Study on the Effect of Various Modifying Agent on the Blast Furnace Slag

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Abstract
Blast furnace slag has modification with different modifying agents, such as iron ore waste rock, fly ash, and the mixture (each 50%). The modifying effect is evaluated from five aspects: acidity coefficient M_k, viscosity coefficient Mη, hydrogen ion index pH of slag, molten slag viscosity, and slag mineral composition. The study shows that modification slag can be used as raw material and meets the requirements for the preparation of slag wool, but they exhibit different modifying effects to different modifying agents. By means of burden calculation, slag parameter calculation and parameter linear regression analysis, the effects of modifying agent were compared as follows, iron ore waste rock is the best modifying agent, mixture is the next and fly ash is the worst.
Key words: SLAG FIBER, BLAST FURNACE SLAG, VISCOSITY, X-RAY DIFFRACTION

Blast furnace slag and solid waste as an additive, such as iron ore tailings, iron ore waste rock and fly ash etc are the main raw material for the production of slag wool. Currently, flush slag craft is preferential disposal method for blast furnace slag crafts, and then re-melting slag produces slag wool. Flush slag process can produce SO_2, H_2S and some harmful gases, and also performs a low-quality heat source without economic recycling after being handled by the hot water. Therefore, flush slag crafts have brought a serious environmental pollution and energy waste problem [1-3]. Discharged liquid slag in the blast furnace was sent to the filled hot furnace for modification, and then used to produce slag wool. It can not only take full advantage of the latent heat of the liquid slag, to achieve green production of iron and steel industry, but also can improve the rate of forming slag cotton, reduce shot content and improve the quality of slag wool[4-7]. The cost of production was reduced greatly for slag wool, which is consistent with the national energy saving policy and demonstrates the reasonable use of resources [8-11]. However, the different substances have the different modification effects, the paper is carried out on the effect of modification of blast furnace slag by iron ore waste rock, fly ash and the both mixture (both 50%) (abbreviated as the mixture)[12].

1 Experimental

1.1 Experimental principle and equipment

In the experiment, RTW-08 type melt property comprehensive tester is employed to measure the molten slag viscosity. According to the actual situation of melt, slag viscosity is measured by being immersed in the body (rotor is cylindrical usually) rotation in the measured melt and crucible maintain a static method in rotation method[9].

1.2 Experimental materials and data

The experiment samples are composed of a steel blast furnace slag, a mining area of iron ore waste rock and a power plant fly ash, whose chemical composition are shown in the table 1.

Table 1. Chemical composition of experiment raw material ,%

	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	FeO	K_2O	Na_2O
blast furnace slag	33.94	33.20	9.57	14.94	0.72	0.83	0.60	0.44
iron ore waste	64.53	3.29	2.25	12.14	3.39	4.42	3.56	2.37
Fly ash	47.62	3.87	1.39	34.67	1.82	0.57	0.98	0.28
mixture	56.08	3.58	1.82	23.41	2.61	2.50	2.27	1.33

The fluidity of the slag has influence on the operation process of drawing into slag cotton, and is demonstrated by the viscosity of slag predominately. When slag melting temperature is about 1673K, the viscosity controlled in 1~3Pa•s meets the requirements of forming slag wool [9]. Compared with chemical composition of blast furnace slag, the formation of slag wool and the chemical composition range of metallurgical slag and igneous in the diagram of SiO_2-Al_2O_3-CaO ternary system (Shown in Fig.1), which reveals that the range of slag composition is out of slag wool. So it is a low wool production making by blast furnace slag with high residue ball content which should be modified. It is found that with addition of iron ore waste rock, fly ash, or both mixture (iron ore waste rock and fly ash, both 50%) (Hereinafter referred to as mixture) to the blast furnace slag, which can be adjusted to the composition of the slag wool to the moderated range.

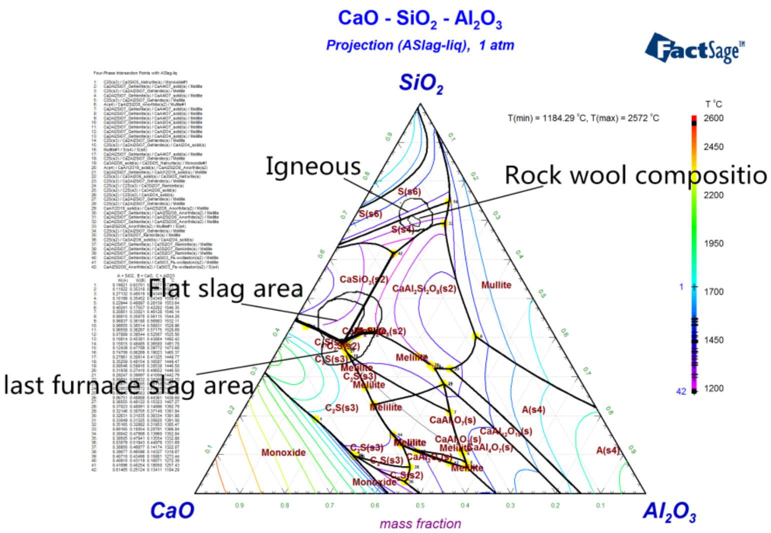


Figure 1. SiO_2-Al_2O_3-CaO ternary system in the state diagram of metallurgical slag and igneous

2 Results and Discuss

The modification slag with different proportions of iron ore waste rock, fly ash or mixture are added to modifying slag respectively, the ingredients terms can be available slag composition of adding different proportions additives, iron ore waste rock proportion is 5%~15%, fly ash proportion is 4%~13%, mixture proportion is 4%~14%. And then contrasting the quenched and tempered effect of three aspects of parameters, viscosity and mineral composition of the slag.

2.1 Comparison of slag parameter

According to the slag composition calculation, the diagrams of the slag acidity coefficient M_k, viscosity coefficient Mη and hydrogen ion index of pH values are draw to contrast the slag changes when iron ore waste rock, fly ash or mixture are added to blast furnace slag.

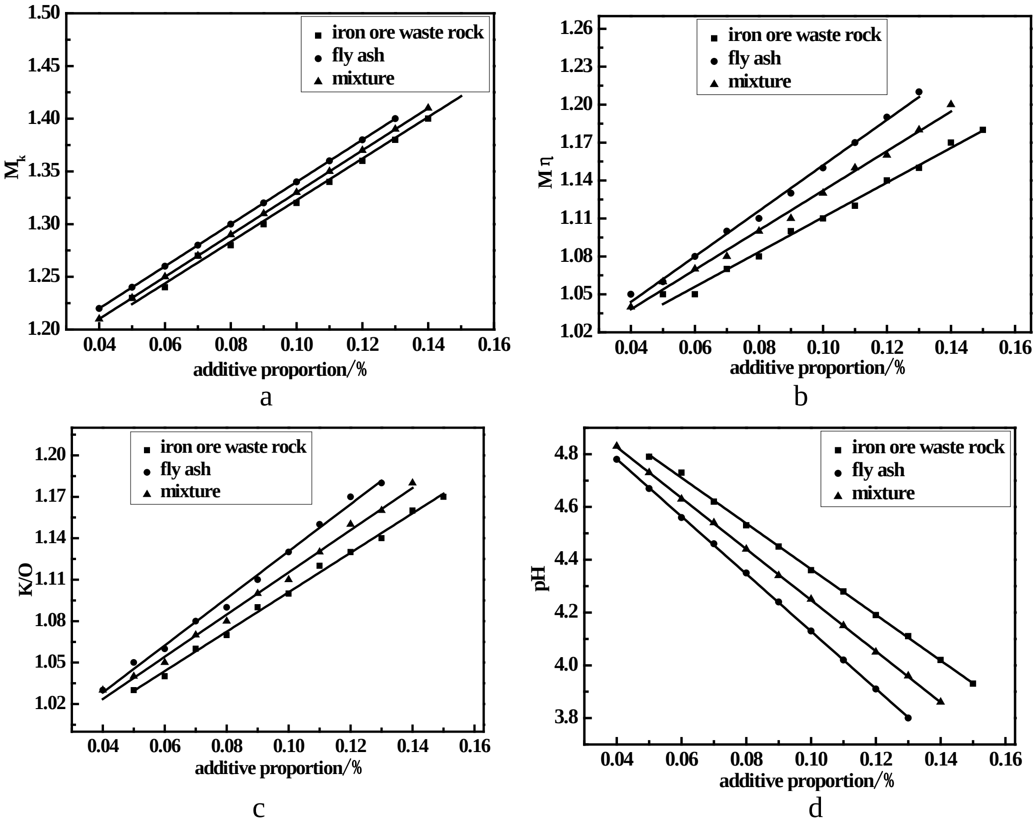


Figure 2. Parameter - quenched and tempered agent ore ratio curve

1) Acidity coefficient

M_k is a specific parameter, which is used for describing the chemical durability of slag wool, controlled in 1.2 to 1.4 within general[12-14]. If M_k is too high, it is possible to obtain longer fiber, improves chemical stability, and increases the use of thermal energy, but slag melts hardly, which makes thicker fiber. A variety of slag's M_k change situations are shown in Fig.2-a. The M_k factor has the linear relationship with additional proportion. The R-Square value of three curves is 0.99458, 1, 1, respectively, which shows an excellent correlation with a very good fitting result. M_k value increases with additional proportion increasing in slag. However, some differences are pointed that the different modifying agents have different modification effect on Mk: the fitting curve slope is about 1.97 for adding iron ore waste rock. The fitting curve slope is about 2.00 for adding fly ash as well as the mixture. In comparison with iron ore waste rock, fly ash and mixture have better modification effect. But all they can be adjusted to reach at the range of acidity coefficient of slag wool preparation.

2) Viscosity coefficient

Mη is a parameter, which is used to measure the melt mobility and indicate the degree of the difficulties of slag wool preparation. The greater Mη value is, the harder raw materials melt. That is to say, the greater the melt viscosity is, the worse the liquidity is, which leads to an undesirable preparation condition for slag fiber.
Fig.2-b shows that the Mη value is almost proportional to additional composition. The R-Square value of three curves is 0.99135, 0.99497, and 0.99343, respectively, which shows an excellent correlation with a very good fitting

result that is Mη value increases with additional proportion increasing in slag .However, various modifying agents have different modification effect on Mη: fitting curve slope is about 1.37 for adding iron ore waste rock, fitting curve slope is about 1.80 of for adding fly ash, and fitting curve slope is about 1.56 for adding the mixture. So fly ash have the best the modification effect, mixture next, iron ore waste stone is the worst. While the greater Mη value is, the stronger slag viscosity is. It is difficult to make slag fiber, which is attributed to melt having a great viscosity. Therefore, in order to obtain better slag fiber, iron ore waste is the best candidate, mixture and fly ash are following.

Acid group ratio K/O is similar with Mη in essence while molecular formula is absolutely used to calculate Mη value, the calculation of K/O is in accordance with molecules number converted into SiO_2 and CaO. But taking the impact of the different contents of Al_2O_3 into consideration, especially, it is a critical value when the content of Al_2O_3 is 8%[12-15]. Al_2O_3 is the role of acidic oxides when the Al_2O_3 content is more than 8%, so that the melt viscosity and chemical stability are improved. The coefficients of some oxide precursors can be interpreted as the correction ones. When coefficient is equal to 1, the oxide can be replaced by the same amounts of ions in the formula.

Fig.2-c the K/O value of slag is almost proportional to additional proportion. The R-Square of the three curves is 0.99591, 0.99427, and 0.99389, respectively, which shows an excellent correlation with a very good fitting result that is K/O value increases with additional proportion increasing in slag. Various modifying agents have different modification effect on K/O value, which is illustrated as the following: fitting curve slope is about 1.43 for adding iron ore waste rock; Fitting curve slope is about 1.70 for adding fly ash; And fitting curve slope is about 1.53 for adding mixture. In a word, fly ash has the best the modification effect, mixture next, Iron ore waste rock is the worst.

3) Hydrogen ion index

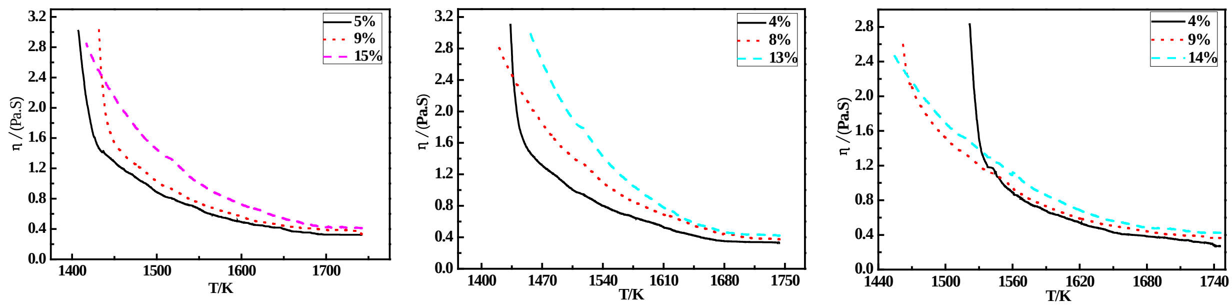
Hydrogen ion index pH is an accurate indicator to probe the chemical stability of the slag wool (anti-air, anti-water). pH <4 is the most stable, pH <5 is stable, pH <6 is moderately stable, pH <7 is less stable, PH> 7 is the most unstable.

Fig.5 shows that the pH of slag has the linear relationship with additional proportion. The R-Squares value of three curves is 0.99925, 0.99991 and 0.99992 respectively, which shows an excellent correlation with a very good fitting result. pH value decreases with additional proportion increasing. The difference is the various curve slope values that means different modification rate of PH with different modifying agent .The results show that fitting curve slope is about minus 8.65 for adding iron ore waste rock; fitting curve slope is about minus 10.87 for adding fly ash; fitting curve slope is about minus 9.67 for adding the mixture. So modification rate of fly ash is the fastest, mixture next, iron ore waste rock slowest. However, the pH of slag is less than 5 when the slag component and M_k have satisfied the raw material requirements of slag wool preparation which has better stability.

Table1 shows that fly ash has the highest total content of SiO_2 and Al_2O_3, mixture next, iron ore waste rock lowest. Conversely, fly ash has the lowest total content of CaO, MgO, Fe_2O_3, FeO, K_2O and Na_2O, mixture next, iron ore waste rock highest. Fly ash has the maximum modification rate of acidity coefficient M_k, viscosity coefficient Mη and Acid group ratio K/O, hydrogen ion index pH of slag, mixture next, iron ore waste rock has the minimum modification rate. However, the iron waste rock, fly ash and mixture, which all can meet the requirements of slag wool preparation.

2.2 Comparison of slag viscosity

Slag viscosity was measured in the condition of addition of 5%, 9%, 15% iron ore waste rock, 4%, 8%, 13% fly ash, 4%, 9%, 14% mixture, and the corresponding slag temperature - viscosity curve was illustrated as shown in Fig.3.



a b c

a. Iron ore waste rock is quenched and tempered agent; b. Fly ash is quenched and tempered agent; c. Mixture is quenched and tempered agent

b.

Figure 3. Temperature - viscosity curve in different additional ratio of slag

Fig.3 shows that each of the three substances as modifying agent of blast furnace slag, modification viscosity increases with the temperature decreasing. The difference is that the slag has different temperature-viscosity gradient descent with different modifying agent. With the proportion of modifying agent changing, the gradient descent of temperature–viscosity is different. The viscosity curves show that when fly ash acting as modifying agent, the slag viscosity is the maximum as well as temperature-viscosity gradient descent; Mixture acting as modifying agent, slag viscosity is smaller, as well as temperature-viscosity gradient descent; Iron ore waste rock acting as modifying agent, slag viscosity is the least as well as temperature-viscosity gradient descent. With adding ratio of modifying agent increasing, for the fly ash acting as modifying agent the temperature-viscosity gradient descent value is the maximum; For iron ore waste rock acting as modifying agent, temperature-viscosity descent value is smaller; For mixture acting as modifying agent, the temperature-viscosity gradient descent is the least. In conclusion, iron ore waste rock is the best modifying agent, mixture next, fly ash is the worst. However, no matter what kinds of material act as modifying agent, slag viscosity is small in the high temperature zone (1573~1743K), which meets the requirements of the preparation of slag wool raw material. Therefore, three substances can be used as modifying agent of slag.

2.3 Comparison of slag mineral composition

With the types and proportions of modification agent change, the slag composition changes and its mineral composition also has corresponding changes. Combined with CaO-MgO-SiO_2 ternary phase diagram which includes the slag phase diagram of the Al_2O_3 content at 15% , as shown in Fig.4, the chemical composition of melilite is SiO_2 whose composition is from 32% to 48%, CaO whose composition is from 25% to 48%, MgO whose composition is from 0% to 15%. Furthermore, modification slag chemical composition in Table 1 is restrained in the above range, indicating that melilite is main crystalline phase in slag [4].

In the experiment, 5%, 9%, 12%, 15% iron ore waste rock, 4%, 8%, 13% fly ash, 4%, 9%, 14% mixture of blast furnace slag are mixed with modifying agent after loaded into the graphite crucible, which is placed in the electric furnace to conduct slag measurement, and then mineral composition analysis is carried out for the re-melting slag. At last, the X-ray diffraction spectrum is measured, shown in Fig.5.

Fig.5 shows that iron ore waste rock acting as modifying agent, when the ratio of iron ore waste rock is 5%, melilite content is the largest, followed by gehlenite, and contains a trace amount of fayalite. When the ratio is more than or equal to 9%, the slag can form infinite solid solution after solidification (vitreous body), mineral cannot be separated. When fly ash acting as modifying agent, whose ratio is 4%, melilite content is the largest, followed by akermanite, and a small amount of gehlenite, hardystonite and fayalite is included. When its ratio is more than or equal to 8%, the slag can form infinite solid solution after solidification, mineral cannot be separated. Similarly, mixture acting as modifying agent, when the ratio is 4%, slag includes large amount of hardystonite, gehlenite, akermanite and melilite, also includes a small amount of fayalite, and when the ratio is 9%, the amount of minerals reduce significantly after solidification precipitation of the slag, and the relative content of melilite increases, the relative content of hardystonite, gehlenite, akermanite decreases significantly. In addition, a trace amount of fayalite is appeared when mixture ratio is 14%, the slag can form infinite solid solution after solidification, and mineral cannot be also separated out.

Different substances acting as modifying agent can lead to slag to include the different types of minerals. Iron ore waste rock acting as modifying agent, slag consists of gehlenite, akermanite, melilite and a trace amount of fayalite. Fly ash acting as modifying agent, which includes a small amount of hardystonite in addition to include the above minerals in iron ore waste rock. And mixture acting as modifying agent, slag including mineral type is the same as fly ash in slag, but the relative content of hardystonite increases significantly. In addition, the different ratios of modifying agents has different effect on forming infinite solid solution after solidification, when iron ore waste rock ratio is greater than or equal to 9%, fly ash ratio is greater than or equal to 8%, mixture ratio is greater than 9%, all slag can form infinite solid solution after solidification.

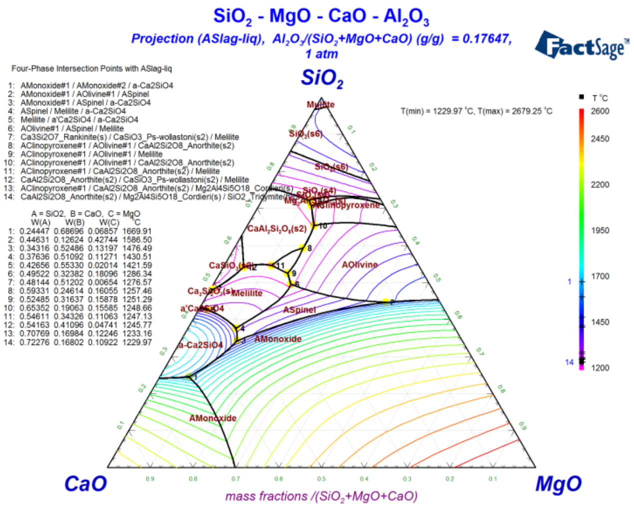
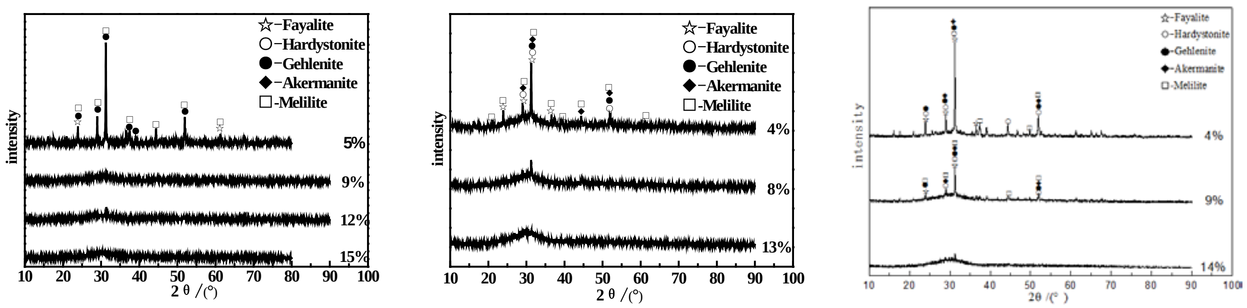


Figure 4. Al_2O_3 content of 15% CaO-MgO-SiO_2 phase diagram



a b c

a. Iron ore waste rock is quenched and tempered agent; b. Fly ash is quenched and tempered agent; c. Mixture is quenched and tempered agent

Figure 5. X-ray diffraction spectra of different proportion additive of slag

3 Conclusion

1) The results show that with fly ash ratio increases in slag, acidity coefficient M_k, viscosity coefficient Mη, acid group ratio K/O and hydrogen ion index pH change intensively, mixtures is next and iron ore waste rock ratio increases in slag with the slowest change rate. They can be used as the slag wool raw material.

2) Using different modifying agents to handle blast furnace slag, viscosity and temperature-viscosity landing gradient are different. However, no matter what kinds of material act modifying agent, the viscosity of slag is small in the high temperature zone (1573~1743K), which meet the requirements as the preparation of slag wool raw material, so the three substances can be used as blast furnace slag modifying agent. Iron ore waste rock acting as modifying agent is the best, mixture next, fly ash the worst.

3) The different substances acting as modifying agent are used to handle blast furnace slag, which induces the mineral composition and the content to be different in slag. When iron ore waste rock ratio is greater than or equal to 9%, fly ash ratio is greater than or equal to 8%, mixture ratio is greater than 9%, the slag can form infinite solid solution after solidification. The slag fiber exhibits an excellent chemical stability.

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