EFFECT OF MODIFIED HUMIC ACID (MHA) BINDER ON ROASTING BEHAVIOR OF MONGOLIAN “TUMURTEI” IRON ORE CONCENTRATE BRIQUETTES

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Abstract. There are two major groups of binder: organic and inorganic binder for agglomeration process for reduction, and sintering for steel production. In this work, effect of composite binder on roasting of Mongolian “Tumurtei” iron ore concentrate briquettes in ambient atmosphere was studied, aiming to clarify optimal parameters of roasting behavior with three different MHA binders for direct reduction. Lignite contains organic and inorganic substances, and according to many previous investigations, it can be raw material for extraction of composite binder. Pressed iron concentrate with MHA binder was subjected to oxidation and reduction process in the electrical furnace. The optimum conditions of experiments were as follows. Parameters of briquetting process were carried out according to the no-binder briquetting test: 0.75 t·cm$^{-2}$ pressure, 5 seconds pressing time, 8% of moisture content, oxidation at 950 °C under air flow for 10 min, and reduction at 1100 °C under CO atmosphere. As a result, MHA binder extracted from “Baganuur” lignite affected the reduction degree higher than another two binders in this study. Total iron content in reduced iron is attained to 98.33% with 1% of MHA extracted from “Baganuur” lignite. Reduction degree can be expressed by loss of oxygen.

Keywords: magnetite, MHA binder, reduction, briquette.

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INTRODUCTION

Steel is one of the most important much applied, and low cost metal materials in modern industry. At present the scale of the steel industry is constantly expending, iron and steel production technology is developing and improving. Direct reduction (DR) technological process is also developing toward compact, efficient, continuous, clean and environmentally friendly directions [1]. According to statistics of the International Iron and Steel Association, the production of crude steel in the world increased in 64 countries reporting 151.7 million tonnes (Mt) in August 2018, a 2.6% increase compared to August 2017 [2].

Direct reduced iron is main source of crude steel making, and its production also constantly increases due to the increase of steel production as shown in Fig. 1 [3]. Mongolia has rich resources of iron ore and coal which evenly distribute throughout the Mongolian territory. Measured geological reserves contain 1 billion tons of iron ore, 162.3 billion tons of coal, and these would obviously increase in the future. There is a lack of steel production from iron ore, especially for direct reduction plants for steel making in Mongolia. According to statistics of the Mineral Resource Agency of Mongolia, mining products account for 16% of gross domestic product (GDP), and 70% of total industrial product at last three years [4].

According to the statistic of Mongolian Customs Agency for last 10 years, 4 million tons of iron concentrate are exported and 140 thousand tons of steel armature for construction are annually imported from foreign various countries (Fig. 2) [5].

Binders are widely used in agglomeration operations, such as briquetting and making pellets, to assure the desired agglomeration properties with regard to subsequent handling, transportation and processing [6].

There are two major binder groups of organics and inorganics. Previously many studies have proved that effect of MHA binder on mechanical strength of pellets is greater than of bentonite. And consumption of MHA binder is low.
er compared with bentonite [7 – 8]. Lignite and brown coal with great resources in Mongolia [9] could be used as the main source of humic substances for the preparation of organic binder. A type of novel organic binders namely modified humic acid (MHA) binder, with high binding property and economic benefits have been developed by Central South University (CSU) in China [10]. The MHA binder is comprised of organic (i.e. fulvic acid, humic acid) and inorganic active fractions [11].

Benefits to using organic binder: Organic binders might be used for a variety of reasons, but perhaps, the most reported benefit is a reduction in pellet silica content. The traditional binder, bentonite clay, generally increases silica content in iron ore pellet by 0.5% depending on bentonite dosage and composition. Organic binders are combusted during the roasting process, and may leave virtually no ash residue among the pellet microstructure of roasted pellet [12]. According to many previous investigations, effect of the most organic binders leads to the required characteristics of roasted pellets [13].

**Materials and methods**

**Materials**

The magnetite concentrate is taken from “Tumurtei” mine in Mongolia. The iron concentrate sample went to size distribution test presented in Table 1. The iron concentrate particle size is too coarse, under below 200 mesh part is 28.13 %, thus it needs to be ground. Then chemical composition of the ground sample was tested by XRF (Table 2). The concentrate sample contained, (% mass.): 65.85 $T_F$, 1.70 Al$_2$O$_3$, 3.44 SiO$_2$ and 1.55 MgO. Particle size distribution and specific surface area of the sample were sepa-

**Table 1**

| Size, mm | +0.100 | –0.1 ... +0.074 | –0.074 ... +0.045 | –0.045 ... +0.032 | –0.032 |
|---------|--------|----------------|-----------------|----------------|--------|
| Content, % | 62.56  | 9.31           | 15.67           | 4.52           | 7.95   |

**Table 2**

| Components | $T_F$ | FeO  | Fe$_2$O$_3$ | CaO | MgO | Al$_2$O$_3$ | SiO$_2$ | TiO$_2$ | Mn |
|------------|-------|------|-------------|-----|-----|-------------|---------|---------|----|
| Content, % |       |      |             |     |     |             |         |         |    |
| 65.85       | 24.08 | 94.15| 0.48        | 1.56| 1.70| 3.44        | 0.49    | 0.069   |    |

| Components | P | S | Cu | K$_2$O | Na$_2$O |  | |
|------------|---|---|----|--------|---------| | |
| Content, ppm | 18.69 | 330.04 | 7.57 | 1,529.97 | 137.68 | | |
rately tested by water sieving method and air permeability method (DBT-127 model), the content of the sample below 0.074 mm after grinding was higher than 80 %. The specific surface area of the sample was 649.53 cm²/g. Texture of the iron ore concentrates which was measured by Leica optical microscope and XRD pattern, is shown on Fig. 3, indicating the main minerals: magnetite, hematite and quartz associated with each other closely.

The main mineral composition of “Tumurtei” iron ore concentrate was identified as principally magnetite (Fe₃O₄) and hematite (Fe₂O₃) as shown on Fig. 4.

In this study, 3 different lignites namely A, B and C – “Baganuu”, “Khuut” and “Liling” were used. Mongolian coal A and B, and coal C from Liling in Hunan Province, China were selected. As well-known, lignite contains organic and inorganic constituents simultaneously [14].

At the beginning, the samples were homogenized and dried, then crushed to powders with the granularity below 0.074 mm [15]. The proximate analysis of lignite indicates that these samples consists of 39.44 %. The proximate analysis of lignite indicates that these samples consists of 39.44, 48.04 and 34.79 % of volatile matter, the ash contents were 10.50, 3.50, 22.58 %, the grade of fixed carbon 41.00, 43.00, 39.43 in coal A, B and C, respectively, measured by Sundy SDTGA5000 analyzer (Table 3).

### Methods

**Extraction of MHA from lignite.**

MHA was extracted from three different lignites (noted above) under same conditions. Powdered and homogenized brown coal was mixed with distilled water chemical pure 0.5 M of sodium-hydroxide in a glass flask. Substances ratio and stirring speed, pH values are obtained from the studies [16]. MHA solution and sediments were subjected to drying until full drying at 60 °C in a drying furnace; then the weight was determined. Finally extraction yield of MHA was calculated according to the balance of products. The extraction flow sheet is shown in Fig. 5.

The chemical composition of varies MHA binder were determined by XRF as presented below:

### Table 3

| Coal | Proximate analysis (%) | W, % | V, % | Ash, % | FC, % | Q, kCal/kg | TC |
|------|------------------------|------|------|--------|-------|------------|----|
| A    | 9.00                   | 39.44| 10.50 | 41.06  | 6,004 | 70.5       |
| B    | 5.39                   | 48.04| 3.50  | 43.03  | 5,775 | 73.1       |
| C    | 3.20                   | 34.79| 22.58 | 39.43  | 5,236 | –          |

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![Graph](image1.png)

**Fig. 3. XRD pattern of magnetite concentrate**

**Рис. 3. Рентгенограмма магнетитового концентрата**

![Graph](image2.png)

**Fig. 4. Single particle microstructure of iron ore concentrate:**  
1 – magnetite; 2 – hematite; 3 – quartz

**Рис. 4. Микроструктура частицы железорудного концентрата:**  
1 – магнетит; 2 – гематит; 3 – кварц

![Graph](image3.png)

**Fig. 5. Extraction flow of MHA binder from lignite**

**Рис. 5. Схема извлечение связующего МНА из бурого угля**
Preparation of binder briquettes.

Preparation of the samples for briquetting process was carried out by mixing a certain amount of magnetite concentrate with different stoichiometric amount of MHA binder ranging from 0.5 up to 1.5 stoichiometric ratios. Those amounts of binders were extracted from selected lignites under alkaline condition.

The mixture of raw materials and 8 % water were input in a mold; then placed in small scale hydraulic presser described on Fig. 6. Green briquette with a diameter 10 mm and a height ≈ 10 mm was produced under different conditions such as pressure and pressing time to making observed optimal condition. The green briquettes were dried at 100 °C to obtain dry briquette. Then the produced briquettes were subjected to mechanical tests including dropping damage resistance test and compressive strength test.

**Mechanical strength tests.**

Ten green briquettes are individually dropped from a height of 50 cm onto a steel plate until breakage. The mean value of the tested briquettes gives their average dropping damage resistance [17].

The compassion strength of green briquettes was determined, at least 10 briquettes sample were compressed on small size hydraulic press until they break onto electric balance. The compression strength of roasted-oxidized ten briquettes was determined by a universal material experimental machine (RHY-100B, China). The mean value for the tested briquettes gives their compressive strength. The observed load corresponds to the compressive strength measured in MPa for briquette [18].

**Reduction, roasting tests and phase characteristic analysis.**

The preheating and roasting tests were observed in a laboratory scale of horizontal electrically heated tube furnace with an internal diameter of 50 mm and an external diameter of 70 mm, schematically described on Fig. 7. Ten dry briquettes which contain 0.5 – 1.5 stoichiometric amount of three different MHA were placed in corundum crucible, and then pushed into the preheating zone of the furnace. The preheated sample was slowly and carefully...
pushed to appointed temperature of roasting zone. Finally, the roasted samples were pulled out and naturally cooled in room temperature [18]. Heating was carried out at different temperatures ranging from 950 °C up to 1150 °C for a different time. To heated at different temperatures, temperature ranging from 950 °C up to 1150 °C for a different time. The gas consumption of CO as reducer was constant (4L/min) at the reduction tests.

**Optical microscope observation.**

The microstructures of polished briquettes before and after reduction were studied using a Leica DMRXE microscope (Germany).

### RESULTS END DISCUSSION

**Effect of binder dosage on properties of green briquette**

The drop damage resistance and compressive strength of the green briquettes are shown in Fig. (4b), with respect to the different stoichiometric amounts of MHA binder under optimized briquetting load of 0.75 ton for fine magnetite (+80 % of –0.074 mm fraction) concentrate. It was found that the drop damage resistance and compressive strength of produced briquettes increased with increasing binder dosage for every constant load and reached its maximum value at 1.5 stoichiometric amounts of binder fines for both concentrate sizes. The compressive strength of “Bg” green briquettes from fine concentrate with Bg MHA reached 12.32 MPa which is higher than for “Li” MHA of briquetts. The results of mechanical strengths tests of green briquettes are presented in Table 4 and Fig. 8.

Parameters of briquetting process were carried out according to the no-binder briquetting test 0.75 t·cm⁻² pressure, 5 seconds pressing time, 8 % of moisture content.

**Effect of binder dosage on properties of roasted briquette**

Firstly the roasting of produced briquettes at different temperatures ranging from 850 °C up to 1100 °C for different time at ambient atmosphere leads to optimized time and temperature. Optimal conditions of roasting-oxidation were 10 min and 950 °C. The temperature range is 10 °C per minute noted other before investigation. CCS of “Kh” is higher than “Bg” and “Li” briquettes, but FeO content of “Kh” increased with increasing MHA dosage (Fig. 9). Organic birders are easily burned out during roasting, leading to the generation of porosity as shown in Fig. 10.

| Green Briquette | Compressive strength, MPa | Dropping number, N |
|----------------|---------------------------|-------------------|
| MHA dosage     | 0.50 0.75 1.00 1.25 1.50 | 0.50 0.75 1.00 1.25 1.50 |
| Bg (coal A)    | 3.50 3.60 4.70 4.99 5.40 | 1.30 1.50 2.20 2.50 2.80 |
| Kh (coal B)    | 6.40 8.20 10.3 12.32 12.43 | 1.70 2.30 4.30 4.30 |
| Li (coal C)    | 7.67 8.33 9.57 9.43 9.23 | 1.90 2.00 2.60 2.70 3.20 |

**Fig. 8.** Effect of MHA dosage on drop damage (a) and compressive strength (b) of green briquettes:

1 – Li; 2 – Kh; 3 – Bg

**Table 4**

Таблица 4. Влияние количества MHA на механическую прочность

![Table 4](image)
Effect of various MHA on reduced magnetite briquettes

The reduction procedure of magnetite briquettes with MHA binders extracted from different lignites was made in laboratory type electrical furnace in the CO atmosphere (Fig. 3).

The reaction of Fe₃O₄ to Fe by CO is:

\[
3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2, \\
\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2, \\
\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2.
\]

The results are presented on the Fig. 3 in terms of the percent reducing extent against temperature due to oxygen.

Effect of MHA dosage on the porosity of roasted briquettes:

- 1 – Li; 2 – Kh; 3 – Bg

Effect of MHA binder dosage on compressive crushing strength (a) and FeO content (b) at 950 °C for 10 min:

- 1 – Li; 2 – Kh; 3 – Bg

Relation between reduction extent and reduction time under different temperature at °C:

- 950 (1); 1000 (2); 1050 (3); 1100 (4); 1150 (5) without binder (a); relation between reduction extent and different stoichiometric amount of various MHA: Li (6); Kh (7); Bg (8) at 1100 °C, 90 min (b)

- 1 – Li; 2 – Kh; 3 – Bg

Fig. 9. Effect of MHA dosage on the porosity of roasted briquettes:

- 1 – Li; 2 – Kh; 3 – Bg

Fig. 10. Effect of MHA binder dosage on compressive crushing strength (a) and FeO content (b) at 950 °C for 10 min:

- 1 – Li; 2 – Kh; 3 – Bg

Fig. 11. Relation between reduction extent and reduction time under different temperature at °C:

- 950 (1); 1000 (2); 1050 (3); 1100 (4); 1150 (5) without binder (a); relation between reduction extent and different stoichiometric amount of various MHA: Li (6); Kh (7); Bg (8) at 1100 °C, 90 min (b)

- 1 – Li; 2 – Kh; 3 – Bg

loss by CO gas which was produced during the reduction. The reduction degree was calculated by mass loss and FeO content was defined as:

\[ R_t = 100 \left( \frac{0.1 W_1 + m_1 - m_2}{m_2 0.43 W_2} \right) \%
\]

\( R_t \) – reduction degree, %; \( W_1 \) – FeO content of oxidized briquettes before reduction, %; \( W_2 \) – total iron content before reduction, %; \( m_1 \) – mass of sample before reduction, g; \( m_2 \) – mass of reduced briquettes, g.

The phase characteristics of the magnetite concentrate before and after reduction at these temperatures were analyzed by XRD [RIGAKU D/Max 2500, Japan] under the conditions of radiation: Cu Kα tube, current and voltage: 250 mA, 40 kV, scanning range: 10 – 80° (2θ), step size 0.02° (2θ) and scanning speed 8°/min (Fig. 12).

**CONCLUSIONS**

The influence of modified humic acid on the carbothermal reduction of a magnetite concentrate by temperature programmed reduction ranging from 950 °C to 1150 °C for different reducing time is shown on microstructure of the samples on the Fig. 13 and can be summarized as follows.

The mechanical strength of oxidized pellet with “Bg” binder extracted from coal A decreased but extent of reduction was stable and higher than with “Kh”, “Li” with increasing binder dosage. The highest reduction ratio is 94.12 % with 1.25 % stoichiometry amount of “Bg” MHA. Relation between both “Kh”, “Li” binder dosage and reduction extent is immediately increasing under the same indicated condition: 1100 °C for 90 min.

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*Fig. 13. Optical micrograph of reduced briquettes:*

*a, b, c, d* for 30, 45, 60, 90 min at 1100 °C; *e, f, g, h* for 90 min at 1000, 1050, 1100, 1050 °C, respectively;

*white zone – iron; grey zone – wustite; dark zone – porosity and hole*

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*Рис. 13. Микроструктура восстановленных брикетов:*

*a, b, c, d* в течение 30, 45, 60, 90 мин при 1100 °C соответственно; *e, f, g, h* в течение 90 мин при 1000, 1050, 1100, 1050 °C соответственно; белая зона – железо; серая зона – вюстит; темная зона – пористость и пустоты*
ВЛИЯНИЕ МОДИФИЦИРОВАННОЙ ГУМИНОВОЙ КИСЛОТЫ (MHA) КАК СВЯЗУЮЩЕЙ ДОБАВКИ НА ОБЖИГ БРИКЕТИРОВАННОГО МОНГОЛЬСКОГО ЖЕЛЕЗОРОДНОГО КОНЦЕНТРАТА «TUMURTEI»

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Аннотация. Существуют две основные группы связующих добавок: органические и неорганические для агломерационного процесса и спекающие для производства стали. В данной работе изучено влияние композиционного связующего на обжиг монгольских брикетов из железорудного концентрата «Tumurtei» в атмосфере воздуха с целью выявления оптимальных параметров их поведения при обжиге с тремя различными связующими MHA для прямого восстановления. Лигнит содержит органические и неорганические вещества и, согласно многим предшествующим исследованиям, он может быть сырьем для извлечения композиционного связующего. Прессованный железный концентрат со связующим MHA подвергли процессу окисления и восстановления в электропечи. Оптимальные условия экспериментов были следующими. Параметры процесса брикетирования выполнены в соответствии с испытанием на сжатие без связующего при давлении 0,75 т·см\(^{-2}\), времени прессования 5 с, содержании влаги 8 %, окислении при 950 °C в потоке воздуха в течение 10 мин и восстановлении при 1100 °C в атмосфере SO. В результате связующее MHA, извлеченное из лингита «Baganuur», повлияло на степень восстановления сильнее, чем два других связующих в этом исследовании. Общее содержание железа в восстановленном продукте достигло 98,33 % с 1 % MHA, извлеченного из лингита «Baganuur». Степень восстановления выражена потерей кислорода.

Ключевые слова: магнетит, связующее MHA, восстановление, брикет.

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