

Metallurgical Properties of Iron Ore Pellet when Using Bentonite Modified by Soda

*Tran Thi Thu Hien**, *Nguyen Quoc Hoang*, *Nguyen Van Thanh*,
Le Viet Quan, *Nguyen Duc Ha*, *Dao Hoang Anh*

School of Material Science and Engineering, Hanoi University of Science and Technology, Ha Noi, Vietnam
**Corresponding author email: hien.tranthithu@hust.edu.vn*

Abstract

The study reported the ability to use soda-modified bentonite applied to the pelletization of iron ore and its effect on metallurgical properties such as green pellet strength, compressive strength and degree of reduction. The properties of the pellets were used in different binders for comparison as bentonite, soda-modified bentonite (1, 2 % per weight of bentonite), and soda. Green pellets were tested for drop numbers. After drying and atmosphere firing, pellets were reduced at 900, 1000 and 1100 °C for 30, 60 and 120 minutes. The obtained results show that when using 1 % soda-modified bentonite as a binder in the pelletization process gives the highest degree of reduction, appropriated green pellet strength and compressive strength. In addition, modifying bentonite by using soda not only increases the adhesion of bentonite without affecting the structure of bentonite but also helps increase the degree of reducibility of iron ore pellets. This modified bentonite by soda can be applied in pellet manufacturing to reduce the bentonite as the binder in pelletization process.

Keywords: Iron ore pellet, metallurgical properties, modified bentonite, soda.

1. Introduction

Nowadays, the iron and steel manufacturing industry plays an important role in the country's modernization and industrialization. The development of this industry requires changing technology to improve product quality. Sintered or/and pellets of iron ores are used often to get better metallurgical properties [1, 2]. Therefore, the manufacturing of sintered ore and pellets is promoted development. Using a binder in iron pellets is an effective way to enhance its quality. The quality of the final product pellets broadly depends on green strength, the type or/and amount of binders, fluxes and additives, and firing conditions. The quality of green pellets depends on raw charging materials like mineralogy, chemistry, size of ore fines, and balling parameters such as initial feed size, moisture content, and size distribution. Physical and metallurgical properties of product pellets depend on the amount and type of binder and flux additions, induration parameters like firing temperature and time, etc. Ingredients of the green pellets react together, during firing, to form different phases and microstructures [3].

In recent years, several different binders have been researched for use in pelletization [1-6], while bentonite is still used widely in real manufacturing. Bentonite is a natural clay mineral, belonging to the smectite group with characteristic properties, therefore, bentonite has potential applications in the

industry. With the development of industry, bentonite is used to make absorption materials, create catalytic agents in organic conversion, in the oil and gas industry and apply in environmental treatment. However, using bentonite increases SiO₂ content, Al₂O₃ in pellets increases consumption energy in metallurgy because of slag increase [7]. The problem is how to decrease bentonite content and still ensure the stability and metallurgy properties of pellets. Some recent research shows the effect of modified bentonite on pellets' mechanical properties [6-9]. On the other hand, various types of binders have been investigated for use in iron ore pelletization. The development of different binders gave good bentonite quality and lower cost without contributing any harmful contaminants to the iron ore [10].

Modified bentonite was used for research and reality applications. So that researching to use these valuable resources and make them become effective material in different fields of a national economy is the duty of scientists. The use of modified bentonite with all the advantages has a set of disadvantages which include dilution of pellets, high cost and scarcity of a binder, high costs for its transportation, substantial energy costs for preparing modified bentonite for the technological process. As an alternative, a modified agent such as soda was investigated.

This research will examine some metallurgical properties such as reducibility, green strength,

compressive strength, structure and morphology of pellets when using modified bentonite as a binder with different soda amounts. Green pellet strength and reducibility are important parameters for the productivity of iron ore pelletizing [6]. The green pellet strength and reducibility, however, are influenced by changes in the crystal structure and morphology of pellets. The results show the change in green pellet strength when changing the soda contents, the degree of reduction and structure in different temperatures of modified bentonite using soda and different reduction times. X-ray diffraction and scanning electron microscopy (SEM) were used for characterization.

2. Experiment

The chemical compositions of raw materials used in this research are presented in Table 1. The experimental procedures are described as follows.

To begin with, soda was dissolved in water, then mixed with bentonite to create a 35 - 40% moisture mixture and kept for 5 minutes. After that, the samples were dried at a given temperature (105 °C) for a certain time (2 hours). Finally, the dried modified bentonite was ground to a size below 2 mm. Soda-modified bentonite was obtained.

Several amounts of soda were examined to investigate the effect on the metallurgical properties of iron ore pellets. Soda with a mass percent is 0, 1 and 2% to the total weight of bentonite (signed as S0, S1 and S2 respectively) was used and 1% soda-modified bentonite (B1) with fine iron ores as signed B1S0, B1S1 and B1S2 respectively. One sample only used 0.1% soda (B0S01) as a binder without bentonite to investigate the effect of the binders with/without soda-modified bentonite.

Pellet production: Pellets were made of bentonite/modified bentonite binder and fine iron ore

mixtures in a pelletizer. The amount of water used to pelletize is usually about 9 - 11%. The diameter of pellets in 12 - 14 mm was selected. The selected pellets were determined free-falling numbers for using the next steps.

Determination of green pellet free-falling number: This test is done to control the required strength of the newly produced green pellet, whether it will keep its firm shape during the conveying operation until it arrives at the plant section where it is indurated. At least 10 green pellets are taken manually; each of them is made subject to free-falling from a 45 cm height and the test is repeated until it is cracked. The number of drops after which the crack occurs is called the “green pellet falling number”. The drop number describes the green pellet strength during a fast impact such as the impact that occurs during unloading from a conveyor belt. This number must be higher than the number of spillages from several conveyor bands onto another conveyor band during carrying until the green pellet arrives at the plant section where it is indurated [3].

Drying pellets: after creating pellets, the pellets were kept inside the oven, which is maintained at 200 °C for drying and removal of moisture for 2 hours. After that, the pellets were taken out and kept in separate plastic pouches.

Induration of pellets: The dried iron ore pellets were fired by heating from room temperature to the predetermined firing temperature (1200 °C) at a rate of about 10 °C /minute. The keeping time at this firing temperature was 30 minutes. After that, the furnace was switched off and the pellets were allowed to cool in the furnace themselves. The pellets were taken out of the furnace and kept separately in different plastic pouches marked with pellet preparation conditions.

Table 1. Raw materials chemical composition

Raw materials	Chemical composition (%)											
	H ₂ O	Fe _{total}	SiO ₂	Al ₂ O ₃	CaO	MgO	Mn	S	P	Pb	Zn	FeO
Iron ores	11.13	65.18	5.48	0.21	0.23	0.27	0.24	0.04	0.01	0.03	0.05	20.92
Bentoni-te	Loss in ignition		P ₂ O ₅	T _{Fe}	SiO ₂	CaO	MgO	Al ₂ O ₃	MnO			
	13.4		0.15	3.24	57.09	3.18	2.03	16.73	0.08			
Coke	W			V			C	S	A			
	10.63			1.24			65	0.47	33.48			
Soda	Na ₂ CO ₃		Others									Moisture
	> 88		≤ 8									< 0.5

Reduction process: After taking the initial weight of a fired pellet, the pellets were inserted into a muffle furnace maintained at a determined temperature with coke. Coke is used to reduce the pellets. All the pellets were reduced for 30, 60 and 120 minutes at the temperature of 900, 1000 and 1100 °C (these temperatures were selected based on Ellingham Diagram and a previous study [4]). To maintain a reduced atmosphere, excess coke was kept surrounding the pellets to ensure that it is a reduced environment as well as Al₂O₃ powder was filled on the surface of the sample inside the cup for preventing carbon is oxidized. Pellets' weight is measured before and after reduction. The amount of the lost oxygen is the initial oxygen content minus the final oxygen content. The reducibility is calculated by measuring the loss of oxygen content compared to the oxygen content in the sample. The reduction reactions are mentioned in the next section. The initial and the final weight of the pellets were measured and used for the percentage reduction calculation, which is used in this formula.

$$\% W = \frac{m \times 100}{m_o}$$

where,

W is degree of reducibility,

m is amount of the lost oxygen (initial oxygen content minus final oxygen content),

m_o is total amount of oxygen initially present in iron ore pellets.

XRD pattern was taken using an X-ray diffractometer with a D8 advanced model. The

radiation applied was CuKα operated at 40 kV and 40 mA on a range of 2θ from 10 to 60°.

The fracture surface of reduced pellets morphology observation was carried out using Scanning Electron Microscopy (SEM) with JSM-7600F type equipment.

3. Results and Discussions

The green strength of pellets is shown in Table 2 (tested drop number of green pellets - times). This is the average value of 10 tests of each sample.

Table 2. The green pellet strength (times) of pelleted iron ores using different binders

Samples	B1S0	B1S1	B1S2	B0S01
Drop number	5.5	5.8	6.1	5.9

Table 2 shows that when using 1% bentonite without modification (B1S0) the green pellet strength of pelleted iron ores is the smallest (5.5 times). When increasing bentonite from 1% to 2%, the green pellet strength of pelleted iron ores increases when using modified bentonite (from 5.8 to 6.1 times). With the sample only using 0.1% soda (B0S01) as binder, the green pellet strength is quite high compared to when using only bentonite (5.9 times). The green pellet strength of all the samples is over 5 times. This result is qualified and fitted with reality and other research [2, 4, 9, 10].

Fig. 1 shows the X-ray diffraction spectrum of bentonite.

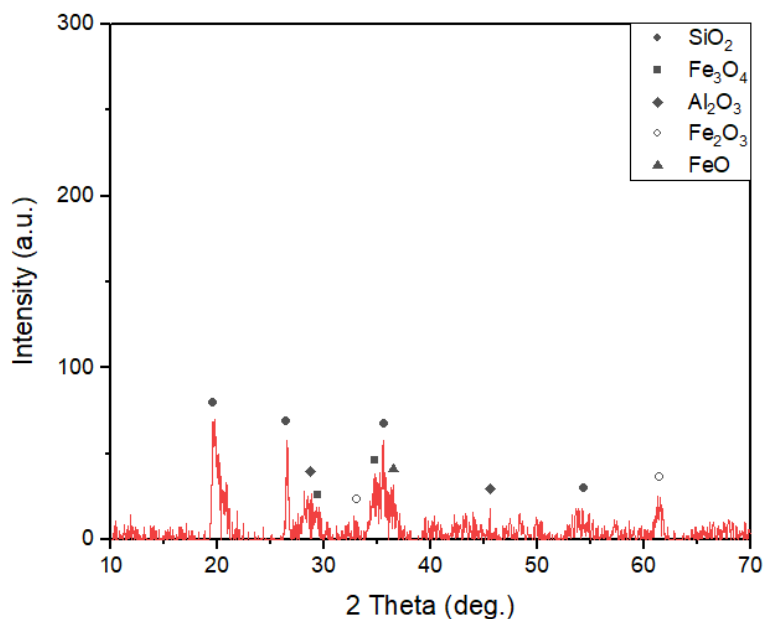


Fig. 1. XRD spectrum of bentonite.

It can be seen from Fig. 1 that the individual structure of bentonite goes through the peaks that are marked in the spectrum. The peaks of bentonite as silica (SiO_2), alumina (Al_2O_3), hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO) are shown in the spectrum. This proved that the structure of bentonite was not changed when modified by soda. Soda was located surrounding bentonite particles. This is clearly seen in the below morphology picture (Fig. 5c).

The structure of bentonite is also shown in the other investigation [9]. So, modifying bentonite by

using soda helps to increase the adhesion of bentonite without affecting the structure of bentonite. This problem will be clarified in the next section.

The structure of bentonite is also shown in other investigations. So, modifying bentonite by using soda helps to increase the adhesion of bentonite without affecting the structure of bentonite. This problem will be clarified below.

Fig. 2 shows the X-ray diffraction spectrum of bentonite and bentonite modified by 1% soda.

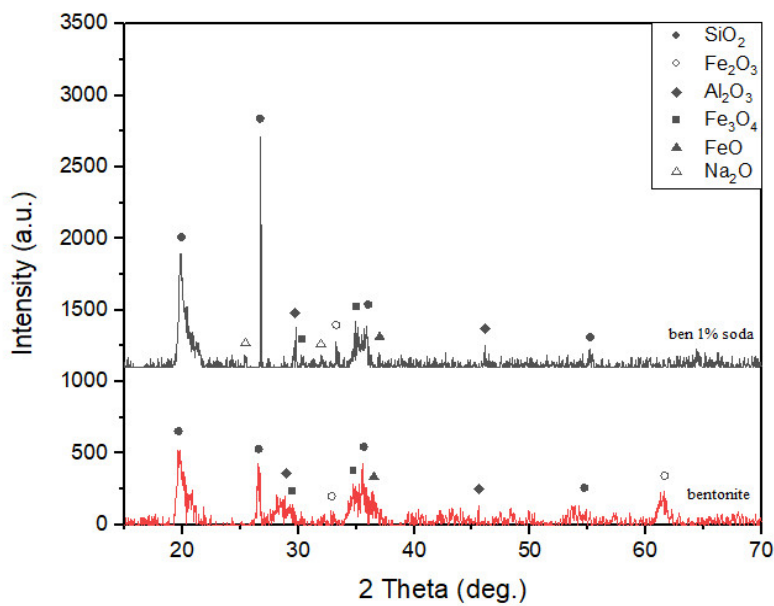


Fig. 2. The XRD spectrum of bentonite and bentonite modified by 1% soda.

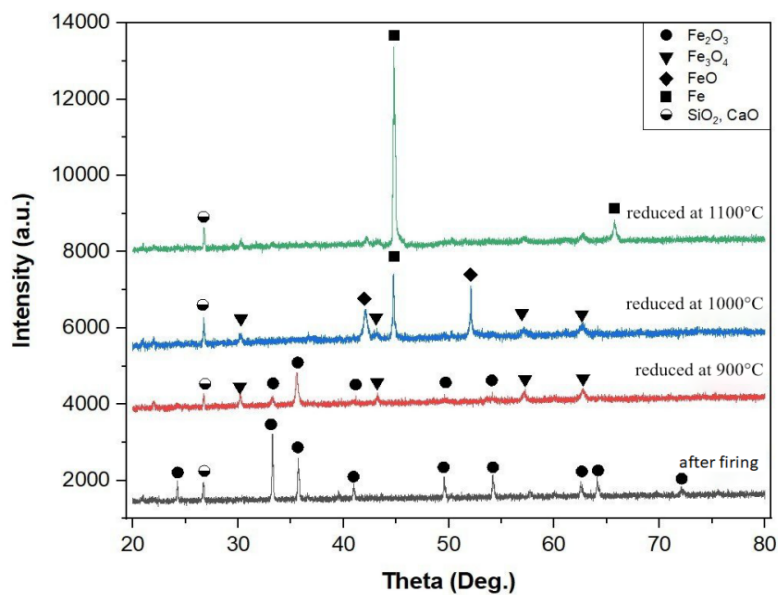


Fig. 3. X-ray diffraction spectroscopy of B1S1 pellet sample after oxidation firing and reduced at 900, 1000 and 1100 °C in 120 minutes

It can be seen from Fig. 2 that the difference in X-ray diffraction pattern between the sample containing soda and without soda. The peak of soda (Na_2O) is quite small because its weight percentage in the pellet is only 1% of the weight of bentonite. In comparison of the composition, the X-ray diffraction shows only a small difference between bentonite modified by 1% soda pellet and the bentonite sample. The peaks of silica (SiO_2), alumina (Al_2O_3), hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO) were observed in both samples with the angle almost the same as each other. From that, it proves that the structure of bentonite was not changed when modified by soda.

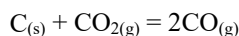
Fig. 3 shows the diffraction of X-ray diagram of a pellet sample using 1% modified bentonite with 1% soda (B1S1) after oxidation firing and reducing at 900, 1000 and 1100 °C in 120 minutes. After oxidation firing, all iron existed in Fe_2O_3 formula. After being reduced at 900 °C, a part of Fe_2O_3 was reduced to Fe_3O_4 . The reduction temperature is raised to 1000 °C, Fe_2O_3 is completely reduced, Fe_3O_4 continued to reduce to FeO and Fe . Iron oxides are completely reduced to Fe at 1100 °C.

Fig. 4 shows the degree of reduction of iron ores pellets changing with different binders, temperatures, and reduction duration.

With different bentonite and soda content, the pellets have different reducibility when reduction times or temperature is increased. This difference shows more clearly when the reduction times are longer. In different conditions, the highest reducibility is iron ore using 1% modified bentonite with 1% soda sample (B1S1). This reducibility reached to 89% when reduced at 1100 °C for 120 minutes. With the same amount of bentonite, when increasing the amount of soda for modification the degree of reduction increases. But the amount of soda increased more (up to 2%), the results show the percentage of reduction decreased. A detailed explanation will be shown below.

The reduction steps of oxides in iron ore through the following reactions [11].

Carbon gasification reaction is



The CO gas produced by this reaction, the reduction of oxides by solid carbon, and by oxidation of carbon, reduces the iron oxides to their lower oxidation states from iron (III) oxide to iron (II, III) oxide to iron (II) oxide and finally iron. The CO_2 gas produced again reacts with solid carbon to form carbon monoxide gas and that carbon monoxide gas again participates in the reduction of iron oxides as following reactions.

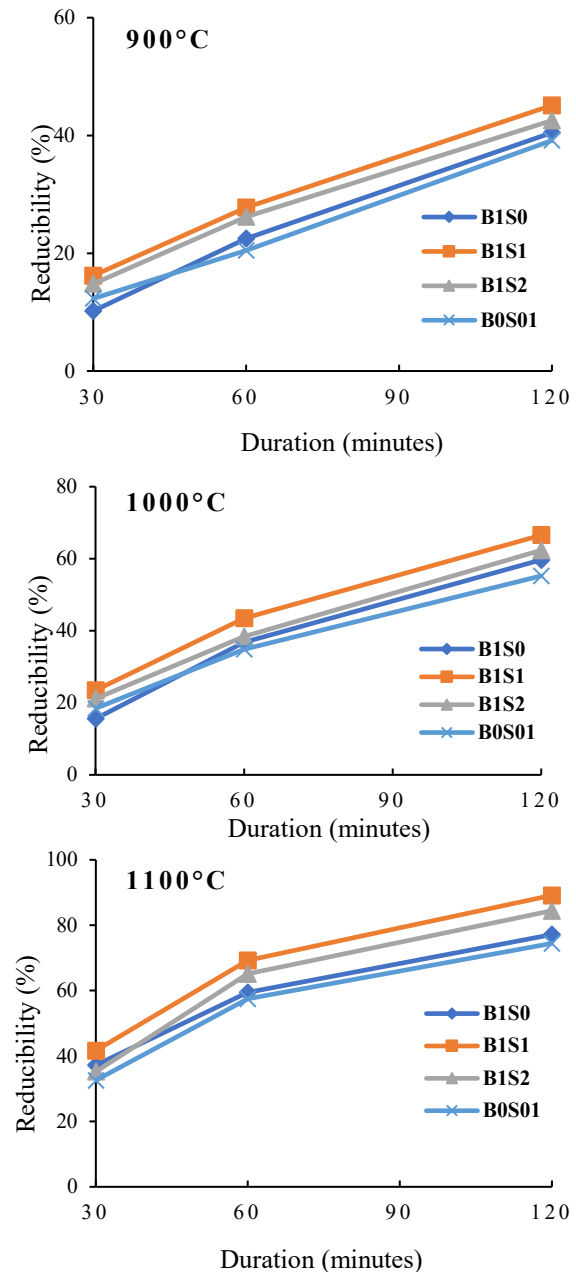


Fig. 4. The degree of reduction of pelleted iron ores with different binders, temperatures, and reduction duration

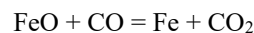
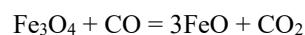
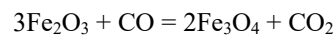


Fig. 5 shows the morphology of pellet samples B1S0, B1S1, B0S01 after being reduced at 1100 °C in 120 minutes.

It shows the difference in grain size structure and the pores. B1S0 (5a) and B0S01 (5c) sample has a condensed, strong structure, less gap, and the big gap distribution is evenly distributed. B1S1 (5b) has a small grain size, small pores but appears more, and

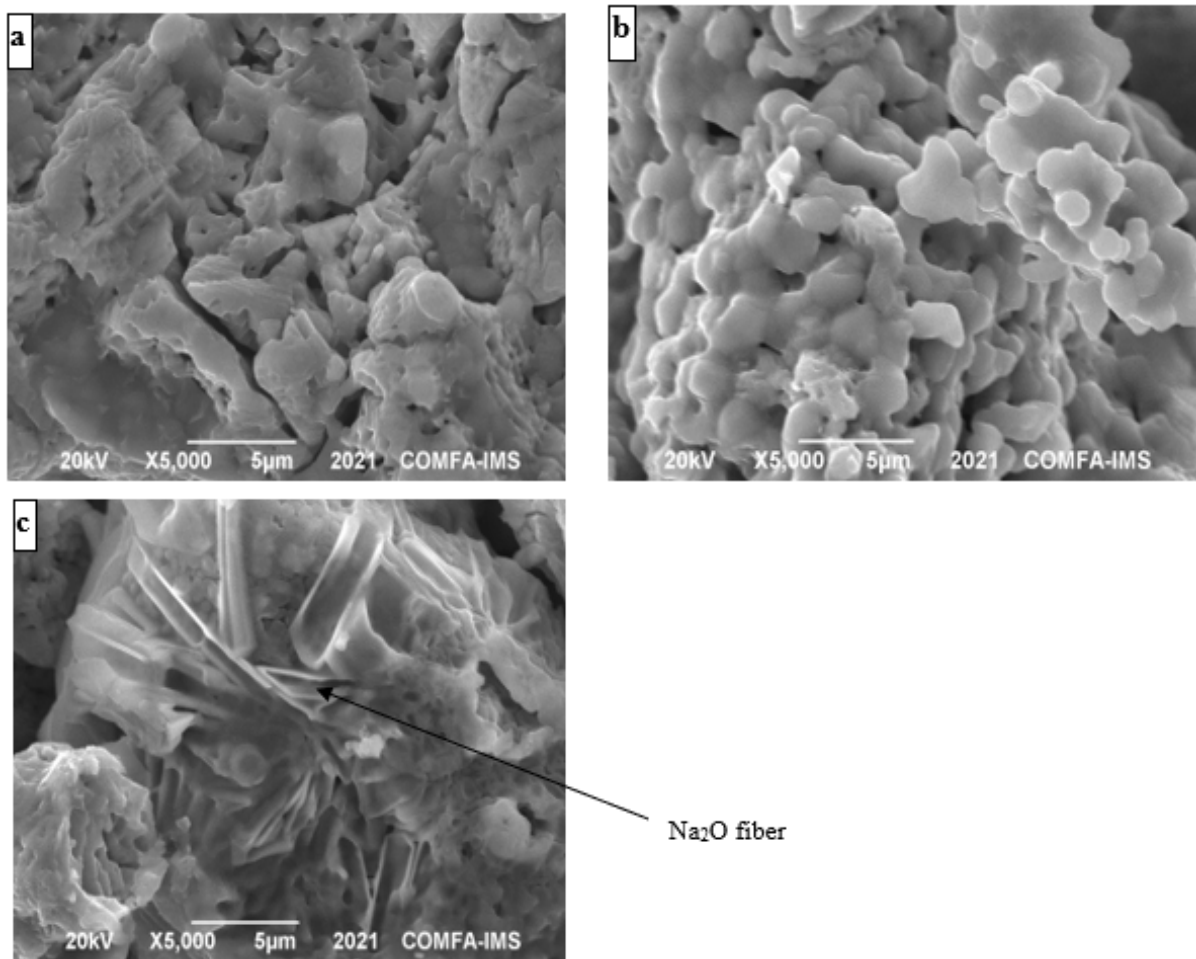


Fig. 5. Morphology of samples using different binders B1S0 (a), B1S1 (b), B0S01 (c) reduced at 1100 °C in 120 minutes.

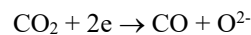
more evenly distributed. This is suitable with the above results when B1S1 samples have higher reducibility than other samples. Besides, in samples only using soda, we can observe that the picture of Na₂O fibers surrounded the grain. This helps to bind the grain and also helps to increase reducibility.

In summary, using modified bentonite with 1% soda as a binder gave the best iron ore pellets metallurgy properties of the pellet (reducibility, green strength) in all tested binders.

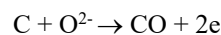
The degree of reduction increases with increased reduction temperature and the effect of the reduction temperature has been explained in the previous section which applies to this section also. However, the presence of Na₂CO₃ within the range of this experiment has been found to exert a positive influence on the degree of reduction. This may be attributed to the fact that at the selected reduction temperature range Na₂CO₃ becomes liquid (melting point 851 °C). This is shown in Fig. 5. In the liquid state, molecules of Na₂CO₃ can be polarized or ionized easily. Therefore, the CO₂ molecules generated by the reduction of iron

oxide are absorbed easily. The possibility of chemical adsorption is also not ruled out. In such a situation polarized or ionized Na₂CO₃ becomes the center of electron transfer. The carbonate ions offer two electrons instantaneously. Two reactions may occur.

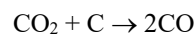
Cathodic reaction is



Anodic reaction is



The overall reaction is



Therefore, it may be inferred that Na₂CO₃ exerts a positive catalytic effect on the generation of CO which means more CO generation and more iron oxide reduction which yields a higher degree of reduction. The interactional effect of Na₂CO₃ has been found to exert a negative influence on the degree of reduction. This may be because with increasing amounts of Na₂CO₃, excess liquid Na₂CO₃ is formed which tends

to fill up the pores and thereby restrict the diffusion of product gases. Probably, a condition of forced equilibrium is set up in the vicinity of the reaction sites. Secondly, the presence of excess liquid Na_2CO_3 in the pores of the pellet is likely to hinder the desorption of CO_2 from the iron oxide surface during reduction. Therefore, absorption/desorption of CO_2 by Na_2CO_3 will be limited. Thus, the generation of CO will be restricted which will yield a lower degree of reduction [8].

4. Conclusion

Using soda-modified bentonite affected the metallurgical properties such as strength, porosity and reducibility.

Using the proper amount of soda for modifying bentonite gives good metallurgical properties such as green strength, porosity and degree of reduction.

Iron ore pellets after using bentonite are modified with 1% soda as a binder to give the best reducibility and still ensure the required green strength of pellets. This pellet can be applied in pellet manufacturing.

Soda-modified pellets can be used as raw materials in blast furnaces for iron-making or direct reduction processes.

Acknowledgment

The authors would like to thank Hoa Phat JSC (Hai Duong) for supplying the raw materials.

References

- [1] T. C. Eisele and S. K. Kawatra, A review of binders in iron ore pelletization, *Mineral Processing and Extractive Metall.*, Vol. 24, No. 1, pp. 1, 2003.
<https://doi.org/10.1080/08827500306896>
- [2] O. Sivrikaya and A. I. Arol, Effects on Physical and Mechanical Properties, XXV Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa & VIII Meeting of the Southern Hemisphere on Mineral Technology, Goiânia - GO, pp. 23-31, 2013.
- [3] O. Sivrikaya and A. I. Arol, Effects on metallurgical and chemical properties, *HOLOS*, Vol. 30, No. 3, p. 104, 2014.
<http://dx.doi.org/10.15628/holos.2014.1759>
- [4] Tran Thi Thu Hien, Bui Duy Tien, Nguyen Dinh Vu, Effect of binder on properties of iron ore pellets, *Conference of National Science in Metallurgy and Advanced Materials Technology*, Hanoi, pp. 67-72, 2016. (Original text in Vietnamese).
- [5] A. K. Mandal, O. P. Sinha, Characterization of fluxed iron ore pellets as compared to feed material for blast furnace, *Journal of Progressive Research in Chemistry*, Vol. 2, No. 1, pp. 71, 2015.
- [6] Gul, A. A. Sirkeci, F. Boylu, G. Guldun, F. Burat, Improvement of mechanical strength of iron ore pellets using raw and activated bentonites as binders, *Physicochemical Problems of Mineral Processing*, pp. 23-36, 2015.
- [7] A. Saidi, M. Shamanian, M. Barati, K. Azari, Hyperactivation of bentonite in pelletizing process, *International Journal of ISSI*, Vol.1, No. 1, pp. 38-41, 2004.
- [8] Amitava Basumallick, Influence of CaO and Na_2CO_3 as additive on the reduction of hematite-lignite mixed pellets, *ISIJ International*. Vol. 35, pp. 1050-1053, 1995.
<https://doi.org/10.2355/isijinternational.35.1050>
- [9] Huang Yan-fang, Zhang Yuan-bo, Han Gui-hong, Jiang Tao, Li Guang-hui, Yang Yong-bin, Xu Bin, Guo Yu-feng, Sodium-modification of Ca-based bentonite via semidry process, *Journal of Central South University of Technology*, pp. 1201-1206, 2010.
<https://doi.org/10.1007/s11771-010-0619-9>
- [10] Larry A. Haas, Jeffrey A. Aldinger, and Robert K. Zahl, Effectiveness of organic binders for iron ore pelletization, *Report of Investigations 9230*, pp. 21, 1989.
- [11] S. Ueda, K. Yanagiya, K. Watanabe, T. Murakami, R. Inoue and T. Ariyama, Reaction model and reduction behavior of carbon iron ore composite in blast furnace, *ISIJ Inter*. Vol. 49, No. 6, pp. 827-36, 2009.
<https://doi.org/10.2355/isijinternational.49.827>