size) lied between 30% and 40% by weight of airborne dust. PM_{10} particulate matter is the material regulated by the U.S. Environmental Protection Agency. The reason of the approximately zero values up to 4-5 μm particle size is the lack of ultrafine particles during Microtrac particle size analyzing. The particle size distribution curves cannot show ultrafine particles since these ultrafine particles penetrated into the filter paper and could not be measured.
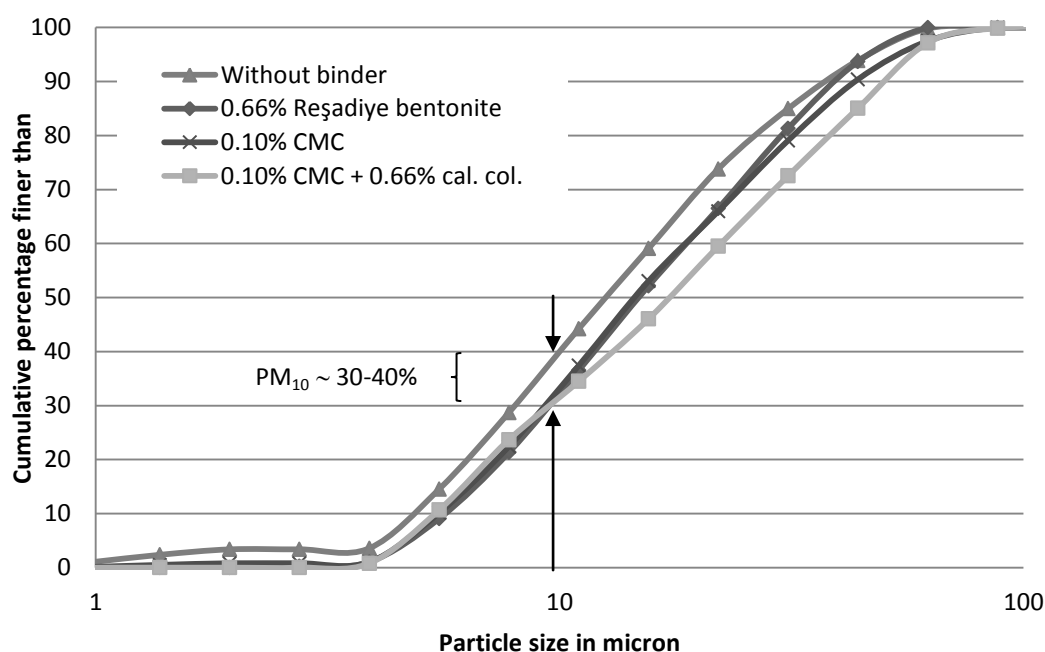
Figure 6. 39 The particle size distribution of airborne dust generated from selected pellets produced without binder, with 0.66% Reşadiye bentonite and with 0.10% CMC and with 0.10% CMC plus 0.66% calcined colemanite

6.8   Mineralogical analyses of pellets : XRD studies of pellets

6.8.1 XRD studies of Divriği magnetite pellets

X-ray diffraction (XRD) studies of Divriği magnetite pellets were carried out with dry magnetite concentrate and thermally treated pellets at different temperatures. A Rigaku MiniFlex II X-ray diffractometer was used to obtain the X-ray diffraction patterns of Divriği magnetite pellet samples. During X-ray analyses, continuous scanning with 0.01^{o}-0.05^{o} step size starting 5° ending 70° was applied with Cu Kα (30 kV beam energy, 10 mA current, λ=1.54050 Å) radiation.

The X-ray diffraction patterns of dry concentrate and pellets thermally treated at 600-800-1000-1300°C were taken to show the mineralogical changing of pellets depend on temperature increase in the presence of either bentonite or calcined colemanite addition. The X-ray diffraction patterns of Divriği magnetite concentrate and pellets produced with 0.50% Reşadiye bentonite or 0.50% calcined colemanite addition and heated at 600°C, 800°C, 1000°C and 1300°C for 30 minutes are given in Figure 6.38.

Figure 6. 40 X-ray diffraction patterns of dry Divriği magnetite concentrate (purple) and pellets made from this concentrate and produced with 0.50% Reşadiye bentonite (red) or 0.50% calcined colemanite (blue) and heated at 600-800-1000-1300°C for 30 minutes

The mineralogy of fired pellets made with calcined colemanite was investigated and compared with bentonite bonded pellets. The base X-ray diffraction pattern was determined with dry Divriği magnetite concentrate and show that magnetite (Fe_3O_4) is the only constituent (M letters show the magnetite peaks, ICCD card no: 19-0629). Since it is a clean concentrate, no impurity (SiO_2 and Al_2O_3) peaks can be detected.

The X-ray diffraction patterns of Divriği magnetite pellets produced with 0.50% Reşadiye bentonite or 0.50% calcined colemanite binder addition and thermally treated at 600^oC indicated that oxidation of magnetite to hematite started before this temperature and an important part of oxidation was completed at 600^oC. However, oxidation is not completed since the X -ray diffraction pattern has three magnetite peaks. Hematite (Fe_2O_3) is the main constituent (H letters show the hematite peaks ICCD card no: 33-0664) and a few peaks still belong to magnetite.

The pellets heated at 800^oC show only hematite peaks, magnetite peaks disappeared. It means at this temperature oxidation of magnetite to hematite was completed. The other pellets contain same amount of binders and thermally treated at elevated temperatures (1000 and1300^oC) have similarly only hematite peaks.

The X-ray diffraction patterns of Divriği magnetite pellets contain either bentonite or calcined colemanite showed no new peaks arising from binder addition. As the addition levels of bentonite or calcined colemanite were very low (0.50% of dry magnetite concentrate), the possible new compounds formation and their differential peaks cannot be detected by XRD analyses.

Oxidation pattern of magnetite pellets and the peaks detected by XRD analyses well confirm with earlier reports.

6.8.2 XRD studies of Brazilian hematite pellets

X-ray diffraction studies (XRD) of Brazilian hematite pellets were carried out with dry hematite concentrate and thermally treated pellets at different temperatures. A Rigaku UltimaVI X-ray diffractometer was used to obtain the X-ray diffraction

patterns of Brazilian hematite pellet samples. During X-ray analyses, continuous scanning with 0.02^o step size starting 10° ending 75° was applied with Cu Kα (40 kV beam energy, 10 mA current, λ=1.54050 Å) radiation.

The X-ray diffraction patterns of dry concentrate and pellets thermally treated at 1000 and 1300^oC were taken to show the mineralogical changing of pellets depend on temperature increase in the presence of either bentonite or calcined colemanite. The X-ray diffraction patterns of Brazilian hematite concentrate and pellets produced with 0.50% Reşadiye bentonite or 0.50% calcined colemanite addition and heated at 1000^oC and 1300^oC for 30 minutes are given in Figure 6.39.

The mineralogy of fired pellets made with calcined colemanite was investigated and compared with bentonite bonded pellets. The base X-ray diffraction pattern was determined with dry Brazilian hematite concentrate and show that magnetite (Fe_2O_3) is the only constituent (H letters show the hematite peaks, ICCD card no: 33-0664). Since it does not contain excessive impurity such as SiO_2 or Al_2O_3, no impurity compound peaks can be detected.

The X-ray diffraction patterns of Brazilian hematite pellets produced with 0.50% bentonite or 0.50% calcined colemanite binder addition and thermally treated at 1000^oC or 1300^oC indicated that hematite (Fe_2O_3) is again the main constituent.

The X-ray diffraction patterns of Brazilian hematite pellets contain either bentonite or calcined colemanite showed no new compounds. No new differential peaks were detected resulted from the addition of these less amounts of bentonite or calcined colemanite. As the addition levels of bentonite or calcined colemanite were very low (0.50%), the possible new compounds formation and their differential peaks cannot be detected by XRD analyses.
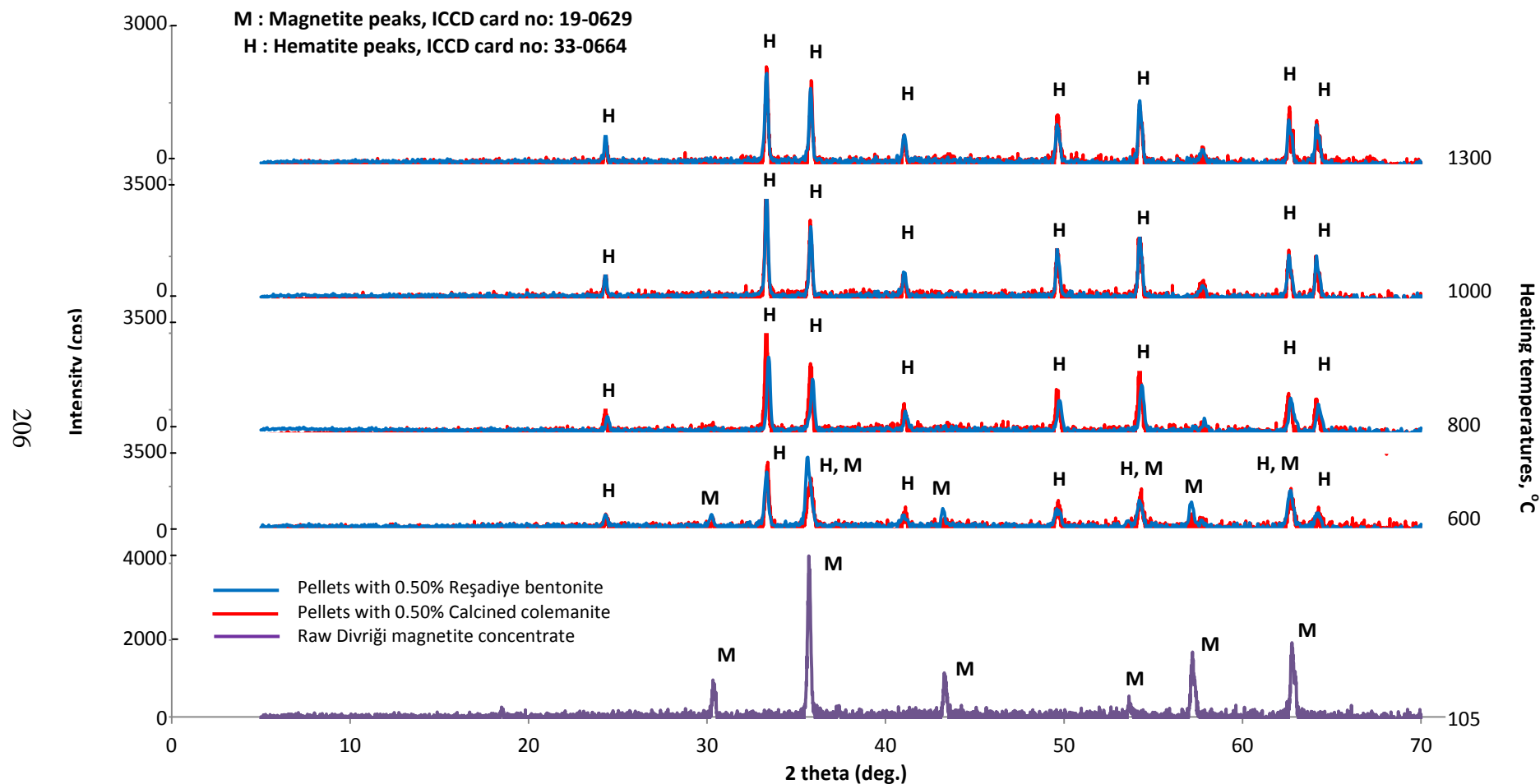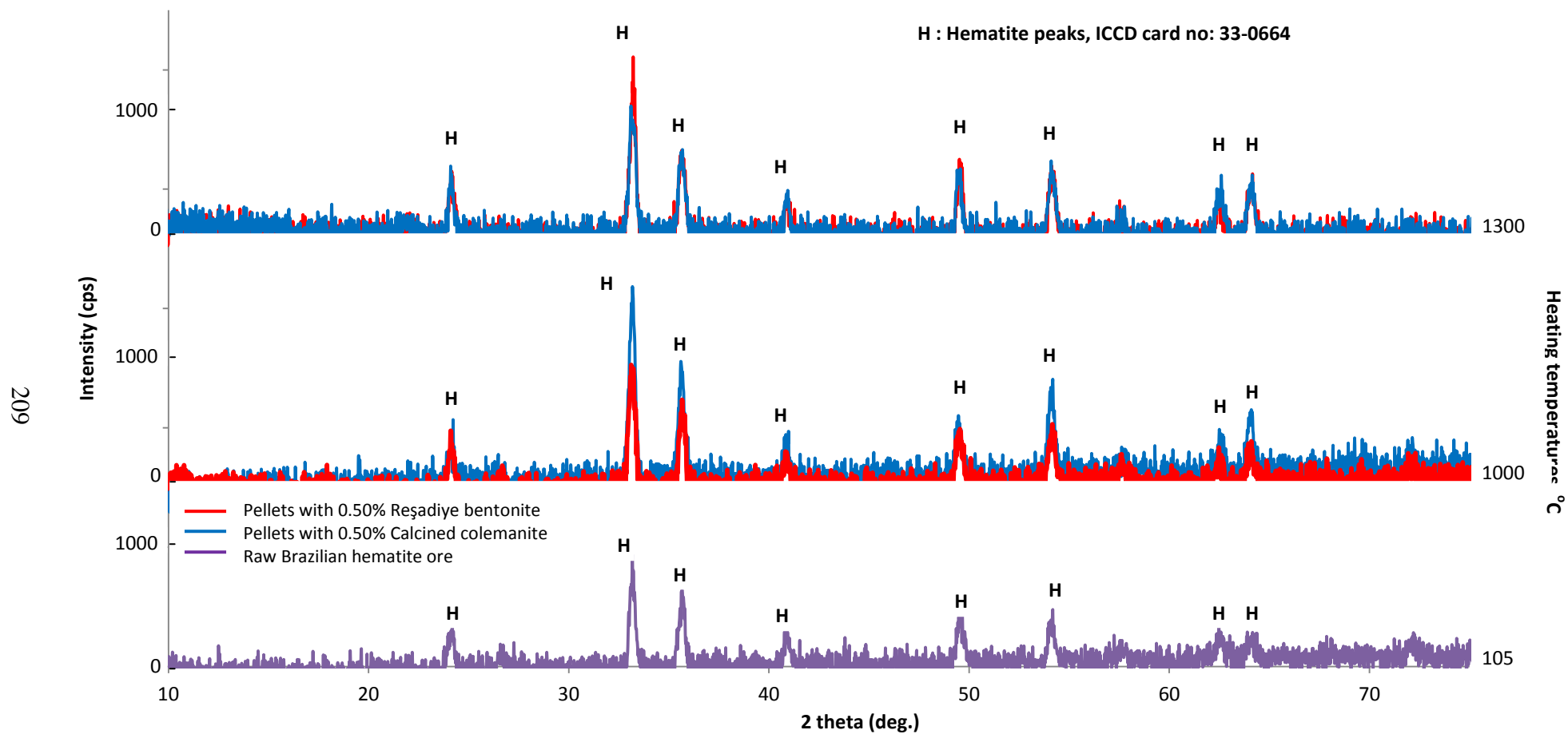
Figure 6. 41 X-ray diffraction patterns of dry Brazilian hematite concentrate (purple) and pellets made from this concentrate and produced with 0.50% Reşadiye bentonite (red) or 0.50% calcined colemanite (blue) and heated at 1000-1300°C for 30 minutes

6.9   Reducibility of pellets

By using the Eq.5 an Eq.6 given in title 4.2.8, percent reducibility of pellets was calculated as a function of time. R% obtained at the end of 180 minutes according to Gakushin reducibility method (ISO 7215-2007), which is a measure of reducibility for different samples.

Divriği magnetite pellets and Brazilian hematite pellets found with sufficient compressive strength were subjected to reducibility test. Results are given in the following sections.

6.9.1 Reducibility tests of Divriği magnetite pellets

Fired Divriği magnetite pellets produced with 0.50% Reşadiye bentonite, 0.50% calcined colemanite, 0.10% technical CMC plus 0.50% calcined colemanite, 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite and 0.10% corn starch plus 0.50% calcined colemanite were reduced at 900°C for 180 minutes.

Percent reducibility versus time for the experimental pellet samples are presented graphically in Figure 6.40.

The reducibility tests of fired pellets at 1300°C revealed that the pellets produced with bentonite binder were more reducible than those of produced with calcined colemanite addition.

The reducibility of Divriği magnetite reference pellets made with bentonite was found to be 45.90% and it was previously found 49.00% for a pellet sample from Divriği Pelletizing Plant by Akşit 2007 with a similar reducibility test setup. The reducibilities of Divriği magnetite pellets made with other binders were found between 25.92% and 34.82%.

While the highest reducibility (45.90%) was found for pellets produced with 0.50% Reşadiye bentonite the lowest one (25.92%) was found for 0.10% DPEP06-0007

polymer plus 0.50% calcined colemanite added pellets. The other pellets contain 0.50% calcined colemanite alone or combination of 0.10% technical CMC plus 0.50% calcined colemanite were found a litter higher than the lowest reducibility. They were found 29.75% and 29.67%, respectively. The reducibility of Divriği pellets added 0.10% corn starch plus 0.50% calcined colemanite was found a little higher; 34.82%, than the other pellets contain calcined colemanite.

The reason of the low reducibilities of calcined colemanite added pellets may be related with the heavy melting of calcined colemanite at 1300°C. While the addition of calcined colemanite contribute to compressive strength of fired pellets through physical melting between ore grains, it most probably blocks the porosity and cause closed pores then make difficult to remove oxygen from the interior part of pellets during reducibility test. Therefore, by means of calcined colemanite addition the mechanical strengths of fired pellets were increased at the same time the reducibility of these pellets were affected adversely. Lower reducibilities of pellets made with calcined colemanite addition are as a result of high temperature selected for firing, namely 1300°C. Hence the lower firing temperatures providing the sufficient industrial compressive strength may recover the low reducibilities of pellets containing calcined colemanite.

The photo of reference Divriği magnetite pellet produced with 0.50% Reşadiye bentonite and photo of 0.50% calcined colemanite added pellet are shown in Figure 6. 41 and Figure 6. 42, respectively. These figures also show the photos of reduced pellets with some cracks of these two pellets due to oxygen removal during reducibility tests. More cracks are observed on pellets contain bentonite than contain calcined colemanite. This also shows the high oxygen removal and high reducibility of those pellets bonded with bentonite.

Figure 6. 42 Reducibility of Divriği magnetite pellets produced with different binder addition and were reduced at 900°C for 180 minutes
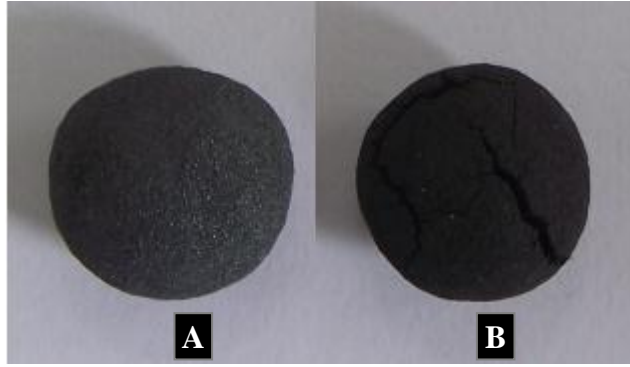
Figure 6. 43 **A)** photo of fired reference Divriği magnetite pellet produced with 0.50% Reşadiye bentonite, and **B)** photo of reduced pellet shows cracks due to oxygen removal during reducibility test
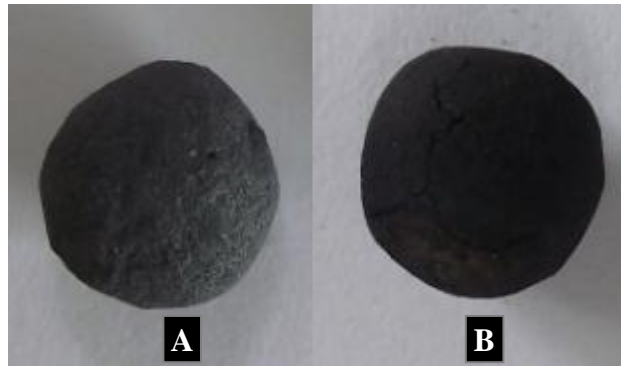
Figure 6. 44 **A)** photo of fired Divriği magnetite pellet produced with 0.50% calcined colemanite, and **B)** photo of reduced pellet shows cracks due to oxygen removal during reducibility test

6.9.2 Reducibility tests of Brazilian hematite pellets

Fired Brazilian hematite pellets produced with 0.50% Reşadiye bentonite, 0.50% calcined colemanite, 0.10% technical CMC plus 0.50% calcined colemanite, 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite and 0.10% corn starch plus 0.50% calcined colemanite were reduced at $900^{o}C$ for 180 minutes. Percent reducibility versus time for the experimental pellet samples are presented graphically in Figure 6.43.

The reducibility of Brazilian hematite pellets made with bentonite as reference pellets was found to be 77.49% and it was previously found 67.40% for a hematite pellet sample from CVRD (Companhia Vale do Rio Doce in Brazil) by Akşit 2007 with a similar reducibility test setup. The reducibilities of Brazilian hematite pellets made with other binders were found between 26.89% and 39.46%.

While the highest reducibility (77.49%) was found for pellets produced with 0.50% Reşadiye bentonite, the lowest one (26.89%) was found for 0.10% DPEP06-0007 polymer plus 0.50% calcined colemanite added pellets. The other pellets contain 0.50% calcined colemanite alone or combination of 0.10% corn starch plus 0.50% calcined colemanite were found a litter higher than the lowest reducibility. They were found 32.85% and 35.41%, respectively. The reducibility of Divriği pellets added 0.10% technical CMC plus 0.50% calcined colemanite was found a little higher; 39.46%, than the other pellets contain calcined colemanite. The reason of the low reducibilities of calcined colemanite added pellets is believed to be similar as explained for Divriği magnetite pellets above. It is related with melting behavior of calcined colemanite at higher firing temperature, which is 1300°C.

6.10 Swelling index tests of pellets

The principle of the swelling index method specified is to determine the swelling of fired iron ore pellets of a specified size range under isothermal reduction using a reducing gas consisting of carbon monoxide and nitrogen. Calculated free-swelling index expressed as a percentage, using the difference between the two volumes; before and after reducibility test at a temperature of 900 °C (ISO 4698:2007).

By using the Eq.6 given in title 4.2.9, percent swelling of pellets was calculated as volume change. Pellets used in swelling determination were obtained at the end of 180 minutes Gakushin reducibility method. The calculated swelling indices of fired Divriği magnetite and Brazilian hematite pellets produced with different binders are given Table 6.25.
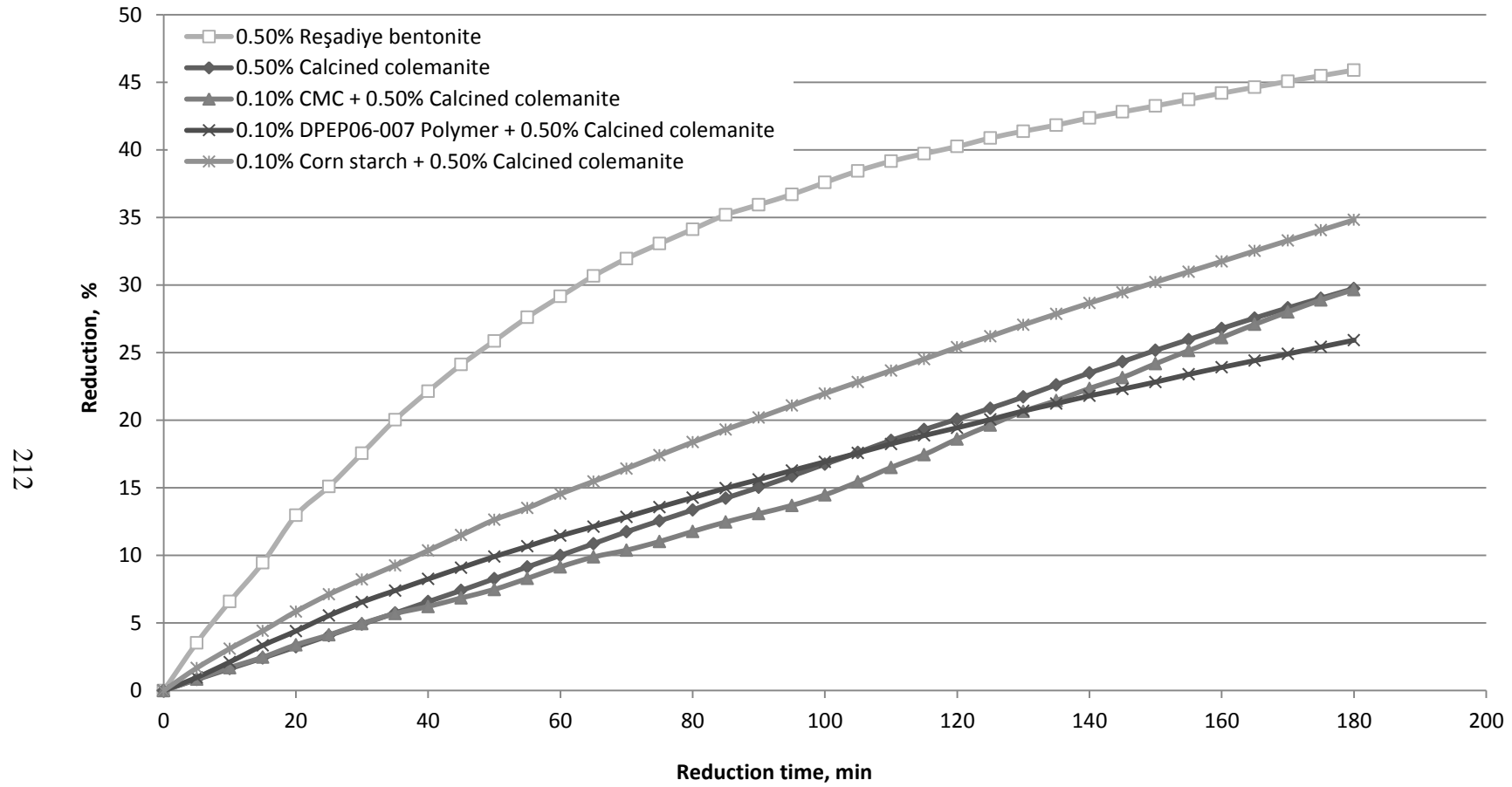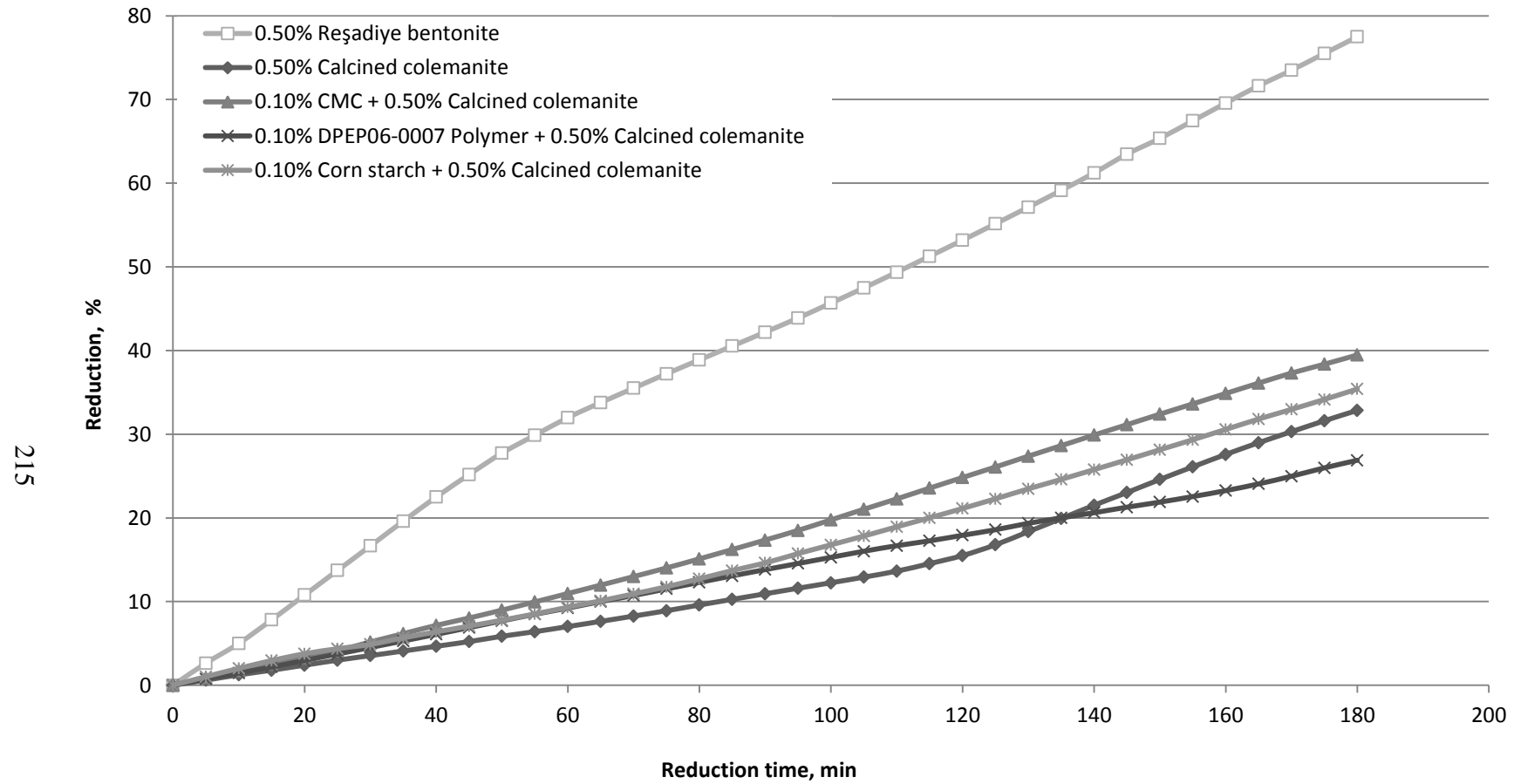
Figure 6. 45 Reducibility of Brazilian hematite pellets produced with different binder addition and were reduced at 900°C for 180 minutes

Table 6. 25 Swelling indices of fired pellets produced with different binders

Pellets	Binder Name and Dosages	Swelling, %
Fired Divriği magnetite pellets	Reşadiye bentonite, 0.50%	16.26
	Calcined Colemanite, 0.50%	12.48
	Technical CMC, 0.10% + Calcined Colemanite, 0.50%	12.62
	DPEP06-0007 Polymer, 0.10% + Calcined Colemanite, 0.50%	11.62
	Corn starch, 0.10% + Calcined Colemanite, 0.50%	14.64
Fired Brazilian hematite pellets	Reşadiye bentonite, 0.50%	17.88
	Calcined Colemanite, 0.50%	11.61
	Technical CMC, 0.10% + Calcined Colemanite, 0.50%	13.93
	DPEP06-0007 Polymer, 0.10% + Calcined Colemanite, 0.50%	10.32
	Corn starch, 0.10% + Calcined Colemanite, 0.50%	12.45

The swelling indices of both fired Divriği magnetite and Brazilian hematite pellets were determined between 10.32% and 17.88%. These swelling indices are in the desired range since the industrially acceptable swelling index should be lower than 20.0% for trouble-free blast furnace operation. Therefore, the additions of tested binders do not have negative effect on swelling behavior of fired pellets.

6.11 Chemical analyses of pellets : XRF studies of pellets

Chemical analyses of pellets produced with Lake Superior magnetite concentrate and fired at 1200°C for 30 minutes were determined with XRF (X-Ray fluorescence spectrometer). The results for chemical compositions of fired Lake Superior magnetite pellets are given in Table 6.26.

The Fe content of concentrate and pellets made with this concentrate were determined to be approximately 65.00%. The main impurities of concentrate were SiO_2 and Al_2O_3 and they were found 4.87% and 0.12%, respectively. No big differences in SiO_2 and Al_2O_3 contents were detected in pellets with addition of tested binders. Since, the addition levels of binders are not so much (0.66% for bentonite and calcined colemanite and 0.10% for organic or organic based manufactured binders). Therefore, the detected contents of product pellets are more or less similar to each other. However, the SiO_2 contents of pellets contain bentonite binders are a little higher than those produced with organic binders or calcined colemanite.

Table 6. 26 Chemical analyses of pellets made with Lake Superior magnetite concentrate. Pellets were produced different binders and fired at 1200°C for 30 minutes

Binder Codes	Binder Name and Dosages	Total Fe %	SiO$_2$ %	Al$_2$O$_3$ %	CaO %	MgO %	Na$_2$O %	K$_2$O %	SO$_3$ %	P$_2$O$_5$ %	TiO$_2$ %
-	Magnetite concentrate	65.52	4.87	0.09	0.44	0.37	-*	0.02	0.03	0.05	0.01
1	No binder	65.42	4.93	0.10	0.58	0.33	-	-	0.02	0.05	0.01
2	Lake Superior bentonite, 0.66%	64.75	5.37	0.14	0.51	0.31	-	-	0.02	0.05	0.01
3	Reşadiye bentonite, 0.66%	64.74	5.44	0.13	0.51	0.45	-	-	0.03	0.05	0.01
4	Calcined Colemanite 0.66%	65.24	4.86	0.06	0.70	0.14	-	-	-	0.05	0.01
5	Technical CMC 0.10%	65.37	4.88	0.05	0.53	0.49	-	0.00	-	0.05	0.01
6	DPEP06-0007 Polymer 0.10%	65.31	4.97	0.05	0.67	0.36	-	-	-	0.05	-
7	Superfloc A150-LMW 0.10%	65.38	4.90	0.10	0.59	0.43	-	-	0.02	-	0.01
8	Technical CMC 0.10% + Calcined Colemanite 0.66%	65.19	4.88	0.06	0.51	0.38	-	-	0.03	0.05	0.01
9	DPEP06-0007 Polymer 0.10% + Calcined Colemanite 0.66%	65.13	4.99	0.05	0.53	0.44	-	-	-	0.05	0.01
10	Superfloc A150-LMW 0.10% + Calcined Colemanite 0.66%	65.18	4.96	0.06	0.67	0.28	-	-	-	0.05	0.01

*Under detection limit of the analyzing equipment

CHAPTER 7

CONCLUSIONS

The aim of the work is the use of boron compounds together with organic binders in iron ore pelletizing. The reasons to test boron compounds together with organic binders can be split into two parts; the first is to overcome the drawbacks of bentonite binder and the second is to improve the low compressive strengths of preheated and fired pellets produced with organic binders alone. The conclusions are summarized below.

1. Good quality green and dry pellets can be produced with organic binders. The fineness of iron oxide is a function on wet pellet moisture content and drop number. Organic binders provide sufficient dry pellet compressive strengths. However, organic binders failed in terms of preheated and fired pellet compressive strengths due to their burning out with almost no or little residue at relatively low temperature.

2. Boron compounds (colemanite, tincal, borax pentahydrate and boric acid) cannot be used as alternative binders alone since they failed to provide sufficient wet and dry pellet qualities. Among the boron compounds colemanite distinguished since it provides better compressive strengths to the preheated and fired pellets. The addition of 0.50% calcined colemanite equally-performed on magnetite pellets, however over-performed on hematite pellets when compared with the performance of reference bentonite binder.

3. Organic binders and colemanite were used together to compensate the shortcoming of either binder. Sufficient wet, dry pellet qualities and improved preheated, fired compressive strengths were obtained with the combined binders.

4. The firing temperature was selected as $1300^{\circ}C$ and rather high compressive strengths were found with the addition of calcined colemanite. Therefore, lower firing temperatures than $1300^{\circ}C$ were tested. Results showed that as low as 0.50% calcined colemanite addition was enough in order to obtain sufficient fired pellet compressive strengths at $1100^{\circ}C$ firing temperature.

5. The micro images of pellets showed that the bonding mechanism of bentonite and calcined colemanite was physical melting at the surface and contact points of iron oxide grains. Calcined colemanite was found to be more effective than bentonite.

6. The porosities decreased from 27-32% for dry pellets to 18-21% for fired pellets with increasing temperature. The reason of the porosity decrease is related with melting characteristic of binders.

7. The airborne dust generation arose from the surface abrasion of product pellets since no pellet breakdown was observed during dust generation test. The amount of particulate matter (PM_{10} which is regulated particles with 10 μm diameter and smaller size) lied between 30% and 40% by weight of airborne dust.

8. The X-ray diffraction patterns of magnetite pellets containing either bentonite or calcined colemanite showed no new peaks arising from binder addition. As the addition levels of bentonite or calcined colemanite were very low (0.50%), the possible new compounds formation and their differential peaks cannot be detected.

9. Bentonite bonded product pellets fired at $1300^{\circ}C$ were more reducible than those of produced with calcined colemanite addition.

10. The swelling indices of product pellets ranged from 10.32% and 17.88% which are in the industrially acceptable limits.

11. The Fe content of product pellets were determined as low as binder addition levels, and SiO_2 and Al_2O_3 contents were as high as impurities added with bentonite. The impurity-free calcined colemanite did not contaminate the pellet chemistry.

CHAPTER 8

RECOMMENDATIONS

In the light of the results of the thesis, a number of studies could be taken up to further investigate the use of boron compounds in iron ore pelletization.

1. The effect of calcined colemanite in pellets on the reduction furnace operation (refractory life, reducibility, distribution of boron element in pig iron and slag etc.) needs to be investigated in greater depth.

2. The effect of calcined colemanite addition on steel properties should be investigated in detail.

3. A cost comparison study should be made between the use of conventional bentonite binder and the use of the suggested alternative binder, namely combination of an organic binder and calcined colemanite.

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PROJECTS

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2. The investigation of enrichment of Bizmişen iron ore.
3. The enrichment of low grade hematite ores by gravity and magnetic separation methods.
4. The use of colemanite with organic binders in iron ore pelletizing TUBİTAK (The Scientific and Technological Research Council of Turkey) Project No:105M348.
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