Hot Slag Modification of BOF Slag for Preventing its Disintegration to Enhance Slag Utilization

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Depending on the utilization of BOF slag, different properties such as good volumetric stability, large grain size, high mechanical strength and low pH are required in BOF slag. Many applications of BOF slag mainly require the coarse aggregate (aggregate sizes larger than 1/4 inch) for providing mechanical strength. However, the disintegration of BOF slag is found to yield a high amount (ca. 55%) of fine powder (<4.75mm) as it is treated by hot pouring and plate chilling in CSC. The production of fine powder limits and lowers the utilization amount of BOF slag. In this study, we prove that a reduction in the basicity of BOF slag is an effective strategy for preventing the disintegration of BOF slag. By remelting 10% and 15% of silica with BOF slag, it was found that modified BOF slag with lower basicity shows less disintegration. The strategy is further proved and applied on hot slag modification station in CSC. The ratio of coarse aggregate of modified BOF slag produced by the hot slag modification station was analyzed. The analytical result shows that the ratio of coarse aggregate, it is found that the expansion value, f-CaO content and pH value are lower than those of the original BOF slag. The modified BOF slag with superior properties show that it is a potential material for road construction, hydraulic engineering and concrete applications, which would enhance the utilization of BOF slag in CSC.

Keywords: BOF Slag, Coarse Aggregate, Volumetric Expansion, Slag Modification, Stabilization

1. INTRODUCTION

Reuse and reutilization of BOF slag has been a vital topic for the circular economy. In Taiwan, BOF slag is significantly utilized in asphalt concrete (AC) pavement construction as its regulations and applications are more mature. For AC applications, larger aggregate of BOF slag (refers to aggregate sizes larger than 1/4 inch, 3/8 inch and 3/4 inch, respectively) is required since its excellent physical properties are a benefit to pavement performance (i.e. resistant to abrasion and rutting). On the contrary, as the mechanical strength of smaller aggregate of BOF slag is less pronounced, it does not have a clear utilization route except for sintering in the factory. However, only about 45% of coarse aggregate can be produced as BOF slag is treated by hot pouring and plate chilling in CSC. The low production of coarse aggregate also reflects the fact that a higher amount (55%) of smaller aggregate (<4.75mm) is produced, which makes reutilization of BOF slag more difficult. Therefore, for increasing BOF slag reutilization, it is necessary to develop strategies to improve the yield of coarse aggregate and reduce the output of smaller aggregate of BOF slag. In this study, it was found that the basicity (CaO/SiO₂) is the key to coarse aggregate formation of BOF slag. Through remelting experiments, more disintegration of BOF slag was observed as the slag basicity was higher. To put the experimental results into practice, hot slag engineering was carried out by injecting silica in to molten slag in our hot stage BOF slag modification plant. After the treatment, the yield of coarse aggregate increases effectively from 45% to 68.2~ 79.5% and the output rate of smaller aggregate is reduced from 55% to 20~30%. Also, the expansion of BOF slag decreases to less than 0.5%, which demonstrates its potential for road construction, hydraulic engineering and concrete applications. Accordingly, this approach has proved to be a good strategy for not only effectively increasing the yield of coarse aggregate but also decrease the expansion of BOF slag, which is believed to be beneficial to BOF slag reutilization in the circular economy.

2. EXPERIMENT

The phase diagram of BOF slag was calculated by SPARK (the software for the calculation of slag property) for estimating if there is any f-CaO in the BOF slag. To study the influence of basicity of BOF slag, the slag modification experiments were carried out in crucibles. By mixing the BOF slag samples with different amounts of silica (e.g.10% and 15%), various basicities of BOF slag can be obtained. The samples were then heated to and held at 1550°C for 1h to ensure the BOF slag melted completely with the silica. Finally, the samples were quenched to room temperature by water. The appearance, crystalline phases and chemical compositions of the collected samples were analyzed. The hot slag modification was done by using the hot stage BOF slag modification (HBM) station established in CSC.¹ The station consists of 2 stands for slag modification (as shown in Fig.1). Each stand is equipped with a lance and a rod as Figure 2 shows. The lance is used for blowing oxygen and injecting reactant (e.g. silica), and the rod is utilized



Fig.1. The HBM setup consists of 2 stands, and both of them can be operated independently to execute slag modification.



Fig.2. Each stand of the HBM setup is equipped with a lance (right) for injecting additives and a rod (left) for breaking solidified slag and collecting samples. The rod covered by molten slag after collecting samples is displayed in this figure.

for breaking solidified slag and collecting for samples for on-line QC examination, respectively. The molten slag is from #2 steelmaking plant of CSC. The slag pot filled with molten slag is transported to a position underneath the stage stand before slag modification starts. Depending on the basicity of the slag, normally, ca. $5\sim10$ wt.% of silica is injected into the molten slag for the modification. The on-line QC examination system is used for measuring the volumetric expansion of the treated slag. The measurement is carried out in a 90°C water bath for 30 mins. If the expansion of the slag is less than 0.4% in 30 mins, it is identified as a successful modification.

3. RESULTS AND DISCUSSION

The disintegration of steel slag is thought as the main reason for the formation of fine powder. The disintegration of steel slag is attributed to the presence of C2S (dicalcium silicate /Ca₂SiO₄) and f-CaO in steel slag.²⁻⁶ It is known that the disintegration is driven by the volumetric expansion of phase transformation from β-C2S to γ -C2S during cooling (as shown in Fig.3).²⁻⁵ However, since β -C2S phase is stabilized by phosphorous in BOF slag, it does not transform to γ -C2S during cooling. Consequently, it is believed that the disintegration of BOF slag is due to the presence of f-CaO which would cause expansion (as shown in Fig.4) as it hydrates and forms Ca(OH)₂.⁶ To prevent the disintegration of BOF slag from f-CaO hydration, decreasing the basicity of BOF slag by remelting f-CaO with silica is considered the key to increase the coarse aggregate of BOF slag.

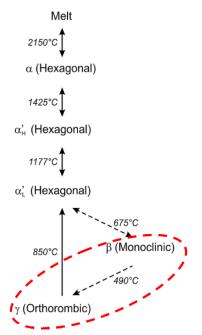


Fig.3. The phase transformation of C2S (Ca₂SiO₄) in steel slag during cooling. The red-dashed ellipse labels β -C2S to γ -C2S transformation at around 490°C.

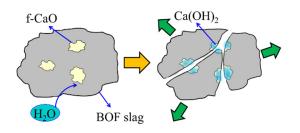


Fig.4. The hydration of f-CaO in BOF slag forms Ca(OH)₂ causes expansion and disintegration of BOF slag.

According to the phase diagram, in the case of BOF slag with a basicity of 4 (shown as a black triangle in Fig.5), f-CaO would exist in the sample. However, as the basicity is reduced to below 2.8 (shown as a red triangle in Fig.5), f-CaO is less likely to form. In addition to the phase diagram calculation, reduction of slag basicity experiments by slag modification were done. By mixing 10% and 15% of silica with BOF slag in crucibles, respectively, the slag modifications were done at 1550°C for 1h for remelting BOF slag and silica. The hot modified BOF slag was then quenched by water and collected for analyses. Each sample was cut in half vertically to analyze its cross section for appearance. As Fig.6a and 6b show, it is clear that the more silica added when remelting the less disintegration of BOF slag is observed. This result confirms that decreasing the basicity of BOF slag would prevent its disintegration. By combining the phase diagram calculation and slag modification experimental results, an adjusted silica injection in the range of

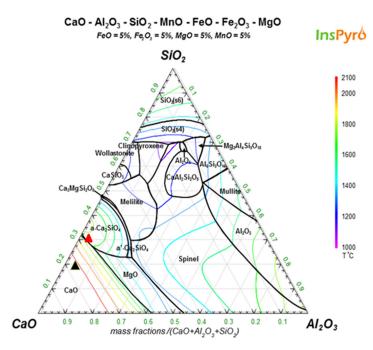


Fig.5. The BOF slag (basicity=4) is labeled as black triangle and the modified BOF slag

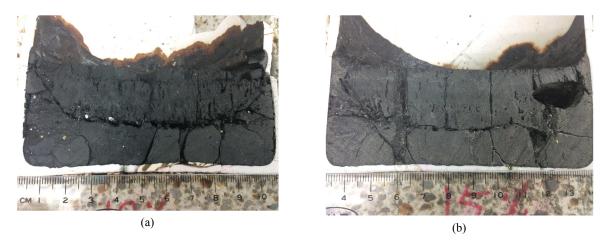


Fig.6a, 6b The appearance of modified BOF slag (with 10% silica addition and 15% silica addition, respectively)

| - | | | | | | |
|-------|--------|--------|--------|---------|------------------|--|
| Batch | AC6 | AC3 | AC2 | AC fine | AC magnetic part | |
| 1 | 37.54% | 14.92% | 15.72% | 31.07% | 0.76% | |
| 2 | 32.16% | 33.18% | 14.16% | 19.79% | 0.73% | |
| 3 | 22.21% | 32.31% | 20.00% | 23.11% | 2.37% | |

Table 1 The analytical result of the ratio of coarse aggregate (AC2/AC3/AC6) in modified BOF slag

(basicity=2.5) is labeled as red triangle in the phase diagram.

 Table 2
 The chemical composition, expansion values, f-CaO and pH values of BOF slag and modified BOF slag, respectively.

| Composition and Property | BOF slag | Modified BOF slag | |
|----------------------------------|----------|-------------------|--|
| CaO % | 43.19 % | 41.15 % | |
| SiO ₂ % | 11.88 % | 16.39 % | |
| Al ₂ O ₃ % | 2.19 % | 2.25 % | |
| MgO % | 8.15 % | 6.91 % | |
| Tfe % | 23.9 % | 21.76 % | |
| MnO % | 2.92 % | 2.97 % | |
| Cr ₂ O ₃ % | 0.19 % | 0.16 % | |
| P2O5% | 3.17 % | 3.40 % | |
| B2 (CaO/SiO ₂) | 3.64 % | 2.51 % | |
| Expansion value | 3~5 % | 0.49 % | |
| f-CaO % | 3.86 % | 1.42 % | |
| pH value | 12.4 | 11.9 | |

5~10% was applied in our hot slag modification station so that the slag basicity could be lowered to below 2.8. Therefore, 5~10% of silica is injected into molten slag in the hot slag modification station, where also, oxygen is blown into the molten slag, which leads to the oxidation reaction of iron (II) oxide, so as to maintain heat, decrease viscosity of the slag and provide a good mixing for the reaction. After modification, the on-line QC examination was applied immediately, to measure volumetric expansion of the modified BOF slag. The QC examination was carried out by immersing a ground modified BOF slag powder into a 90°C water bath for 30 mins. For a successful modification, the volumetric expansion should be less than 0.4 % by our QC examination. For every 1000 tons of modified BOF slag produced, the ratio of coarse aggregate (include AC2, AC3 and AC6 which refer to aggregate sizes larger than 1/4 inch, 3/8 inch and 3/4 inch, respectively) was analyzed. Totally, 3 batches (1000 tons/batch) of samples were analyzed. The analytical result is shown in Table 1. Based on the result, it was found that the ratio of coarse aggregate of modified BOF slag is in the range of 68.2~79.5%, which is higher than BOF slag (ca. 45%).

Besides the ratio of coarse aggregate, the chemical composition, expansion and pH value of the modified BOF slag were analyzed. Table 2 shows the comparison of chemical composition, expansion and pH value of BOF slag and modified BOF slag, respectively. It was found that the basicity of the modified BOF slag is 2.51 which is lower than the original BOF slag, so that the expansion value, f-CaO content and pH value are lower than those of the original BOF slag. With superior properties of high ratio of coarse aggregate, good volumetric stability and low pH value, it is believed that the modified BOF slag is a potential material for road construction, hydraulic engineering and concrete applications.

4. CONCLUSION

For the utilization of BOF slag, several applications such as road construction, hydraulic engineering and concrete products mainly require the coarse aggregate (aggregate sizes larger than 1/4 inch) for providing mechanical strength. However, the disintegration of BOF slag was found to yield a high amount (ca. 55%) of fine powder (<4.75mm) as it was treated by hot pouring and plate chilling in CSC. The production of fine powder limits and lowers the utilization amount of BOF slag. The presence of f-CaO in BOF slag is believed to cause the disintegration of BOF slag as it is hydrated to expand. Thus reducing the basicity of BOF slag is believed to be an effective strategy for preventing the disintegration of BOF slag. By remelting 10% and 15% of silica with BOF slag, it was found that modified BOF slag with lower basicity shows less disintegration. The strategy is further proved and applied on the hot slag modification station in CSC. For every 1000 tons of modified BOF slag produced, the ratio of coarse aggregate was analyzed. The analytical result shows that the ratio of coarse aggregate of modified BOF slag is in the range of 68.2~79.5%, which is higher than BOF slag (ca. 45%). In addition to the ratio of coarse aggregate, it was found that the expansion value, f-CaO content and pH value are lower than those of original BOF slag. With superior properties of high ratio of coarse aggregate, good volumetric stability and low pH value, it is believed that the modified BOF slag is a potential material for road construction, hydraulic engineering and concrete applications, which would enhance the utilization of BOF slag in CSC.

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