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A review on the humic substances in pelletizing binders:

Preparation, interaction mechanism, and process characteristics

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Humic acid is inexpensive, and has a wide range of sources and a strong adsorption force with the surface of iron ore, and the size of its adsorption force is affected by some factors such as humic acid concentration, pH of the solution, and metal cations. The modified humic acid pellet binder (MHA) with strong adhesion and high viscosity was obtained through the separation and purification of solid wastes such as lignite and weathered coal and chemical modification treatment and successfully applied in the production process of iron ore pellets. After industrial tests, MHA can significantly improve the strength of green and dry pellets, less residue after high-temperature roasting, less metallurgical pollution, high strength of fired pellets, and can partially or completely replace bentonite.

**KEYWORDS:** Humic acid binder; Adsorption mechanism; Green pellet drop number; Dry pellet compressive strength; Fired pellet compressive strength
1. Introduction

Pellet ores become one of the high-quality furnace materials for modern metallurgy because of their uniform particle size, high strength, suitability for long-distance transportation and storage, high iron grade, good metallurgical properties, and conducive to improving the permeability of the smelting column and reducing the coke ratio\textsuperscript{1, 2}. The pellet binder is an essential additive in the production of pellets, which can not only bring the fine iron ore together to form uniform-sized green pellets but also significantly improve the pelletizing rate and metallurgical properties\textsuperscript{3}. After long-term research and development, three types of pellet binders such as an inorganic binder, organic binder, and composite binder have been gradually formed. However, the majority of Chinese enterprises are still using some poor quality bentonite as a traditional additive for iron ore pellets, with additions as high as 2~3%, much higher than the foreign level of 0.5~0.7\%\textsuperscript{4}. According to the production experience, for every 1% of bentonite added, the iron grade of pellet ore will decrease by about 0.6\%\textsuperscript{5}, and the iron content will decrease by about 7 kg/ton\textsuperscript{6}. A 1% increase in the SiO\textsubscript{2} content of the pellet feed will result in an increase in the cost of steelmaking by 4~7 USD/ton\textsuperscript{7}. The organic binders not only significantly regulate the internal moisture of the pellets and improve the pelletizing rate as well as the green and dry pellet strength, but also leave almost no residue in the pellets after high-temperature roasting, which greatly reduces the level of metallurgical pollution\textsuperscript{8, 9}.

However, many experimental and industrial test studies have found that although the strength of green and dry pellets is almost the same or better than that of bentonite when organic binders are used instead of bentonite, almost all studies concluded that the preheated and fired pellet compressive strength is insufficient, especially for the chain grate-rotary kiln process\textsuperscript{10, 11}. This is the main reason why Peridur and Alcotac binders are widely used in foreign but have difficulties in meeting the
production requirements in China. The fundamental reason for the low preheated and fired pellet strength is the lack of sufficient liquid slag bonding force inside the pellets after high-temperature volatilization of organic binders, which results in high porosity\textsuperscript{12, 13}. While the new modified humic acid binder (MHA) is an organic polymer binder containing traces of inorganic substances obtained from solid wastes such as lignite, weathered coal, and peat through chemical purification and modification treatment. After experimental studies, it was shown that the active ingredient humic acid (HA) and fulvic acid (FA) in MHA adsorbs to the surface of magnetite and hematite through ligand exchange, electrostatic interaction and hydrogen bonding to enhance the adhesion between iron ore and humic acid, thus improving the green and dry pellet strength\textsuperscript{14-16}. At the same time, the high-temperature combustion of MHA leaves a trace amount of inorganic silicate phase, which enhances the solid phase bridging within the pellets and inhibits the significant reduction of the preheated and fired pellet strength. Therefore, humic acid pellet binder can partially or completely replace bentonite and meet the requirements of various iron ore pellet production\textsuperscript{17}.

2. The extraction of humic acid from humic substances

Humic acid is widely distributed in nature and is found in low-order coals such as peat, lignite, and weathered coal, of which the composition content of humic acid is shown in Table 1. Peat is a product of the initial stage of decay of plant residues, lignite is a product of the pre-coal-forming stage with a laminar structure, and weathered coal is a kind of metamorphic coal formed by long-term weathering action when exposed to air\textsuperscript{18}. According to statistics, the weathered coal reserves are more than 100 billion tons, peat is about 12.4 billion cubic meters, and lignite is as high as 130.3 billion tons in China\textsuperscript{19}. The content of humic acid in different low-rank coals varies and is closely related to the type, mining location, and extraction method. As a general solid waste, peat, lignite and weathered
coal have long been under-appreciated for their exploitation, resulting in the occupation of a large number of land resources and environmental pollution, but the extraction of humic acid after artificial treatment and its application in many fields has not only reduced environmental hazards but also realized the reuse of solid waste resources.

Humic acid is very strongly bound to non-humic acid-like substances and is often difficult to separate. The current extraction methods of humic acid include acid extraction, alkali-soluble acid precipitation, chemical oxidation, and microbial degradation, while alkali-soluble acid precipitation is the main method. For the extraction of common humic acid is relatively simple, and the soluble HO-HA/FA-COONa or HO-HA/FA-COOK can be formed by an ion-exchange reaction between NaOH/KOH and HO-HA/FA-COOH to achieve separation. However, for humic acid with high calcium and magnesium content, Ca and Mg ions in FA/HA need to be replaced by Na$_2$CO$_3$ and Na$_4$P$_2$O$_7$ to form soluble HA sodium salts and insoluble calcium carbonate or pyrophosphate to separate.

The coal-alkali ratio and liquid-solid ratio make the main factors affecting the extraction of humic acid from lignite. Insufficient alkali will make the humic acid can not dissolve completely, while excess will cause the extracted humic acid to form an insoluble colloidal solution, thus reducing the extraction rate. Also, excess alkali is a contaminant and deteriorates product quality. The liquid-solid ratio will affect the diffusivity of humic acid, the smaller the liquid-solid ratio, the worse the diffusion and the lower the extraction rate. The addition of auxiliary reagents can also improve the extraction rate of humic acid, Jiang, et al. used anthraquinone AQ under alkaline conditions to break the association between humic acid and inorganic minerals, which is more conducive to the separation of the two, thus improving the extraction rate of humic acid, reducing the amount of alkali, extraction
temperature and time, and the obtained humic acid have higher aromatization and polymerization, larger relative molecular mass and more polar functional groups \(^{24}\). At the same time, the adsorption capacity of the humic acid-based pellet binder prepared in this way was greatly improved, as were the pellet strength and burst temperature\(^ {25}\).

3. Properties, structure, and types of humic substances

Humic acid and fulvic acid are a complex mixture of large aromatic aliphatic molecules with similar chemical structures obtained by chemical purification of humic substances. The molecules mainly contain phenolic hydroxyl, carboxyl, alcohol hydroxyl, carbonyl, amine groups, and other active functional groups\(^ {26-28}\). According to the solubility of extracts from the humic substance in different solvents, humic substances are divided into HA and FA. FA is soluble in acid, alkali, acetone, and ethanol solutions, HA refers to a substance that is extracted with an alkaline solution and precipitated with an acid\(^ {29}\), and there is no unified report on the specific and clear chemical structural formula of both, but the structural models of FA\(^ {30}\) and HA\(^ {31}\) were proposed by some scholars through modern detection techniques, as shown in Fig.1 and Fig.2.

FA and HA not only have different chemical structures but also have significant differences in the content of chemical components and functional groups in their molecules, as shown in Table 2. From the analysis of the table, it can be seen that the main elements of FA and HA are C, O, H, and N in order, and a small amount of ash. H/C is an important parameter indicating the aromatic polymerization degree of FA/HA, and the value in the table reflects that HA>FA; the ratio of O/C reflects the amount of oxygen-containing functional groups and bridge bonds, and the value in the table reflects that FA>HA. Meanwhile, the number of carboxyl groups and total acidic groups in FA molecule is higher than HA, so FA is more soluble than HA, and it contains more oxygen-containing
functional groups, has higher chemical and biological activity, and its physicochemical properties and biological properties are significantly better than HA\(^{32}\).

FA is a variable-charge organic colloid with strong complexation ability with metal ions and mineral surfaces and is tightly bound to mineral ions in lignite\(^ {33}\). The surface of HA molecules exhibits acidic properties in solution due to a large number of acidic functional groups such as carboxyl, phenolic hydroxyl, and alcohol hydroxyl, the presence of hydrophilic and hydrophobic groups makes it highly surface-active, and it is easy to interact with high-valent metal ions such as Fe\(^{3+}\), Al\(^{3+}\) to produce ion exchange and complexation. Under higher concentration conditions, it becomes a negatively charged hydrophilic colloid\(^ {34}\). However, it has poor thermal stability, does not melt when heated, and is easily oxidized at high temperatures, leading to its deformation and loss of original activity\(^ {35}\).

4. The Interaction mechanism of Humic acid binder in the pellets

Green pellets are the primary step in the production of iron ore pellets, and the formation process mainly consists of three stages: the formation of cue pellet, the growth of cue pellet, and the compaction of green pellet\(^ {36}\). Under the cue pellet is rolled continuously, and the excess capillary water inside is squeezed to the surface, which in turn bonds the surrounding mineral powder and thus grows continuously\(^ {37}\). The best strength of the green pellet is obtained by pressing out the excess capillary water as the pellet is rolled, which is the green pellet compaction process\(^ {38}\).

During the pelletizing process, the capillary forces, adhesion between the binder and mineral particles, the cohesion of the binder, and hydrogen bonding between mineral particles and water are mainly formed inside the green pellet\(^ {39}\). When a sufficient amount of organic binder is added, the organic molecules absorb water and form an inactive sticky layer on the surface of the mineral particles,
which binds the mineral particles together by adhesion and cohesion\textsuperscript{40}. The mechanical strength of the binder is called cohesion and refers to the net interaction force between the binder molecules \textsuperscript{41}, the magnitude of which depends on the chemical structure, molecular weight, and the degree of cross-linking and branching\textsuperscript{42}. Adhesion force is the sum of the van der Waals, electrostatic, magnetic, and other forces, hydrogen and chemical bonds at the interface between the iron ore particles and the binder \textsuperscript{43}. Qiu, Jiang et al. \textsuperscript{44} concluded that organic binders contain solidophilic and hydrophilic groups such as carboxyl and hydroxyl groups and have a high degree of polymerization, which allows organic binders to establish strong adhesion and surface interactions with mineral particles.

4.1 Effect of pH on the adsorption of FA/HA with hematite/magnetite

Both FA and HA are large organic molecules with aromatic structures and molecular weights ranging from hundreds to tens of thousands, while both contain a large number of functional groups such as carboxyl and hydroxyl groups, which provide important conditions for the adsorption of mineral particles by the active components of HA\textsuperscript{45}. After a long-term study, it was found that the adsorption mechanism of humic acid and minerals mainly includes physical adsorption based on van der Waals forces and electrostatic forces\textsuperscript{46} and chemical adsorption based on ligand exchange and ion complexation reactions\textsuperscript{47, 48}, and the mechanism of action is shown in Fig.3. And factors such as pH value, the concentration of humic acid, metal cations, contact time, and temperature can affect the type and strength of adsorption forces between humic acid and mineral surfaces, thus affecting the green and dry pellet strength.

The pH value and the concentration of humic acid had a significant effect on the adsorption of humic acid on the surface of magnetite and hematite. Zhou, Zhang, et al.\textsuperscript{49} investigated the effect of the pH value of humic acid solution purified from weathered coal on the adsorption density on the
surface of magnetite and hematite, and the results are shown in Fig.4 and Fig.5. The experimental study showed that at the same initial concentration of humic acid, the adsorption density of humic acid on the surface of magnetite and hematite decreased with the increase of the pH value of the humic acid solution. At this time, the adsorption forces of humic acid molecules with magnetite and hematite were electrostatic attraction and ligand exchange as well as partial hydrogen bonding.

In the presence of moisture, the surfaces of magnetite and hematite are hydroxylated and the surface hydroxyl groups adsorb H\(^+\) or OH\(^-\), resulting in different electrical properties on the mineral surfaces. In acidic solutions, the surface hydroxyl groups of magnetite and hematite adsorb H\(^+\) from the solution to form Fe-OH\(^{2+}\), making the magnetite and hematite surfaces positively charged, while some of the carboxyl functional groups in HA and FA molecules ionize to produce HO-HA-COO\(^-\) or HO-FA-COO\(^-\), exhibiting negative electrical properties. At this time, HA and FA molecules have opposite charges to the mineral surface, so HO-HA-COO\(^-\)/HO-FA-COO\(^-\) and Fe-OH\(^{2+}\) on the mineral surface will generate electrostatic attraction force, while they will further interact with each other to form ligand exchange of HO-HA-OC-O-Fe/ HO-FA-OC-O-Fe \(^{50}\), and the reaction process is shown in (1-5).

\[
\text{Fe} + \text{H}_2\text{O} \rightleftharpoons \text{Fe} - \text{OH} \quad (1)
\]
\[
\text{Fe} - \text{OH} + \text{H}^+ \rightleftharpoons \text{Fe} - \text{OH}_2^+ \quad (2)
\]
\[
\text{HO} - \text{HA/FA} - \text{COOH} \rightleftharpoons \text{HO} - \text{HA/FA} - \text{COO}^- + \text{H}^+ \quad (3)
\]
\[
\text{Fe} - \text{OH}_2^+ + \text{HO} - \text{HA/FA} - \text{COO}^- \rightleftharpoons \text{Fe} - \text{OH}_2^+ \text{O}^- - \text{OC} - \text{HA/FA} - \text{OH} \quad (4)
\]
\[
\text{Fe} - \text{OH}_2^+ + \text{HO} - \text{HA/FA} - \text{COO}^- \rightleftharpoons \text{Fe} - \text{O} - \text{CO} - \text{HA/FA} - \text{OH} + \text{H}_2\text{O} \quad (5)
\]

FA and HA establish a strong adsorption force with the mineral surface through electrostatic force and ligand exchange, while they are not fully ionized in the acidic environment and a partially agglomerated state, wrapping and adhering to the magnetite or hematite surface, resulting in a higher
adsorption density, which improves the adhesion force and amount of humic acid binder with iron ore, and significantly increases the strength of green and dry pellets\(^{51}\).

However, as the pH value of the humic acid solution increases, the magnetite/hematite surface gradually adsorbs OH\(^-\) from the solution and becomes Fe-O\(^-\); and the surface potential changes from positive to negative potentials. Meanwhile, FA and HA continuously ionize H\(^+\) under alkaline conditions and combine with OH\(^-\) to produce water molecules, prompting the ionized conversion of HO-FA-COOH and HO-HA-COOH that are in agglomerated state and have larger molecular weight into HO-FA-COO\(^-\) and HO-HA-COO\(^-\) dissolved in water, thus the surface negativity of FA and HA molecules is enhanced\(^{52}\), and the reaction process is shown in (6-7).

\[
Fe - OH + OH^- \rightarrow Fe - O^- + H_2O \quad (6)
\]
\[
HO - HA/FA - COOH + OH^- \rightarrow HO - HA/FA - COO^- + H_2O \quad (7)
\]

At this time, the Fe-O\(^-\) of magnetite/hematite surface and HO-FA-COO\(^-\)/HO-HA-COO\(^-\) carry opposite charges and exhibit significant electrostatic repulsion. On the other hand, as the pH value increases, the humic acid molecules adsorbed on the magnetite/hematite desorb from the surface, which leads to a significant decrease in the adsorption density\(^{53, 54}\).

### 4.2 Effect of FA/HA concentration on the adsorption of FA/HA with hematite/magnetite

Although the adsorption density of magnetite and hematite surfaces decreases with the increasing pH of the humic acid solution, it can increase with the increasing concentration of humic acid. Wu\(^{55}\) purified FA and HA using lignite and investigated the effect of humic acid solution concentration on the adsorption density of magnetite/hematite surfaces at different pH values of both, and the experimental results are shown in Fig.6 and Fig.7. The experimental study showed that the adsorption density of FA and HA on magnetite or hematite increased continuously with the increase of
concentration at the same pH value, and the increase was much higher under acidic conditions than under alkaline conditions, and the adsorption of FA/HA on magnetite was greater than that on hematite$^{56}$.

With the increase of humic acid concentration, the number of FA and HA molecules in solution keeps increasing, especially under alkaline conditions, HA is converted from an ionic state to a molecular state, forming a colloidal macromolecular. When there are mineral particles in the solution, the colloidal particles will cross-link and entangle with each other, forming a huge spatial mesh structure, which networks the mineral particles and thus flocculates each other. Therefore, although the mineral particles and HA have a large electrostatic repulsion under alkaline conditions, HA still flocculate and adsorb on the mineral surface as the concentration of HA increases, and this effect obviously increases the adsorption density and adsorption force between humic acid and magnetite/hematite surfaces, which are more easily aggregated to form agglomerates and contribute to the improvement of green and dry pellet strength$^{57}$.

### 4.3 Effect of metal cations on the adsorption of FA/HA with hematite/magnetite

In the humic acid-mineral particle system, in addition to the influencing factors of pH and humic acid concentration, metal cations in the system also affect the adsorption behavior of humic acid on the surface of mineral particles. On the one hand, metal cations affect the stretching and curling of humic acid molecules and change the viscosity of humic acid solutions. On the other hand, metal cations affect the interaction of functional groups with mineral surfaces, thus affecting the adsorption behavior of humic acid on mineral particles$^{58, 59}$. Zhou, Zhang, et al.$^{60}$ used lignite to purify FA and explored the effect of metal cations on FA on the adsorption density on magnetite/hematite surface, and the experimental results are shown in Fig.8 and Fig.9. The experimental results showed that the
addition of metal cations increased the adsorption density of HA with iron ore particles and the relative viscosity of the HA solution. The addition of metal cations (Al$^{3+}$, Fe$^{3+}$, Ca$^{2+}$, Mg$^{2+}$) not only interacts with the negatively charged FA, counteracts part of the negative charge of FA, reduces the electrostatic repulsion between FA, and promotes the free FA molecules in solution to be adsorbed through multilayer adsorption$^{61}$, but also compresses the double electric layer on the iron ore surface, bringing the FA molecules closer to the iron ore surface, which facilitates the coordination of FA with the mineral surface$^{62,63}$. Therefore, metal cations act as a bridge between FA and magnetite particle surfaces, which induces FA to coalesce together, thus increasing the adsorption density and relative viscosity of FA solutions.

The study of factors influencing the adsorption of humic acid molecules on the surface of iron ore showed that factors such as pH, concentration, and metal cations of humic acid solution would have significant effects on the relative viscosity of the humic acid solution and the adsorption density on the surface of iron ore. Therefore, the pH and metal cations can be reasonably adjusted to obtain the suitable humic acid adsorption density and viscosity, which can improve the pelletizing rate and the compressive strength of green and dry pellets.

5. The application effect of HA and FA pellet binder

Humic acid has received close attention and intensive research from pellet workers due to its low price, wide source, and excellent adsorption and flocculation ability with iron oxides. In order to prepare a high-performance humic acid pellet binder Funa, a natural polymeric iron ore pellet binder containing humic acid salts was made from weathered coal extracted by NaOH solution at Central South University. The study showed that Funa is an organic polymeric binder with surfactant and colloidal properties, which can reduce the surface tension of water, improve the hydrophilicity of the
concentrate, and bind by chemisorption on the surface of iron ore concentrate, and has good thermal stability. Qiu, Jiang et al. found through pelletizing experiments that the green and dry pellet strength increased with the addition of the Funa binder, and when the addition of Funa was 1.75%, the green pellets drop number and the dry pellet compressive strength reached the greatest value of 24 times/0.5m and 280N/pellet, respectively. Compared with the pellets with bentonite as the binder, Funa significantly improves the pelletization and compressive strength, and also has a higher reduction ratio and iron grade.

The successful application of pellet binder Funa in pellets has led many pellet workers to study the separation and purification and chemical modification treatment of humic substances from different sources to prepare a cost-effective modified humic acid pellet binder (MHA) for total or partial replacement of bentonite to obtain high-quality pellets. Zhou, Wattanaphan et al. mixed lignite powder and NaOH at a mass ratio of 10:1, dissolved by heating and stirring in a water bath at 75°C, removed and left to stand and poured the supernatant into a container and dried completely at 75°C, crushed and ground into powder samples to make MHA and mixed with hematite to make pellets. The experiments showed that the green/dry pellet quality of 0.6 wt.% MHA binder was comparable or even better than that of 0.66 wt.% bentonite pellets, all well above the least requirement of pellet strength.

Spectralite has poor hydrophilicity and pelletization, and poor reactivity at high temperatures, which restricts its large-scale application in pellet production. Zhou, Zhang et al. used MHA binder instead of bentonite to prepare qualified specularite pellets. and the results showed that the organic functional groups in the MHA binder had strong chemical adsorption with spectrality particles, which improved the green pellet strength. Compared with pellets made of bentonite, the microstructure of the fired pellets made with MHA binder was denser and the Fe₂O₃ grains were better recrystallized. Under
optimal conditions, the pellet strength of 0.75 wt.% MHA binder was comparable to or better than that of 2 wt.% bentonite pellets, and the total Fe content was 1.06% higher than that of 2% bentonite pellets. Meanwhile, Bai, Zhang et al.\(^{69}\) used an MHA binder to prepare spectrality pellets. When the dosage of MHA binder is 1.0 wt.%, the green pellet drop number was 3.7 times/0.5m and the green pellet compressive strength was 12.5 N/pellet. Under the optimal experimental conditions of a firing temperature of 1280°C and firing time of 10 min, the compressive strength of fired pellets was 2747 N/pellet, and the finished pellet strength meets the requirements of blast furnace ironmaking.

Vanadium/titanium-bearing magnetite is not only an important source of iron but also associated with vanadium, titanium, nickel, and other beneficial components, which have high comprehensive utilization value. Han, Zhang et al.\(^{70}\) reduced the amount of MHA binder to 0.25% by wet grinding vanadium-titanium magnetite powder with MHA binder. Under the same preheating conditions, the preheated pellets had higher strength than Peridur pellets. The iron grade of 0.5 wt.% MHA fired pellets was 0.9% higher than that of the 2.0 wt.% bentonite pellets. The quality of pellets made with MHA binder meets the requirements for pellets produced by the grate-kiln method. Zhang, Zhou, et al.\(^{71}\) used MHA binder instead of bentonite to prepare vanadium-titanium magnetite pellets, and the results showed that when the MHA dosage was 0.25%, the compressive strength of the preheated pellets was 522 N/pellet at a preheating temperature of 950 °C and time of 10 min, and the compressive strength of the fired pellets was 3702 N/pellet at firing temperature of 1250 °C and time of 10 min. Compared with 2.0% bentonite pellets, the compressive strength of finished pellets made by MHA was slightly lower, while the TFe grade was significantly higher by 1.11%.

To further investigate accurately the extent to which each chemical component within humic acid affects the quality of pellets, Han, Huang et al.\(^{72}\) systematically investigated the effects of Na-FA and
Na-HA and their mass ratios on the strength of green, dry, and fired pellets, as shown in Fig.10. The experimental data showed that Na-HA had a higher green pellet drop number than Na-FA for the same amount of addition. When the mass ratio of Na-HA to Na-FA was increased to 7:3, the green pellet drop number reached 11.7 times/pellet. With the increase in Na-HA to Na-FA mass ratio, the strength of the dry and fired pellets increased significantly. Especially when the mass ratio of the binder was 6:4, the dry pellet compressive strength started to increase significantly. Therefore, the mass ratio of Na-HA and Na-FA has a significant effect on the performance of the MHA binder, and the optimization of the mass ratio of Na-HA and Na-FA can optimize and balance the decision of MHA binder pelletizing performance.

The data about the effect of humic acid pellet binder addition on the strength of green, dry, and fired pellets in references[94~101] are systematically summarized in Fig.11. The analysis of the figure shows that Funa/MHA pellet binder shows excellent performance in iron ore pellets, especially significantly improving the strength of green and dry pellets, but there is also a problem that the fired pellet compressive strength decreases with the increase of MHA addition. However, when the binder addition is less than 1%, the fired pellet strength is still greater than 2500N/pellet, which fully meets the basic production requirements of pellets. The fundamental reason is that although humic acid binder contains a certain amount of inorganic substances, humic acid will still burn and decompose at high temperatures, which leads to a decrease in the fired pellet compressive strength. To remedy this defect and improve the high-temperature performance of pellets, Zhou and Kawatra73) prepared a modified humic acid-bentonite composite pellet binder (MCB) by extracting humic acid salts from lignite and mixing them with cheap calcium bentonite, and investigated the effect of its addition on the strength of green, dry and fired pellets, and the experimental results are shown in Fig.12. The
results showed that the strength of green, dry, and fired pellets with MHA or MCB binders added to the pellets was significantly increased compared to that of bentonite. Functional groups such as hydroxyl and carboxyl groups in HA adsorbed onto the bentonite surface through complexation and hydrogen bonding, which increased the adsorption density and force between bentonite and iron ore, and HA reduced the contact angle and enhanced hydrophilicity on the iron ore surface\textsuperscript{74} and improved the binder in dispersion between iron ore particles and increased the viscosity inside the pellets, thus significantly improving the green and dry pellet strength\textsuperscript{75}. Meanwhile, the presence of calcium bentonite provided a sufficient slag phase for the pellets and improved the fired pellet compressive strength. Therefore, humic acid binder prepared from humic substances can partially replace bentonite and reduce the amount of bentonite\textsuperscript{76}.

6. Conclusion

Humic acid, as a product with great utilization value obtained after the processing of humic substances waste resources widely existing on the earth, has been noticed and used by various industries in society. The successful application of humic acid in iron ore pellets also confirms that the performance of humic acid has obvious advantages over bentonite and traditional organic binders.

Compared with bentonite, modified humic acid pellet binder as an organic additive reduces the introduction of a large amount of SiO\textsubscript{2} in bentonite, which reduces metallurgical pollution and metallurgical cost. At the same time, the presence of humic acid can better regulate the internal moisture and viscosity of pellets, thus effectively controlling the pelletizing rate. Humic acid molecules contain a large number of solidophilic and hydrophilic functional groups such as carboxyl and hydroxyl, which improve the adsorption and aggregation ability between humic acid and mineral particles, enabling close filling between pellet particles and reducing the internal porosity of green
pellets, thus significantly improving the green and dry pellets strength.

Compared with traditional organic binders such as CMC, starch, and polyacrylamide, the preheated and fired pellet strengths prepared with MHA have a less negative impact at the same addition level, due to the fact that a portion of silicon oxide is still present in the chemically treated humic acid, which reacts with the internal oxides of the pellets after the high-temperature firing process to produce a trace liquid phase. After the pellet is cooled, a solid phase bridge effect is established between the mineral particles, thereby improving the fired pellet compressive strength.

Modified humic acid pellet binder has many advantages of both organic and inorganic binders, and can be used not only as a single additive for iron ore with poor pelletizing performance but also in combination with bentonite for other types of iron ores. As far as the environment is concerned, the vigorous promotion and use of humic acid in pellet binder can greatly reduce the consumption of high-value crops such as cotton, corn, and wheat, and the pollution and damage to the environment caused by the large number of by-products produced by enterprises' large-scale chemical synthesis of polymers. In terms of cost, humic acid is inexpensive, widely available, and simple to chemically modify and treat, which can significantly reduce the cost of iron ore pellet binders, while it can completely or partially replace bentonite, thus reducing metallurgical pollution and costs.

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94) S. Yan, N. Zhang, J. Li, Y. Wang, Y. Liu, M. Cao, and Q. Yan: Scientific Reports, 11(2021),15381. https://doi.org/ 10.1038/s41598-021-94949-0.
Caption List

Table 1  Composition and content of humic acid in peat, lignite, and weathered coal

Table 2  Chemical composition and content of FA and HA

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Fig.10 The influence of Na-FA、Na-HA and mass ratio of Na-FA to Na-HA of MHA on the green dry and fired pellet compressive strength (MHA binder keeps 0.5% dosage) (Data from Ref. [100])

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Fig.12 Green dry and Fired pellet compressive strength with 0.5 wt% binders. MCB = 0.333 wt% MHA + 0.167 wt% Ca-Bent. (Data from Ref. [105])
<table>
<thead>
<tr>
<th>Type</th>
<th>Region</th>
<th>Ash(%)</th>
<th>HA(%)</th>
<th>FA(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat</td>
<td>Marais de Mazerolles (France)</td>
<td>33</td>
<td>37</td>
<td>3</td>
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</tr>
<tr>
<td>Woody Peat</td>
<td>Indonesia</td>
<td>9.7</td>
<td>53.48</td>
<td>4.74</td>
<td>78.</td>
</tr>
<tr>
<td>Peat</td>
<td>Yuyang District (Shaanxi, China)</td>
<td>-</td>
<td>24.74</td>
<td>20.08</td>
<td>79.</td>
</tr>
<tr>
<td>Fraga Rizzo peat</td>
<td>Cravinhos (São Paulo, Brazil)</td>
<td>28.32</td>
<td>35.50</td>
<td>1.37</td>
<td>80.</td>
</tr>
<tr>
<td>Zhongdian Peat</td>
<td>Zhong Dian (Yunnan, China)</td>
<td>17.9</td>
<td>30</td>
<td>-</td>
<td>81.</td>
</tr>
<tr>
<td>Woody Peat</td>
<td>Indonesia</td>
<td>9.7</td>
<td>53.48</td>
<td>4.74</td>
<td>78.</td>
</tr>
<tr>
<td>Shengli lignite</td>
<td>Xilinhaote (Inner Mongolia, China)</td>
<td>16.69</td>
<td>23.1</td>
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<tr>
<td>Thar Lignite</td>
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<tr>
<td>Konin Mine lignite</td>
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<td>Huolinhe lignite</td>
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<tr>
<td>Shaotong lignite</td>
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<tr>
<td>Weathered coal</td>
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<td>26.4</td>
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<tr>
<td>Weathered coal</td>
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<td>C (%)</td>
<td>H (%)</td>
<td>N (%)</td>
<td>O (%)</td>
<td>H/C</td>
<td>O/C</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>-----</td>
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<tr>
<td>HA 55.0</td>
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</tr>
<tr>
<td>HA 60.5</td>
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<td>1.8</td>
<td>30.32</td>
<td>0.95</td>
<td>0.38</td>
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<td>3.97</td>
<td>38.33</td>
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<td>0.39</td>
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<tr>
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<td>3.50</td>
<td>0.83</td>
<td>38.46</td>
<td>0.73</td>
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</tr>
<tr>
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<td>1.02</td>
<td>0.58</td>
</tr>
<tr>
<td>FA 52.3</td>
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<td>2.9</td>
<td>40.7</td>
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<td>0.58</td>
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<tr>
<td>FA 48.58</td>
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<td>2.36</td>
<td>43.88</td>
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<tr>
<td>FA 39.98</td>
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<td>2.43</td>
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<td>FA 52.06</td>
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<td>1.76</td>
<td>40.77</td>
<td>0.88</td>
<td>0.59</td>
</tr>
</tbody>
</table>

HA: Humic acid    FA: Fulvic acid
Graphical Abstract

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