ALTERNATIVE BINDERS TO BENTONITE FOR IRON ORE PELLETIZING : PART II : EFFECTS ON METALLURGICAL AND CHEMICAL PROPERTIES

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ABSTRACT

This study was started to find alternative binders to bentonite and to recover the low preheated and fired pellet mechanical strengths of organic binders-bonded pellets. Bentonite is considered as a chemical impurity for pellet chemistry due to acid constituents (SiO_2 and Al_2O_3). Especially addition of silica-alumina bearing binders is detrimental for iron ore concentrate with high acidic content. Organic binders are the most studied binders since they are free in silica. Although they yield pellets with good wet strength; they have found limited application in industry since they fail to give sufficient physical and mechanical strength to preheated and fired pellets. It is investigated that how insufficient preheated and fired pellet strengths can be improved when organic binders are used as binder. The addition of a slag bonding/strength increasing constituent (free in acidic contents) into pellet feed to provide pellet strength with the use of organic binders was proposed. Addition of boron compounds such as colemanite, tincal, borax pentahydrate, boric acid together with organic binders such as CMC, starch, dextrin and some organic based binders, into magnetite and hematite pellet mixture was tested. After determining the addition of boron compounds is beneficial to recover the low pellet physical and mechanical qualities in the first part of this study, in this second part, metallurgical and chemical properties (reducibility - swelling index – microstructure – mineralogy - chemical content) of pellets produced with combined binders (an organic binder plus a boron compound) were presented. The metallurgical and chemical tests results showed that good quality product pellets can be produced with combined binders when compared with the bentonite-bonded pellets. Hence, the suggested combined binders can be used as binder in place of bentonite in iron ore pelletizing without compromising the pellet chemistry.

KEYWORDS: iron ore pelletizing; bentonite; organic binder; boron compounds; colemanite, chemical and metallurgical properties.

1. INTRODUCTION

Bentonite is the most widely used binder in iron ore pelletizing. The use of bentonite is favorable in terms of physical, mechanical and metallurgical pellet qualities, however, because of its acid constituents (SiO_2 and Al_2O_3) it is considered as an chemical impurity especially for concentrate with high SiO_2 content. These acid oxides are known for their adverse effects on the iron-steel making economy. For example, the addition of 1% bentonite, containing 85% SiO_2+Al_2O_3, decreases the iron content of pellets by 0.6-0,7% by wt (de Souza *et al*.,1984, Kater and Steeghs, 1984).Any increase in silica content can lead to appreciable cost increases of the steel production (Chizhikova *et al*., 2003, Schmitt, 2005). 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. Therefore alternative binders to bentonite have been tested for many years. Because of good binding properties without contaminating the product pellets, organic binders have attracted attention among researchers. (Eisele and Kawatra, 2003, Sivrikaya, 2011).

Organic binders provided good wet pellet strength; however, they have found limited application in industry. Ripke and Kawatra (2000) gave a statistic about the pellet plants in USA. Eight of the nine plants utilized bentonite clay as a binder, while the ninth plant used an organic binder. The reason behind the failure of organic binders in industry is their low burning temperatures. Organic binders which burnt out at relatively low temperatures (<250^{o}C) with virtually no or little residue can not provide bonding to iron oxide grains at higher induration temperatures. Therefore, in literature the results showed that organic binders produce good quality wet and dry pellets. However, they fail to impart enough strength to the pre-heated and fired pellets as a result of reduced slag bonding (Kater and Steeghs1984, Goetzman *et al*., 1988, Sivrikaya, 2011) which is especially more important in pelletizing of hematite ores due to lack of oxide bonding. 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 pre-heated 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 (Sivrikaya, 2011). A few researchers have investigated the use of boron compounds in iron ore agglomeration and found promising results on physical and chemical properties of product pellets (Köroğlu, 1980, Timuçin *et al*., 1986, Malysheva *et al*., 1996, Schmitt, 2005, Akberdin and Kim 2008)

This study was conducted to investigate how insufficient preheated and fired pellet strengths can be improved when organic binders are used as binder. Boron compounds free in acidic contents are suggested to overcome the lack of slag forming constituents encountered with organic binders as they are known for their low melting temperatures and also to decrease the melting temperatures of silicates. Addition of a slag bonding/strength increasing boron compounds into pellet recovered the low preheated and fired pellet strength with the use of organic binders (Sivrikaya and Arol, 2013).

In this part of the study, the effects of addition of boron compounds such as colemanite, tincal, borax pentahydrate, boric acid together with organic binders such as CMC, starch, dextrin and some organic based binders (OBB), into magnetite and hematite pellet mixture was tested on metallurgical and chemical qualities of product pellets. Metallurgical and chemical properties of thermally treated pellets (reducibility - swelling index - microstructure - mineralogy - chemical content) of pellets produced with combined binders (an organic binder plus a boron compound) were determined and presented.

2. MATERIALS AND METHODS

Detailed information about raw materials used in the pelletizing experiments, their characterization and the pelletizing experiment procedure are given in the first part of this study (Sivrikaya and Arol, 2013).

2.1. Determination of chemical and metallurgical pellet properties

2.1.1. Reducibility of pellets

Reducibility is the degree of ease with which oxygen can be removed from pellet composition. In standard, the product pellets is heated upto 900^{o}C under nitrogen and then the reducing test gas is passed through the pellets at this temperature with the required flow rate. Gakushin reducibility test method standatds were utilized for reducibility experiments. The reducibility experiments of product pellets was carried out with an reducibility apparatus consisting of a vertical split furnace, a sensitive balance and a control unit.

2.1.2. Swelling index of pellets

Pellets tend to swell during chemical reduction process in the reduction furnaces. Swelling of the product pellets should not exceed 20% by volume for a trouble-free operation in the reduction facilities. Swelling index of reduced pellets according to Gakushin method was calculated according to volume change of pellets before and after reducibility test.

2.1.3. Microstructures of pellets

In order to understand the reason for compressive strength increase of pellets containing boron compound, the microstructures of thermally treated pellets were examined under a scanning electron microscope. The bonding mechanism of combined binders added to magnetite pellets was explained by the physical changes (crystal change and crystal growth) in mineral grains of pellets after thermal process. JEOL JSM-6400 scanning electron microscopy was used to obtain micro images of pellets heated at 800-1300^{o}C to see the effect of heating temperature and different binders on crystal changes.

2.1.4. Mineralogy of pellets

In order to understand the reason underlying the strength increase after addition of boron compound, changes in the mineralogy of the fired pellets were investigated by XRD method. A Rigaku MiniFlex II XRD analyzer (X-ray diffractometer) was used to obtain the mineralogy of thermally treated pellets.

2.1.5. Chemical content of pellets

Iron and chemical impurity contents are important for product pellets in terms of an economic iron production in reduction facilities. In order to see the efect of addition of different binders on pellet chemistry, chemical analyses of product pellets were determined with XRF method using a Spectro IQ X-Ray fluorescence spectrometer.

3. RESULTS AND DISCUSSION

The results of the physical and mechanical tests are presented in the first part of the study (Sivrikaya and Arol, 2013) and according to those results; pellets with sufficient physical and mechanical qualities were selected to determine their chemical and metallurgical properties. The results of chemical and metallurgical tests of selected pellets are presented below and all results were presented in the Ph.D. dissertation by Sivrikaya, 2011. The mean values of 20 randomly pellet samples were given with the 95% confidence level (P95) in the graphs.

3.1. Reducibility of pellets

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 (Figure 1). 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 increases the 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 sintering, namely 1300°C. Hence the lower firing temperatures such as 1100°C which provided the sufficient industrial compressive strength may recover the low reducibilities of pellets containing calcined colemanite.

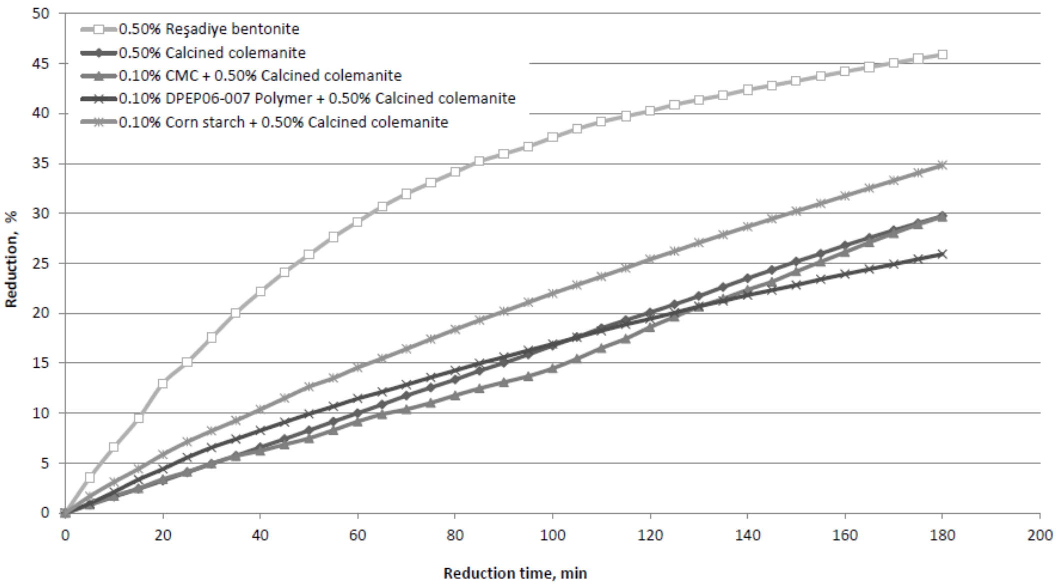

Figure 1. Reducibility of magnetite pellets sintered at 1300°C and reduced at 900°C for 3 hour

3.2. Swelling index of pellets

The swelling indices of both fired magnetite and hematite pellets were determined between 10.32% and 17.88% (Table I). These swelling indices are in the desired range since the industrially acceptable swelling index should be lower than 20% for trouble-free reduction furnace operation. Therefore, the additions of tested alternative binders do not have negative effect on swelling indices of product pellets.

Table I. Swelling indices of pellets sintered at 1300ºC and reduced at 900ºC for 3 hours

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

3.3 Microstructures of pellets

SEM micro-images of pellets thermally treated at 800-1300ºC were taken and only images for pellets sintered pellets at 1100ºC are given in Figure 2. In the images, separate grains of pellets can be seen and the grains of pellets seem to be granular, sharp, cubic or angled (not rounded) for pellets heated at 800 and 1000ºC. The grains start to be rounded for pellets contain calcined colemanite and heated at 1100ºC as a result of relatively high temperature. However, this rounded grain surface cannot be observed entirely for pellets bonded with bentonite and heated at same temperature.

At 1200 and 1300ºC 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).

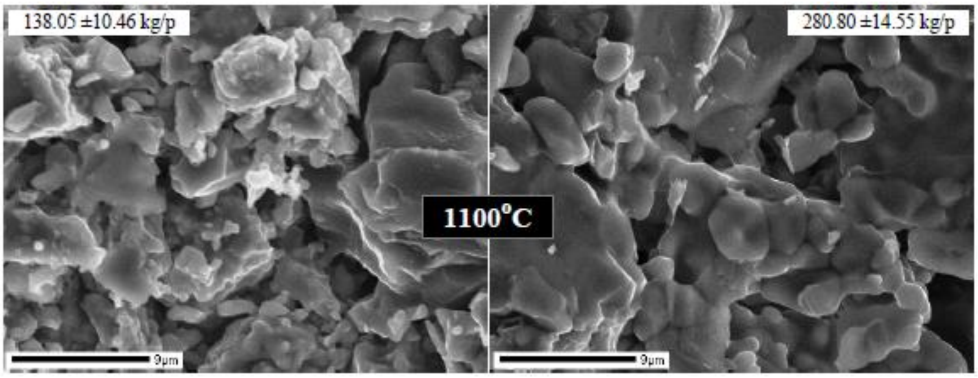

Figure 2. Microstructures of pellets; bentonite bonded at left, calcined colemanite bonded at right.

3.4. Mineralogy of pellets

The X-ray diffraction patterns of magnetite pellets contain either bentonite or calcined colemanite showed no new peaks arising from binder addition (Figure 3). 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.

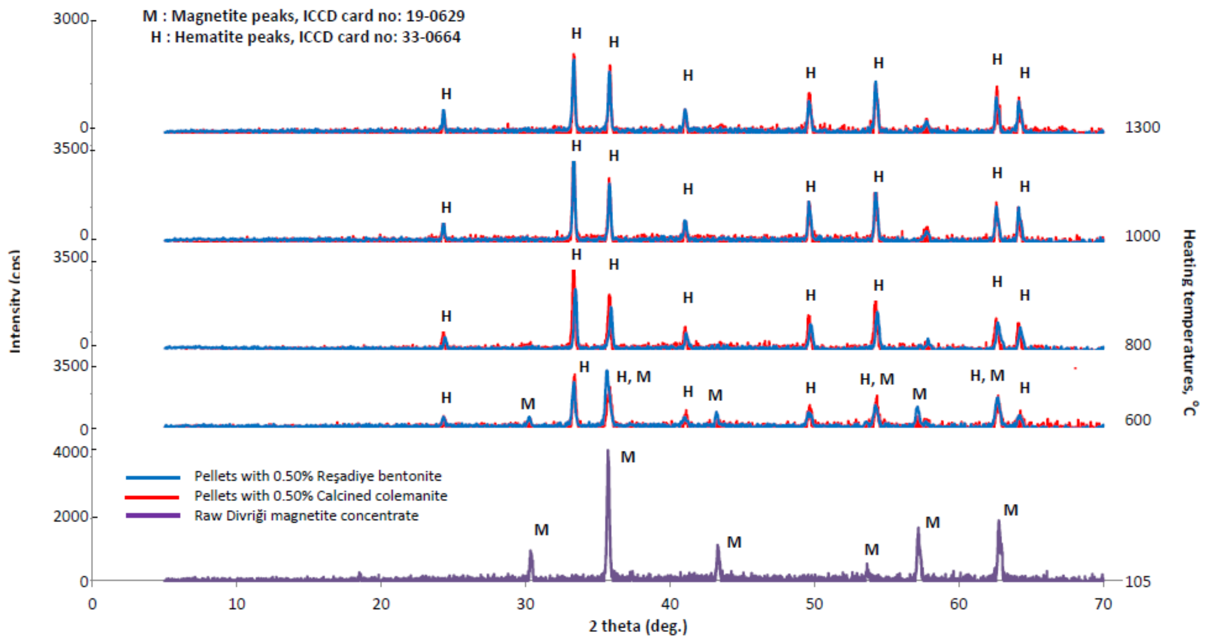

Figure 3. X-ray diffraction patterns of dry magnetite concentrate (purple) and pellets made from this concentrate and produced with 0.50% bentonite (red) or 0.50% calcined colemanite (blue) and heated at 600-800-1000-1300ºC for 30 minutes.

3.5. Chemical content of pellets

The Fe content of magnetite concentrate and product pellets made with this concentrate were determined to be approximately 65.00%. (Table II) The main impurities of concentrate were SiO_2 and Al_2O_3 and they were found 4.87% and 0.09%, respectively. No big differences in SiO_2 and Al_2O_3 contents were detected in pellets with addition of alternative tested binders. Since, the addition levels of binders are not so much. 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 greater than those produced with organic binders or calcined colemanite combination.

Table II. Chemical analyses of product pellets produced with different binder addition.

Binder Codes	Binder Name and Dosages	Total Fe %	SiO_2 %	Al_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	SO_3 %	P_2O_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

4. CONCLUSION

In the first part of the study, the addition of boron compounds into pellet mixture was found to improve the lower preheated and fired pellet physical strength encountered with use of organic binders. According to those results found in first part, pellets with sufficient physical qualities were selected to determine their chemical and metallurgical properties. The results showed that good metallurgical and chemical quality product pellets can be produced with combined binders when compared with bentonite-bonded reference pellets. Swelling indices of reduced pellets were found in the range of industrial desired values. The other reducibility, microstructure and mineralogy of pellets produced with combined binders were found to be comparable to those of bentonite-bonded reference pellets. It was found that, organic binders and boron compounds did not contaminate the pellet chemistry and thus not interfere with iron making, since the organic binders are being eliminated during thermal processes and boron compounds do not contain acidic impurities. As a result, the suggested combined binders can be used as binder in place of bentonite in iron ore pelletizing without contaminating the pellet chemistry.

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