

Influence of the Binder on the Mechanical Properties of the Chromite Self-Reducing Pellets

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Abstract

Cold and hot mechanical strengths of the chromite self-reducing pellets agglomerated using different binders was evaluated by means of compression and repeated falling tests. The behavior of hot strength was evaluated, actually at room temperature, after the pellets were submitted at thermal treatment at 1173, 1273, 1373, 1473 and 1573K (900, 1000, 1100, 1200 and 1300° C). The binders used were: bentonite, hydrated lime, molasses, carboxymethylcellulose (CMC) and sodium silicate. Initially materials (chromite, ferro-silicon, petroleum coke and binders), were characterized by chemical and particle size analysis. After that, the materials were agglomerated in the form of pellets P1, P2, P3, P4, P5, P6, with additions 0, 0.25, 0.5, 0.75, 1% bentonite and 1% bentonite with 0.2% CMC, respectively. Pellets P7, P8, P9, P10, P11, with additions of 0, 0.25, 0.5, 0.75, 1% bentonite with 12% hydrated lime, respectively. Pellets P12, with additions of the 2% molasses and 8% hydrated lime. Pellets P13, P14 and P15 with additions 1, 2 and 4% sodium silicate respectively. The compression test of these green pellets were measured during 28 curing days. After that they were dried and also submitted for the thermal treatments to evaluated the strength behavior after these treatments. The best result was found with the pellet P15, containing 4% sodium silicate as binder, presented a cold compression strength of 5 kgf/pellet and after thermal treatment at temperatures at 1173 and 1273K the compression strengths were of 15 kgf/pellet and did not decrepitate.

Keywords: ferro-chromium; self-reduction; self-reducing agglomerates; chromite.

1. Introduction

The production of high carbon ferrochromium using self-reducing pellets by the self-reduction process presents technological advantages due to the intimate mixing between oxide and reducer, resulting on fast reducing reaction rate achieving unitary reaction fraction at 1500°C (1773K) on 5 minutes⁽¹⁻⁶⁾. The chromium recovery is improved, reaching 95% in comparison with 90% at conventional smelting process. The self-reduction processes are not new and presently many processes are based on this principle, such as: Tecnoled, ITmk3, Fasmets, Inmetco, PTC and others. In these processes, two characteristics must be satisfied: The first is the transfer of heat to agglomerate because the overall reaction is endothermic and there is difference on reduction progress of particles chromite from the surface and inner of the agglomerate (self-reducing pellet)⁽¹⁾.

The second, the self-reducing pellets cannot be fired, that is the agglomerate should get the strength at low temperature⁽¹⁻⁵⁾.

Production of chromite self-reducing pellets using Portland cement as binder requires high amounts of it (more than 10%) to achieve enough cold strength for industrial use. Another critical point is its loss of strength when submitted at high temperature. This is because hydration reactions that occur during curing suffer dehydration at the temperature range of 873-1173K (600-900°C). In this range, by calcination, decomposition occurs with loss of chemical bonds decreasing the hot strength.

Therefore the evaluation the properties of the pellets is very important, since chromite self-reducing pellets of high quality and high content significantly increase the production of the furnace. This paper tries to evaluate the strength of self-reducing pellet with different binders.

1.1. Characterization of the pellets

The experiments of the pellet characterization provide parameters to predict the behavior of the binder when used in industrial scale and try to predict the behavior of the pellets obtained with ore or concentrate with respect to handling and their behavior in the reduction furnace.

1.2. Binders used in the production of conventional iron ore pellets

Bentonite is currently the binder used for pelletizing iron ore, since the clays have the ability to absorb water through their structural layers and form gels. The lime is an important binder in pelletizing contributing to the improvement of the quality of green pellets. Sodium silicate is used as a binder for foundry sands. In addition to the lime and clays, several other compounds have been used as binders for pelletizing as hydrated magnesium chloride, magnesium oxide and calcium chloride. The main reason for using organic reagents comes from the fact that after firing pellet, these reactants are eliminated without leaving appreciable residue. This can be of fundamental importance for the production of some types of steel, where the amount of impurities should be minimal. In addition, obviously search for new reagents that may make the process more economical. In fact, although in general, the cost of organic binder per unit mass is more expensive than inorganic as bentonite, the amount added is much lower. The use of cellulose derivative reagent consisting of a long chain molecules with many carboxyl and hydroxyl radicals, wherein the binding agent is carboxymethyl cellulose sodium, having as main characteristic their high viscosity and higher water absorbency.

These organic products do not contain silica and its additions do not dilute the iron, after firing of the pellets and also do not leave residues. They present great homogeneity, reducibility improvement due to increase of porosity after firing. The main disadvantages, besides the high cost, is that organic binders are highly hygroscopic, easily polymerizing in water and produces pellets with lower compressive strength, both dry and green. The hot and cold properties of the chromite self-reducing pellets are functions of several variables. Among the main highlights are: particle size distribution of raw materials (ore or waste, coal or coke, binders and fluxes); porosity of raw materials, chemical compositions of raw materials; composition of the pellet itself; pelletizing process and pellet size. It is required currently that 90% of the pellets be between 9 and 16 mm and a maximum of 5% below 5 mm diameter. In this work it was studied the behavior of the chromite self-reducing pellet with minimum amount of binder and to present enough strength for handling.

2. Materials and methods

The materials used were Brazilian chromite fines, petroleum coke fines, ferrosilicon fines and as binders: bentonite; molasses; lime and sodium silicate. The materials were mixed and pelletized. Table 1 and Table 2, show the chemical composition of materials and the composition of the self-reducing pellets respectively. The pellet size was calibrated to 15mm diameter. Molasses presented a weight loss of 88-92% by calcination, in air, at 1000°C (1273K). The chemical analysis of the residue of 8-12%, after calcinations, is shown in the Table 1. The carboxymethyl cellulose (CMC) is an organic compound derived from cellulose with high viscosity and solubility in water and is often used as a stabilizer and binder.

After curing and drying, the pellets were evaluated the cold and hot strength by compression and successive falls tests.

Figure 1 shows the equipment (furnace) used to submit the pellets for isothermal cycles (1173, 1273, 1373, 1473 and 1573K).

The equipment used for strength, sputtering and repeated falls experiments of pellets, it is shown in Figure 2 a, b and c, respectively.

2.1. Compression test of the green self-reducing pellets

Compression green strength was measured for green pellets during curing time, every 4 days until 28th day. The procedure used was: 15 of pellets, with diameter of 15 mm, were subjected to compression test one by one. The results shown are the average value.

2.2. High temperatures compression test.

The chromite self-reducing pellets, previously dried at 393K (120°C) during 3 hours, were submitted at temperatures thermal cycles of 1173, 1273, 1373, 1473 and 1573K to evaluate the pellets compression strength, after cooling down to room temperature. Procedure for the test was the same as described above for green pellets

2.3. Decrepitation test

Procedure used for test: 32 pellets are dried at 413K, during 4 hours, and then subjected a thermal shock, that is, the dried pellet at room temperature is submitted directly to the test temperature, for example, at 1273K, keeping it during 5 minutes at the temperature and then removed to calculate the decrepitation index (DI):.

$$DI = \text{pellets decrepitated number} \times 100/32$$

2.4. Repeated falls test

Procedure used for repeated falls test: 15 pellets, one by one is dropped from a height of 45 cm onto a thick steel plate repeatedly until the appearance of cracks. The result is the number of falls of each pellet support up to crack, not included the fall where it occurred. The average from 15 results was considered the final result for each set of test.

2.5. Compression strength of dried pellets

A set of 15 pellets, dried at 393K for 3 hours and after cooling in air, was tested with the same procedure already described.

3. Results and Discussion

3.1. Compression strength of dry pellets

The results of compression strength of 15 different pellets composition are shown in Figure 3. It was observed that the pellet P15, with 4% sodium silicate as binder, presented highest compression strength (5 kgf/pellet).

3.2. Compression test of the self-reducing green pellets

Figures 4-6 show the compression strength of the self-reducing green pellets, measured every four days until the 28th.

Figure 4 shows that strength of the pellets with additions of bentonite (0 - 1%), present small difference in strength (in the range of 1-2 kg-f/pellet) with bentonite content in the range of 0.25-1%, but good improvement in comparison with no bentonite addition. Pellets with additions of 1% bentonite and 0.2% CMC reached strength in the range of 4-3 kg-f/pellet, probably due to an increase in viscosity of the mixture. It is observed that almost no influence of curing days on the strength.

Figure 5 shows the pellets strength with additions of bentonite (0 - 1%) with additions 12% hydrated lime in the self-reducing pellets P7, P8, P9, P10 and P11. They show a small increase of strength with curing days, reaching a strength 2.6 kg-f/pellet for the pellet 11 (1% bentonite, 12% hydrated lime). Again the addition of bentonite improves the strength but the influence of content of it in the range of 0.25-1% is small. P12 pellet (2% molasses and 8% hydrated lime) presented a compression strength 5.5 kg-f/pellet, which is more than double of obtained with bentonite. The results are within the expected ones.

Figure 6 show the compression strength results of pellets P13, P14 and P15 with additions of 1, 2 and 4% sodium silicate, respectively. It was observed a decrease of compression strength for the three investigated pellets, with the curing days, probably due to hygroscopic behavior of sodium silicate absorbing moisture. The influence of content of sodium silicate is high. P15 containing 4% of it presented highest strength.

3.3. Experiments of mechanical behavior at high temperatures

3.3.1. Influence of binder

Figures 7- 11 show the compression strength of the self-reducing pellets P1-P15, at temperatures of 1173, 1273, 1373, 1473 and 1573K, observing the influence of the binder. Figure 7 show that the P15 pellet reaches compression strength of 15 kg-f/pellet after two hours at 1173K.

Same behavior can be observed at temperatures 1273, 1373, 1473 and 1573K of self-reducing pellets P1-P15, reaching the compression strength of 15.5, 17, 17.5 and 19 kg-f/pellet respectively, as shown in Figures 8, 9, 10 and 11. Self-reducing pellet with 4% sodium silicate (P15) gave the best results of cold and hot compression strength.

3.3.2. Micrographics Analysis

Microscopic analysis (SEM with microanalysis) were made for P14 and P15 pellets, due to their results of strength

Figures 12 and 13 show the central portion of the pellets after submitted at 1573K for 120 minutes. It can be seen that the phase composition is similar (Tables 3 and 4) with formation of an incipient slag formed, mainly of silica (SiO_2) dissolving chromite particles (point 1, Figures 12a and 13a) forming a silicate with aluminum, magnesium, chromium and iron oxides (point 4, Figures 12b and 13b).

The high strength obtained with sodium silicate, within these set of binders and their contents tested, is credited to an incipient slag formation.

3.3.3 Decrepiation experiments.

The pellets P1-P15, have been tested at 1173, 1273, 1373, 1473, 1573K for 5 minutes. None of them presented decrepitation (DI = 0)

3.3.4 Repeated falls tests

All the pellets presented good behavior for this test. The best result was obtained with dried pellet P15 (4% sodium silicate), which supported an average of 5 falls. **4**

4. Conclusions

The results obtained from the experiments can be concluded that:

- a) The best result of the dry pellets compression strength was obtained by pellets, with 4% sodium silicate (5 kg-f/pellet).
- b) The best result of cold compression strength after 28 curing days was obtained by P12 pellets, with 2% molasses and 8% hydrated lime (5.5 kg-f/pellet).
- c) The best results of the hot compression strength was provided by P15 pellets (4% sodium silicate), with results of 15 and 20 kg-f/pellet at 1173 and 1573K, respectively.
- d) All tested pellets did not present decrepitation.
- e) Analysis by EDS shows the pellets P14 and P15 have incipient formation of slag phase (silicates), which confer higher compressive strength

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Table 1: Chemical composition of materials (% wt).

Components	Chromite	Petroleum coke	Fe-Si	Sodium silicate	Bentonite	Molasses	Lime
Cr ₂ O ₃	41.2						
FeO	16.9				7.3	0.6-2.0	
SiO ₂	5.7			27.6	55.7	27.6	1.9
Al ₂ O ₃	17.3				28.4	0.2-1.0	
MgO	15.6				2.9	4-8	0.5
CaO	0.4				1.0	60-70	90
Volatil material		10.8					
Fe total	13.1		25.0				
P	0.007						
C fixed		88.8					
Ash		0.4					
S		0.8					
Si			4.16				
Ca			0.14				
ZnO					2.75		
Na ₂ O				8.6			
H ₂ O				63.5			
Others						0.6-1.2	7.6

Table 2: Composition of the pellets (% wt)

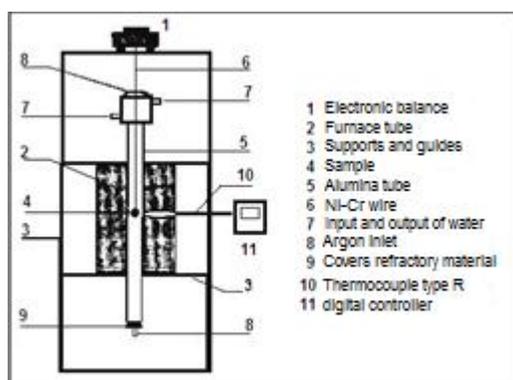
Type	Chromite	Petroleum Coke (20% excess)	Fe- 75%Si	Sodium silicate (hydrated)	Bentonite	Molasses	Hydrated lime	CMC
P1	80.08	17.92	2	-	0.0	-	-	0.0
P2	79.88	17.87	2	-	0.25	-	-	0.0
P3	79.67	17.83	2	-	0.50	-	-	0.0
P4	79.47	17.78	2	-	0.75	-	-	0.0
P5	79.26	17.74	2	-	1.0	-	-	0.0
P6	79.10	17.70	2	-	1.0	-	-	0.2
P7	70.28	15.72	2	-	0.0	-	12.0	-
P8	70.08	15.67	2	-	0.25	-	12.0	-
P9	69.87	15.63	2	-	0.50	-	12.0	-
P10	69.66	15.59	2	-	0.75	-	12.0	-
P11	69.47	15.53	2	-	1.0	-	12.0	-
P12	71.90	16.10	2	-	-	2.0	8.0	-
P13	79.26	17.74	2	1 (2.7)	-	-	-	-
P14	78.45	17.55	2	2 (5.5)	-	-	-	-
P15	76.81	17.19	2	4 (11)	-	-	-	-

Table 3: Chemical composition P14 pellet (core), analyzed by EDS in SEM. Temperature of 1573K (120 minutes). Figure 12.

% weight	O	Mg	Al	Si	Ca	Cr	Fe
1	12.26	11.73	15.25	0.73	0.29	41.78	17.95
2	18.92	5.29	12.36	0.42	0.27	40.93	21.82
3	27.06	23.38	1.47	42.21	0.39	1.24	4.25
4	20.29	0.52	15.99	60.57	1.41	0.77	0.45
5	Resin						

Table 4: Chemical composition P15 pellet (core), analyzed by EDS in SEM. Temperature of 1573K (120 minutes). Figure 13.

% wt	O	Mg	Al	Si	Ca	Cr	Fe
1	14.62	16.66	15.57	0.27	0.31	41.40	11.16
2	26.40	26.98	1.22	40.08	0.20	1.49	3.63
3	14.40	13.98	14.22	0.08	0.20	41.49	15.63
4	20.26	23.10	3.33	43.14	2.51	2.09	5.58
5	Resin						



(a)



(b)

Figure 1. (a) Schematic representation of the electric resistance furnace. (b) View of the resistance furnace and its auxiliary equipment.

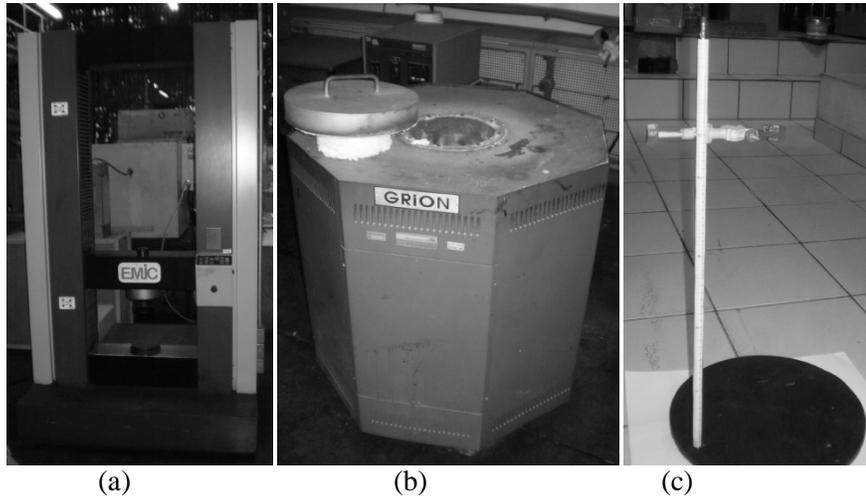


Figure 2. (a). Press EMIC, (b). electric resistance furnace, (c). equipment for repeated falls test.

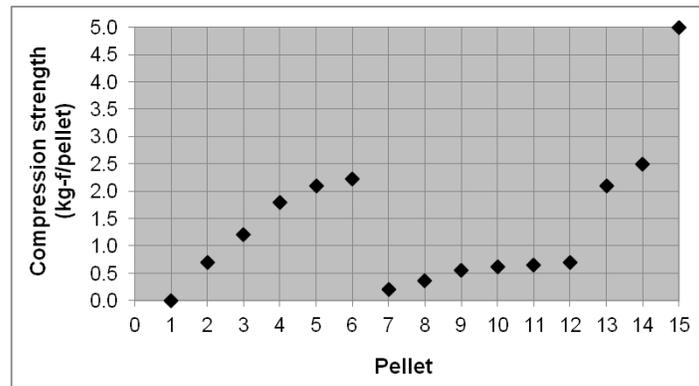


Figure 3. Compression strength of the pellets after dried at 393K during 3 hours.

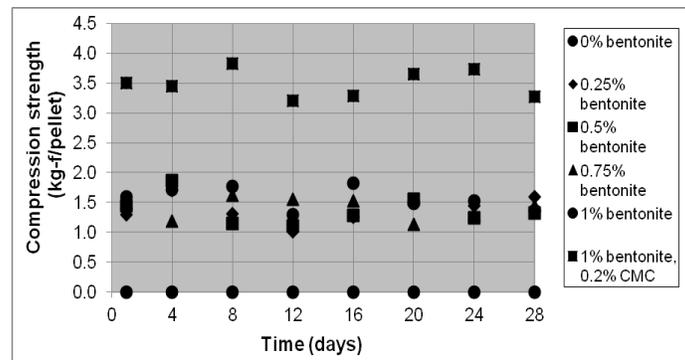


Figure 4. Compression strength of the chromite self-reducing pellets (P1, P2, P3, P4, P5 and P6) bonded with 0, 0.25, 0.5, 0.75 and 1% of bentonite respectively and 1% of bentonite with 0.2% of CMC

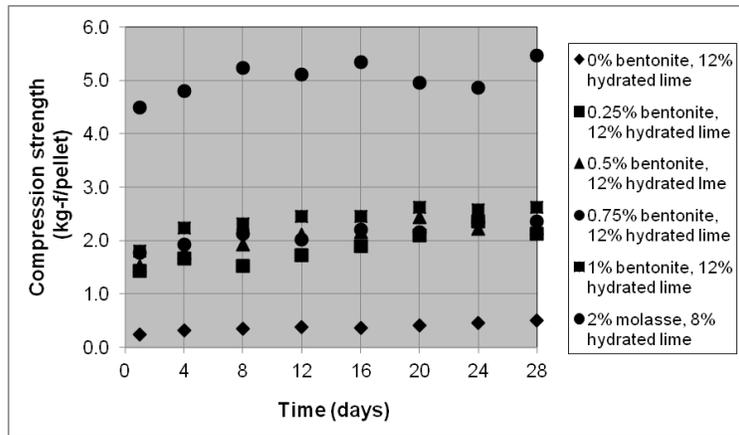


Figure 5. Compression strength of the chromite self-reducing pellets (P7, P8, P9, P10, P11 and P12) bonded with 0 (bottom), 0.25, 0.5, 0.75 and 1% of bentonite with 12% hydrated lime (all at middle) respectively and 2% of molasses with 8% of hydrated lime. (highest)

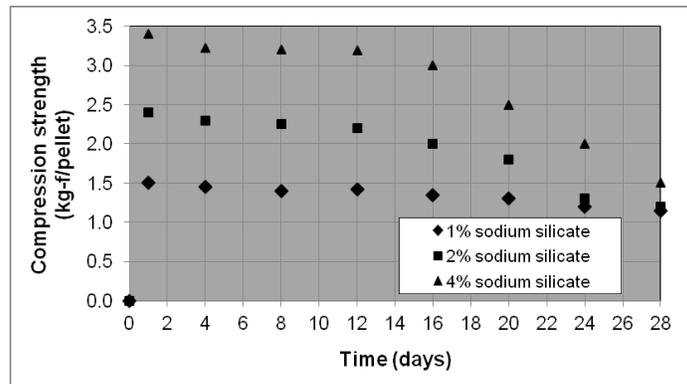


Figure 6. Compression strength of the chromite self-reducing pellets (P13, P14 and P15), bonded with 1, 2, and 4% of sodium silicate.

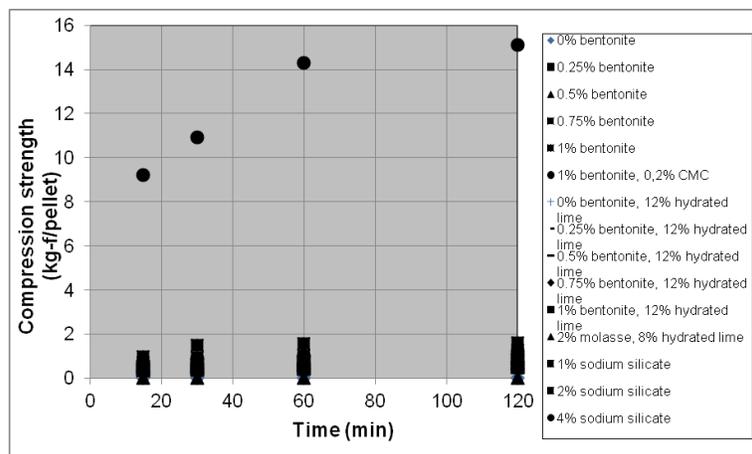


Figure 7. Compression strength of the pellets (P1-P15) at 1173K. P15 is the highest.

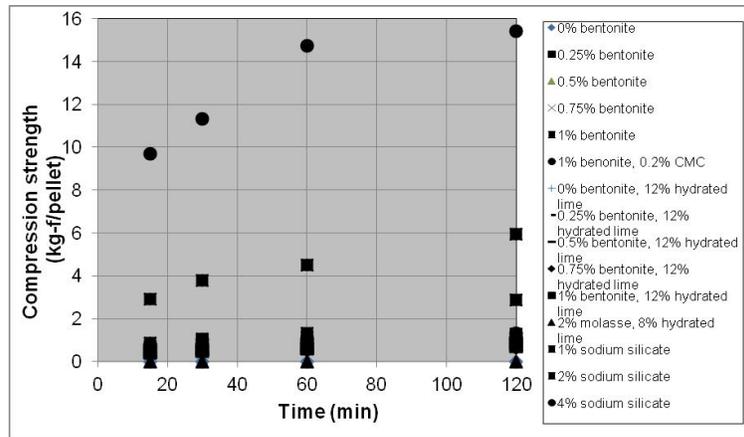


Figure 8. Compression strength of the pellets (P1-P15) at 1273K.

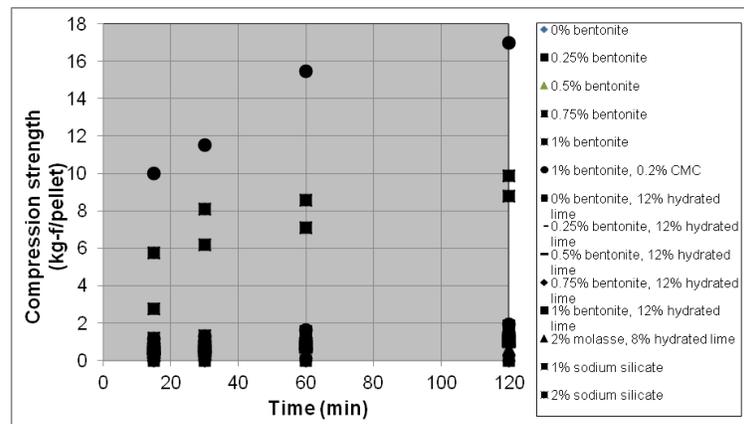


Figure 9. Compression strength of the pellets (P1-P15) at 1373K.

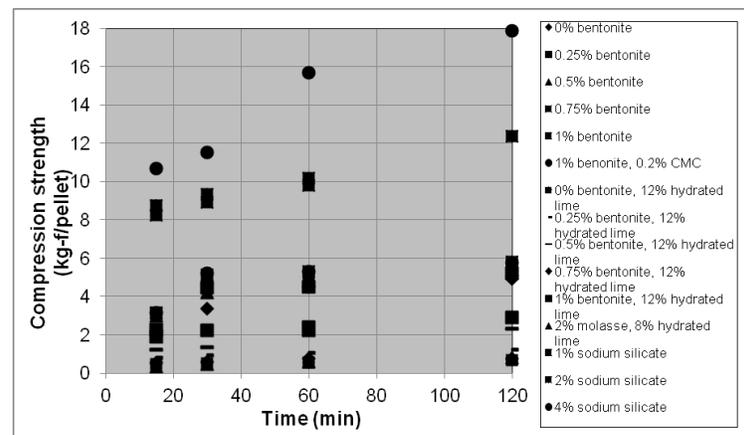


Figure 10. Compression strength of the pellets (P1-P15) at 1473K.

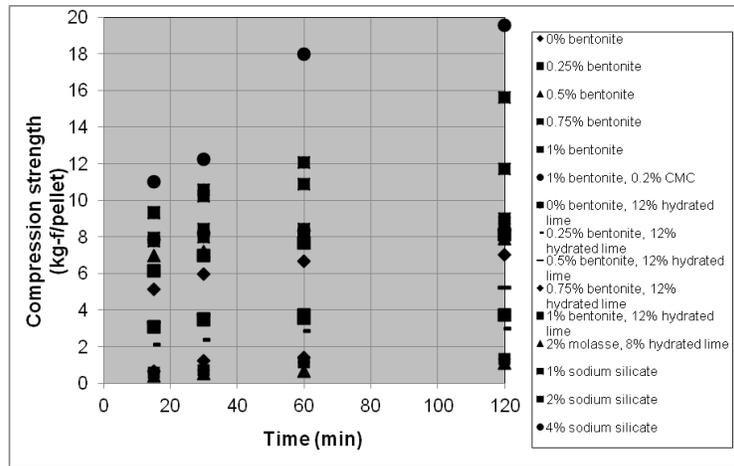


Figure 11. Compression strength of the pellets (P1-P15) at 1573K.

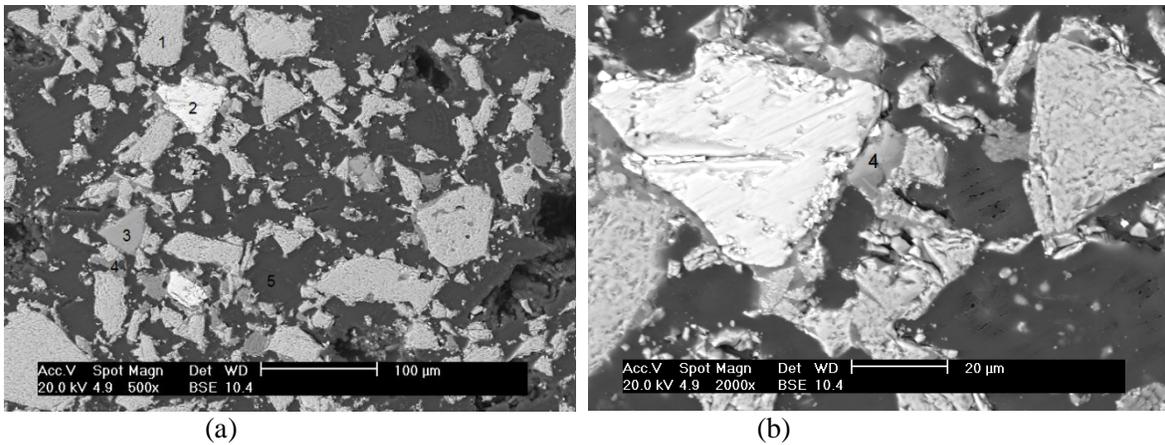


Figure 12. Backscattered electrons P14 pellet (2% of sodium silicate) at 1573K, 120 min. (a) 500X, (b) 2000X.

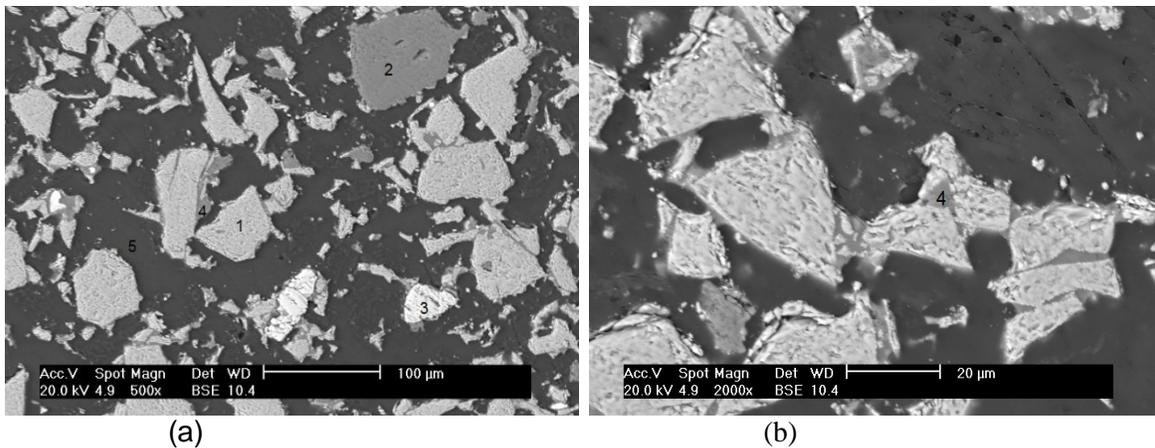


Figure 13. Backscattered electrons P15 pellet (4% of sodium silicate) at 1573K, 120 min. (a) 500X, (b) 2000X