Polymeric Binders for Agglomeration in Ferrous Metallurgy

Willy Cilengi*; Dr Aitber Bizhanov**

*Ex-BASF, Box 2801 Halfway House, South Africa 1685, wcilengi@gmail.com. (Retired in 2021)
**J.C.Steele&Sons,Inc., 710 South Mulberry Street, Statesville, NC 28677 USA. abizhanov@jcsteele.com

Introduction

Agglomeration of natural and anthropogenic iron-containing fine raw materials plays a very important role in ferrous metallurgy, allowing the recycling of significant volumes of sludge and dust, which otherwise could lead to a significant negative impact on the environment and to the ineffective use of large areas for their disposal [1]. The most widely used industrial agglomeration technologies in ferrous metallurgy are sinter production, pelletizing and briquetting.

In two of these technologies, bonding materials play a significant role - in pelletizing and in briquetting. Bentonite is the main binder used in pelletizing. Starch and other materials such as molasses, hydrocarbons, coal and lignosulfonates may not be attractive to the indurated pellet market, which requires a stable, high-volume binder supply [2].

A wide variety of different binders (inorganic and organic) are used in briquetting. The type of inorganic binder used is largely determined by the briquetting method. Currently, the most widespread are the following main industrial briquetting technologies - roller briquetting, vibrocompression and stiff vacuum extrusion. (Figure 1). Large values of the applied pressure in roller briquetting make it difficult to use hydrated binders (cement) due to the limitations on the moisture content of the briquetted mass (no more than 5%); vibrocompression is possible only with the use of a binder showing thixotropic properties (cement); stiff vacuum extrusion allows to agglomerate wet masses (12-16%), allowing the use of hydrated binders.

The use of organic binders also has its limitations in combination with roll briquetting due to the possibility of its extrusion during pressing; there are practically no restrictions on the use of organic binders when using stiff extrusion.

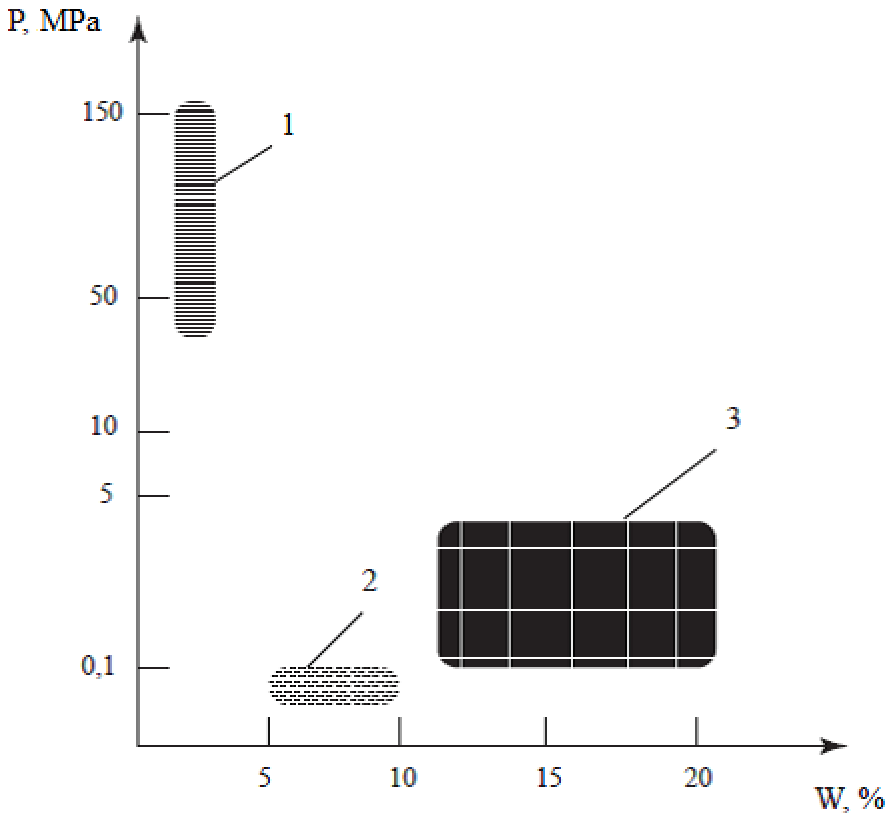


Figure 1 Comparison of technologies of briquetting according to the parameters of briquetting (applied pressure P and moisture content of the charge W). 1 - roller pressing, 2 - vibropressing, 3 – stiff vacuum extrusion

A significant drawback of most inorganic binders is that achieving the required levels of mechanical and so-called "hot" strength (the ability to maintain integrity before melting in a metallurgical furnace) requires a significant consumption of such binders. Therefore, for example, the minimum required amount of cement for the production of blast furnace and ferroalloy briquettes is rarely below 6-7%, and when using vibration compression it exceeds 10-12% of the briquette mass.

The use of polymeric BASF binders makes it possible to achieve the properties of agglomerated products required by metallurgists at a significantly lower consumption, which, as a rule, does not exceed 1% of the briquette mass. It is clear that with the same number of briquettes on the inorganic binder and on the organic BASF binder in the furnace charge, a noticeably larger amount of the leading element enters the metallurgical furnace when using BASF binders.

Comparison of other organic and inorganic binders is given in Table 1.

Table 1 Organic and Inorganic Binders comparison

BINDER TYPE	**POSITIVE FEATURES**	**DRAW-BACKS**
Bentonite	Green strength	High volumes needed. Calorific Value reduction and global ore quality is on the decline
Polyvinyl Alcohol	Waterproof when cured	Capex & Opex to run boiler as well as excessive fines produced during briquetting processes
Polymers	Strength & Waterproofing	Expensive per kilogram although cost of operation are comparable
Molasses + Lime	Cured strength	High volumes needed and can produce excessive fines.

In 1980's – 90's, Allied Colloids published patents on polyacrylamide (PAM) as organic binders. Allied Colloids evolved to become part of BASF through CIBA Holding AG acquisitions in 2009. Two main product types were developed:

- Carboxy methyl cellulose (CMC) polymers
- Anionic polyacrylamides – Alcotac® product range.

Since then BASF developed and implements effective solutions using a number of original organic polymer binders. Currently, BASF's collection of such binders includes the following grades (Table 2):

Table 2 BASF binders for agglomeration

Alcotac® Series	Application Areas	Chemical Nature
Alcotac® CB8, CB11	Nickel, Coal agglomeration	Polyacrylate, aqueous solution
Alcotac® FE14	e.g. coal, ferro-alloys, and mixed fines agglomeration	Anionic polyacrylamide
Alcotac® FE16	Iron ore pelletization	Anionic polyacrylamide blend

Alcotac® CS, CS-A	Iron ore pelletization	Modified anionic polyacrylamide blend

1. **BASF solutions for Pelletizing**

Bentonite as a binder makes it possible to achieve high strength of iron ore pellets due to the increased concentration of silica. However, increased concentration of bentonite dilutes the concentrate and increases the cost of hot metal production. Traditional organic binders (carboxymethylcellulose or polyacrylamides) improve the quality of the charge while decreasing the strength of the raw pellets. The mechanical properties of raw pellets achieved with bentonite have so far not been achieved with organic binders.

Over the past few years, BASF has carried out a large amount of research and made many attempts to develop new chemistry that could significantly improve the performance of organic polymers when using them. The result of these studies was the development of a new organic binder Alcotac® CS, with the help of which it is possible to replace a significant proportion of bentonite in the industrial pelletizing process of iron ore or laterite. Among its other advantages, Alcotac® CS is the only product on the market that effectively operates in conditions of high Ca and Mg salt content in the pelletizer feed.

The utilization of Alcotac® CS increases the mechanical strength of the pellets in a ratio between 2.6 and 4.2 times higher than the strength obtained with Standard HPAM binder (Alcotac® FE16, conventional partially hydrolyzed polyacrylamide). The increase in the mechanical strength of the pellets with the addition of Alcotac® CS in comparison with Standard Hydrolyzed Polyacrylamide HPAM and bentonite is illustrated in Figure 2, [3].

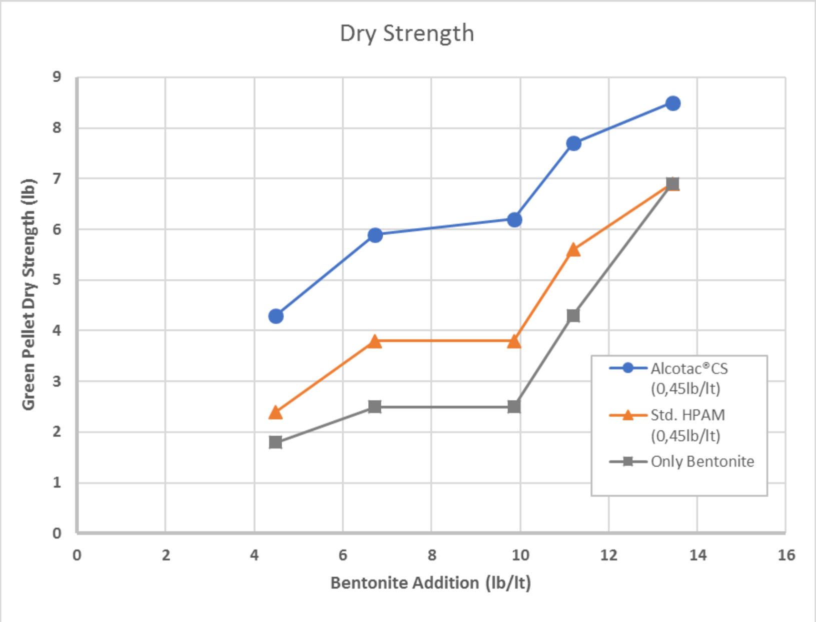
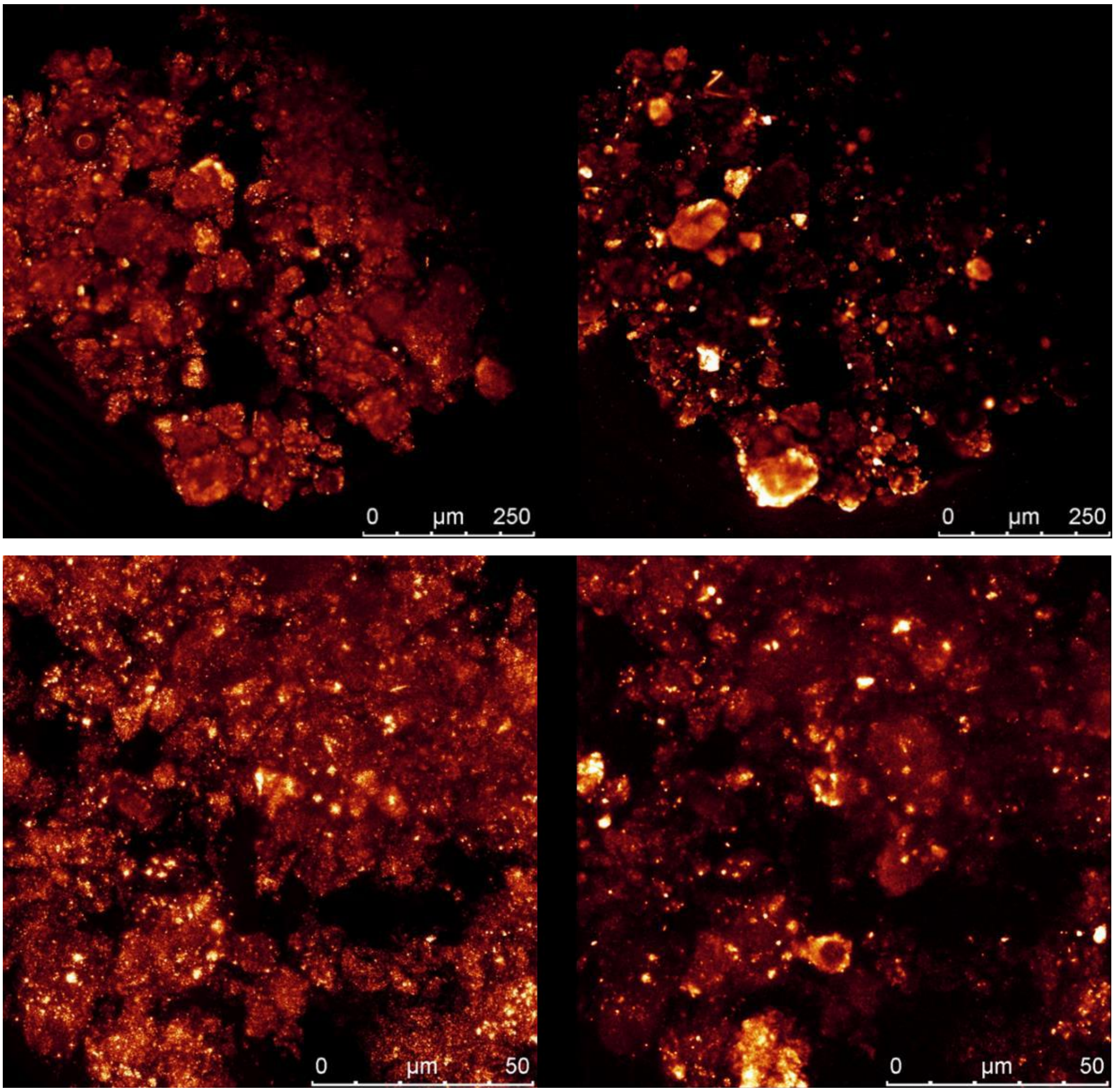


Figure 2 Dry strength of pellets obtained from agglomeration experiments [3].

The floc-type structure is also obtained like in the case of Standard HPAM. However, from the fluorescence images (right side), the degree of adsorption of the Alcotac® CS molecules are much higher than Standard HPAM and it is not only limited to the outer areas of the floc but it is found in the entire the surface of the bentonite. This unique high level of adsorption is congruent with the SEM structures and serves as a hypothesis to explain the superior mechanical properties of the pellets produced with Alcotac® CS and bentonite (Figure 3, [3]).



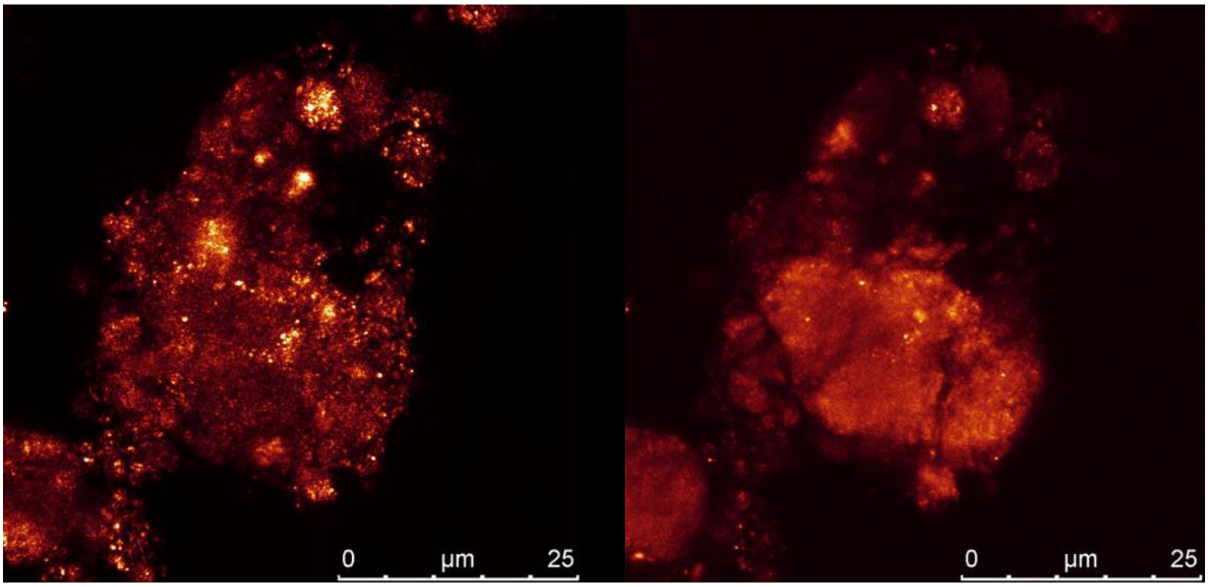


Figure 3. Confocal Laser Scanning Microscopy (CLSM) images of bentonite suspension with Alcotac® CS polymer binder added. Left: reflected light. Right: emitted fluorescence.

2. <u>BASF solutions for Ironmaking Applications</u>

2.1. Study Case 1

The research results have shown the high efficiency of using a BASF binder for agglomeration of iron-containing materials in relation to blast furnace (BF) production. The content of BASF binder in briquettes is 0.3% by weight. On a laboratory extruder, three BASF binders (Alcotac® CB6, Alcotac® CS and Alcotac® FE14) were used for briquetting iron ore concentrate. Bentonite (2% mass) was also added when using CS. Figure 4 shows the process of making extruded briquettes (BREX, [4]) with Alcotac® CB6 (0.3%) and the finished samples. The mechanical strength of the BREX with Alcotac® CB6 and Alcotac® FE14 reached 12-15 MPa, with Alcotac® CS - 20 MPa.

Figure 4 Experimental BREX production and finished samples

Figure 5 shows the BREX on the three mentioned binders after holding at 900 ºC in the furnace. As can be seen, all the samples showed high heat resistance.

Figure 5 BREX after 5 minutes exposure at T = 900 ºC

Results of the mineralogical analysis of raw and reduced at 1100 ºC samples of BREX are presented in Figure 6. The analysis of mineral phases in polished sections was carried out on an automated instrumental complex MLA 650 (FEI Company), including a FEI Quanta 650 SEM scanning electron microscope equipped with an X-ray spectral microanalysis system with two detectors. The main mineral phases were determined by X-ray diffraction analysis using the analytical complex ARL 9900 Workstation IP3600 (combined design "X-ray fluorescence spectrometer with top tube position + θ-θ diffractometer").

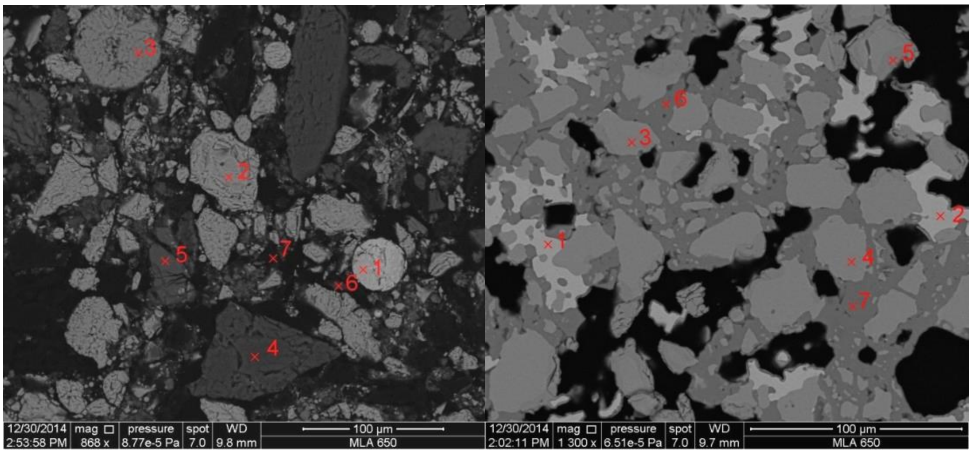


Figure 6 Mineralogical analysis data of raw and reduced BREX sample with Alcotac®CB6. Left - raw BREX (1-iron, 2-magnetite, 3-calcium ferrite, 4-SiO_2, 5-CaO, 6-tridymite, 7-carbon); on the right - reduced briquette at a temperature of 1100 ºC (1,2 - iron, 3,5 - Hematite, 4 - magnetite, 6,7 – olivine)

The Figure 7 shows that in the reduced sample, the integrity of the BREX is ensured by the formation of iron-silicate structures and a metallic framework.

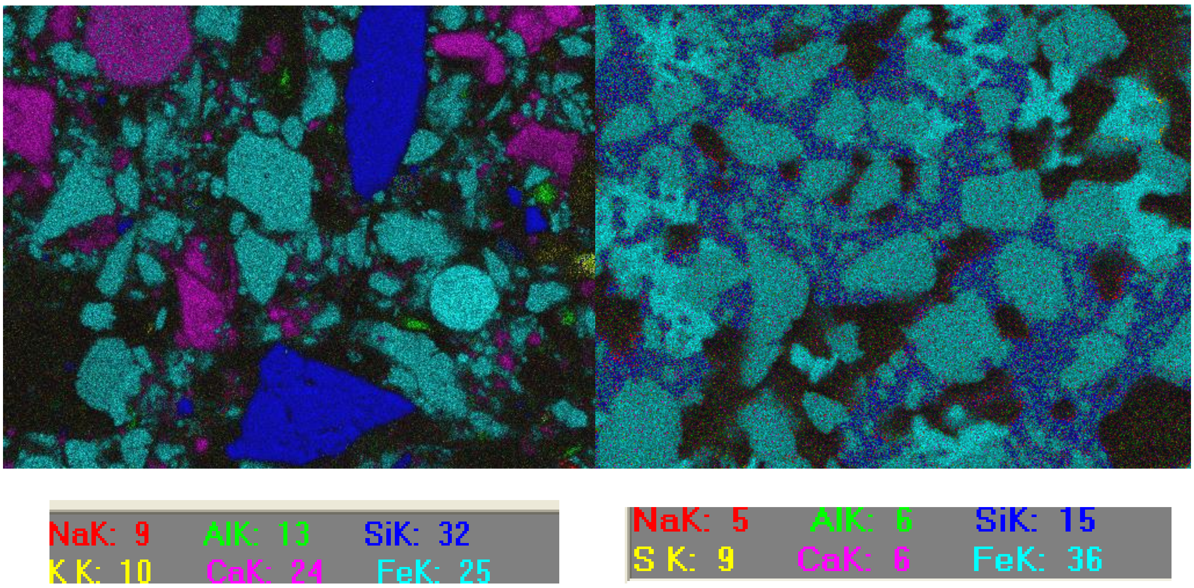


Figure 7 Raw (left) and reduced samples. Image combined in the characteristic radiation of the elements

It is known that the system CaO-FeO-SiO_2 has a eutectic (25% CaO•SiO_2 and 75% FeO•SiO_2) with a crystallization temperature of 1030 °C (Figure 8). There are also fields with a crystallization temperature close to 1150 °C.

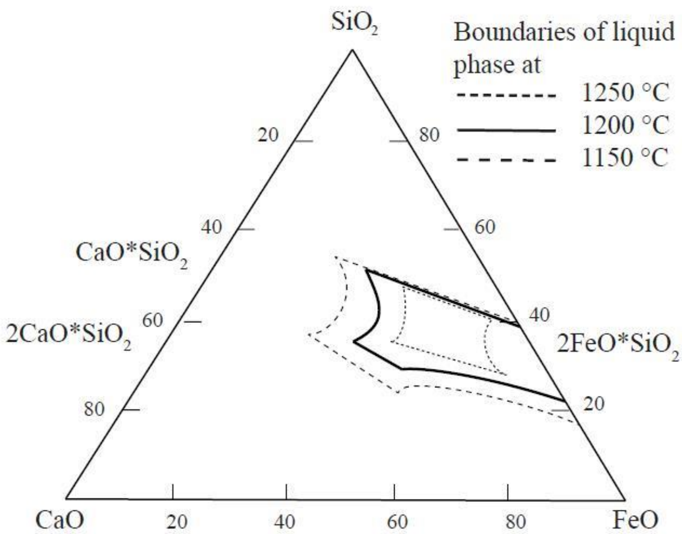


Figure 8 Phase diagram of CaO- FeO- SiO_2

Apparently, because of the limited time in the furnace at a temperature of 1150°C and above, the iron-silicate phase does not reach a liquidus temperature and remained in a plastic condition without violating the integrity of the briquette in the already established frame of metallic iron with a melting point above 1500°C.

Thus, the BASF polymer binder contributes to the preservation of the integrity of blast furnace BREX up to the moment of action of the following strengthening mechanisms - metallization and the formation of iron-silicate bonds.

2.2 Study Case 2

Due to the possibility of closing the sinter plant as part of a steel plant, a study was conducted on the feasibility of operating local blast furnaces on pellets and briquettes. In particular, the metallurgical properties of the BREX bonded by BASF Alcotac® CB6 polymer binder were studied. A minimum of 1% sodium bentonite addition was required as a plasticizer/extrusion aid. The BREX had a circular cross section of 2.5 mm in diameter and 1.5-2.0 mm in length. The average moisture content of the freshly formed BREX was 11%. The vacuum level in the working chamber of the extruder was maintained at 38-48 mm Hg. The BREX remained somewhat elastic during the testing period (up to four days).

Strength was evaluated by drop test. A 460-gram sample of pellets was placed in a sealed 25mm square plastic bag and dropped from two meters onto a steel plate five times. Then the fallen sample was sieved and the mass fraction of particles with sizes less than 5.00 mm was determined. Table 3 shows the results of the drop testing of BREX after 24 hours and four days of strengthening. Figure_ shows negligible amount of fines generated after drop testing.

Figure 9 Drop testing of experimental BREX results (left – fines generated; right – dropped samples)

Table 3 Physical-mechanical properties of BREX

Property	BREX #1	BREX #2
Wet Base Moisture (WBM), %	12.3	11.6
Density, kg/m^3	2.60	2.90
Drop strength (green), %	0.9	0.8
Compressive strength 24 hours (MPa)	1.1	1.3
Compressive strength 4 days (MPa)	1.7	2.4

These samples were also heated to 900°C, returned to ambient conditions and then observed for general appearance and integrity (Figure 10). Good thermal shock stability was demonstrated.

Figure 10 Appearance of experimental BREX (left – raw; right – partially reduced) after heating to 900°C

Tumble testing in accordance with ISO 3271: 2015 showed that the average impact strength (tumble index, TI) of BREX is not less than 85%, and abrasion resistance (abrasion index, AI) - not more than 12.3% (Table 4).

Table 4 Tumble testing results

Initial briquette weight	$\mathbf{m_0}$	**grams**	15012
+ 6.30 мм	$\mathbf{m_1}$	**grams**	12917
+ 500 microns	$\mathbf{m_2}$	**grams**	239
- 500 microns	$\mathbf{m_3}$	**grams**	1690
$\mathbf{m_0-m_1-m_2-m_3}$	**d**	**grams**	166
$\mathbf{d/m_0}$	**D**	**%**	1.1
$\mathbf{(m_1/m_0)}$	**TI**	**%**	86.0
$\mathbf{(m_0-m_1-m_2)/m_0}$	**AI**		12.4
		TI	86.2
		AI	12.3

The tumble test results show that the BASF binder is capable of imparting the required impact strength and abrasion resistance to blast furnace briquettes.

2.3. Study Case 3

A ferro-minerals trading company with access to over 35 million tons of low-grade magnetite (~ 53% Fe) and planning to build a processing plant to upgrade to an Fe content of over 63% has studied the agglomeration process (extrusion) using organic binders.

The material with a moisture content of 0.9% WBM was wetted to 8.5% WBM. Alcotac® FE14 and Alcotac® CB6 were selected for the tests. The mixer was charged with 12 kg of finely dispersed magnetite. While mixing, 1 kg of water was added and mixed for 3 minutes. Then 72 g of Alcotac® FE14 was added and mixed for 3 minutes. The mixture was then extruded as 18 mm diameter BREX, which were then placed in a drum that rotated 10 times for 30 seconds. Thereafter, the BREX were fired at 250 °C for 3 minutes. A batch of 12 kg was repeated 5 times.

The rate of strength gain of the BREX is from 297 N for green briquettes to 383 N after a day of aging, 652 N after three days and 1112 N after a week. After three minutes of firing at a temperature of 250 C, the strength increased to 1230 N.

Another sample on which Alcotac® CB6 was tested (0.60 % and addition of bentonite at 1 %). The green strength of the sample - 352.2 N and after 20 minutes in muffle furnace at 1100 °C strength increased to value 3214.4 N.

Figure 11 shows the green and fired samples. The samples do not blister or crack but remain in good condition.

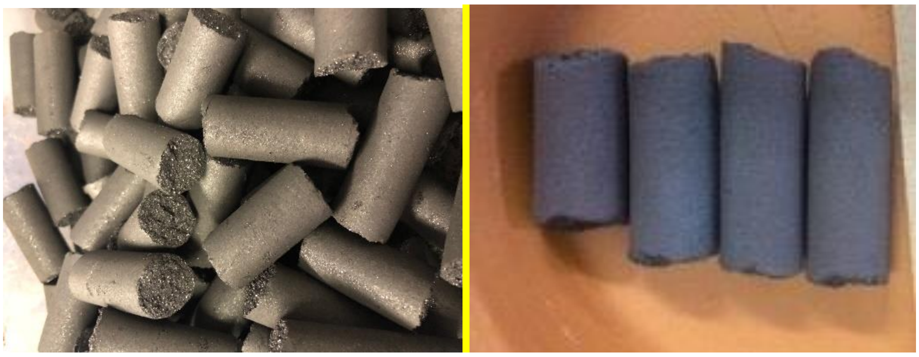


Figure 11 Green (left) and fired Magnetite BREX

3. <u>BASF solutions for Ferroalloys Production</u>

3.1 Study Case 4

Another study for the benefit of a mining trading company was carried out using a BASF binder for extrusion agglomeration of chrome-containing fines. The material was successfully extruded using the BASF Alcotac® FE14 at 0.2% w/w dosage and 18.3% w/w moisture. The BREX produced showed good green and dry compression strength. The hot test consisted in introducing BREX into the muffle oven at 1200 °C for 15 minutes. The BREX came out of the oven glowing, intact and stable.

The rate of compressive strength gain of the BREX is from 279 N for green briquettes to 311 N after a day of aging, 529 N after three days and 913 N after a week. Compressive strength after 2 weeks reached values of 1128 N and 1837 N after three weeks hardening. After only three minutes of firing at 250 °C, the strength of green BREX increased to 1230 N. A quick hot test performed on BREX at 1200 °C after Day 14 in a muffle oven showed BREX glowing, stable and intact. The compressive strength of the BREX extracted from the furnace was 2526.44 N. The 12 figure shows the appearance of briquettes when tested for thermal stability and immediately after being removed from the oven.

Figure 12 Appearance of the BREX during thermal stability testing (left) and after extraction from the furnace

Cured BREX were placed in water in a beaker for 24 hours. They were removed from water, weighed again and showed no mass increase or loss.

Conclusions

The study cases as elaborated above have demonstrated the possibility for efficient usage of the BASF organic binders in the ferrous metallurgy. The usage of BASF organic binders can be combined or complimented with inorganic binders such as sodium bentonite or other materials to increase thermal stability and to improve the behavior in the furnace (slagging and easing of different metallization phases). The low dosage of BASF organic binders required in the ferrous material, increase the charge of desired material into the furnace, which indicates there is an economic benefit to be obtained.

References

1. A. Bizhanov, V. Chizhikova Agglomeration in Metallurgy. Springer, Berlin, 2020, p 454

2. T. C. Eisele, S. K. Kawatra A Review of Binders in Iron Ore Pelletization. Mineral Processing & Extractive Metall. Rev., 24: 1-90, 2003

3. A. Villanueva, S. Hoff, A. Michailovski: Novel Binder Technology from BASF: Study of Bentonite Modification. SME Annual Meeting Feb. 25-28, 2018, Minneapolis, MN

4. BREX. Certificate of trademark (service mark) No. 498006, application No. 2012706053 of 02.03.2012. Right holder AM Bizhanov. (in Russian)