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Application and Breakthrough of BOF Slag Modification Technique

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It has been a challenge to reuse and recycle the Basic Oxygen Furnace (BOF) slag for steel companies worldwide. Due to the existence of f-CaO in slag, the volume of slag expands during hydration, limiting the uses of BOF slag. Accordingly, removing f-CaO to prevent BOF slag from expansion is the key for slag utilization. Despite many post-treatments of BOF slag having been tried, none of them have proved to effectively decrease the amount of f-CaO/MgO. Consequently, the core technology, namely, hot stage BOF slag modification (HBM), was developed by China Steel (CSC) to solve the volumetric expansion problem. By treating BOF slag with HBM technology, a reaction with f-CaO/MgO and silica was done to form calcium/magnesium silicates so that the volumetric expansion of the slag was inhibited. Currently, the success rate of the BOF slag modification is higher than 96% after refining several experimental parameters during HBM operation. Besides slag modification, it is equally important to utilize the modified slag as raw materials for road construction, concrete-based materials as well as asphalt concrete aggregates etc. Herein, pavement / grass bricks and concrete-based revetment blocks were made by using modified BOF slag as a raw material. The performance of the pavement bricks, such as compressive strength, is higher than 70 MPa. Most importantly, the volumetric stability of bricks and revetment blocks was examined. The stability of the modified BOF slag-based products was revealed after testing them outdoors for at least 8 months. Further volumetric stability outdoor tests of these concrete products is ongoing. In addition to conventional uses, novel applications of modified BOF slag (e.g. ceramic tiles) are being developed. On the basis of results aforementioned, we believe that the development of BOF slag modification technique at CSC will shed light on the utilization and reuse of BOF slag.

Keywords: BOF slag, Volumetric expansion, Slag modification, Stabilization, Valorization

1. INTRODUCTION

BOF slag, the by-product of steelmaking, has now encountered great difficulties in reuse and utilization. The reasons that cause the utilization difficulties are mainly due to the existence of f-CaO/MgO in BOF slag. As a result of the presence of f-CaO/MgO in BOF slag, the volume of the slag expands during hydration, which limits the uses of BOF slag in engineering materials[1,2]. Consequently, developing an approach to diminish the amount of f-CaO/MgO in BOF slag is vital if one would like to make good use of it.

Much effort has been devoted to develop strategies for reducing f-CaO/MgO in BOF slag. Among these strategies, HBM (hot stage BOF slag modification)[3-8] shows promise for solving volumetric expansion problems caused by the presence of f-CaO/MgO in BOF slag. As environmental legislation worldwide becomes stricter, the volumetric stability of BOF slag is strongly called for if BOF slag is to be used as an engineering material. Also, for utilizing BOF slag in a variety of applications, it is crucial to improve the volumetric stability of BOF slag. Thus, the HBM technique was adopted by CSC to solve the volumetric expansion problem of BOF slag.

The principle of HBM involves, (1) the introduction of silica sand into the molten slag to react with the f-CaO/MgO to form the stable minerals of calcium/ magnesium silicates and ferrites, and (2) complementary additions (e.g. oxygen) to generate heat so to maintain the molten state of the BOF slag for proceeding the reaction. Theoretically, f-CaO/MgO can react entirely with silica so as to form calcium/ magnesium silicates if a completed reaction is achieved. However, several experimental parameters such as slag temperature, the amount of silica and oxygen addition and the control of the inherent properties of the BOF slag etc. should be considered and optimized so as to achieve a satisfactory success rate of BOF slag modification.

In 2012, the HBM station was established at CSC. Although the success rate of modification is merely 27% in the beginning, after refining experimental parameters during HBM operation, currently, the success rate is steadily improving to more than 96%. This work aims to present the industrial practices of the production and utilization of modified BOF slag at CSC.

2. EXPERIMENT

The hot stage BOF slag modification station consists of 2 stands for slag modification (as shown in Fig.1). Each stand is equipped with a lance and a rod as Fig.2 shows. The lance is used for blowing oxygen and injecting reactant (e.g. silica), and the rod is utilized 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. As the process begins, the lance is inserted into the molten slag, which then blows oxygen and injects reactant (e.g. silica) into the molten slag. In addition to the injection of the reactant, the lance can move forward into the molten slag and stir it, increasing the rate of the reaction. Depending on the properties of the slag, normally, ca. 10-15 wt.% of silica is injected into the molten slag for the modification. For a single modification, it takes around 30 min to finish the modification of the slag. After the modification, a rod equipped with three containers, is inserted into the treated molten slag, to collect samples of the molten slag for the on-line QC examination system. The on-line QC examination system is used for measuring the volumetric expansion of the treated slag.

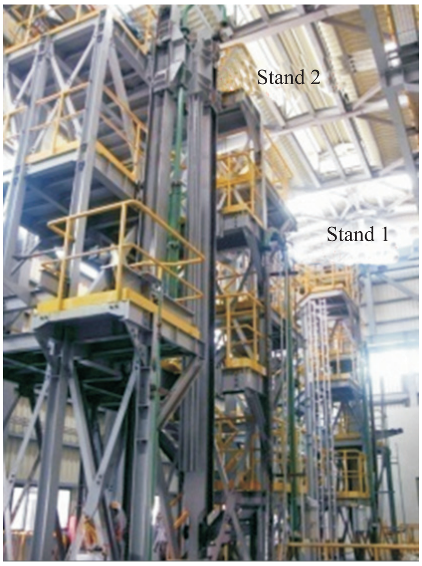


Fig.1. The HBM setup consists of 2 stands and both of them can be operated independently to execute slag modification.

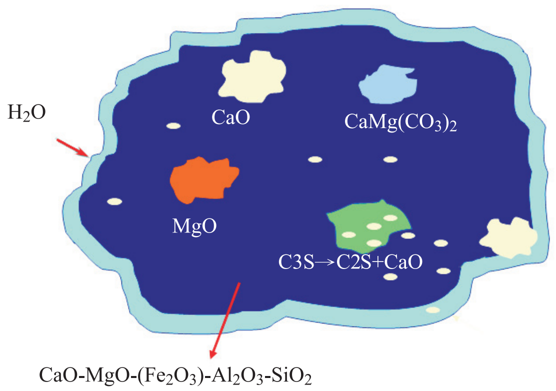
Fig.2. Each stand of the HBM setup is equipped with a lance (right) for injecting additives, a rod (left) for breaking solidified slag, and collecting samples. The rod covered by molten slag after collecting samples is displayed.

The measurement is carried out in a 90°C water bath for 30 min. If the expansion of the slag is less than 0.4% in 30 min, it is identified as a successful modification.

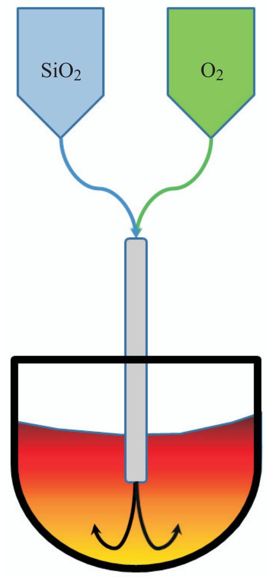
3. RESULTS AND DISCUSSION

The volumetric instability of BOF slag originates from the existence of f-CaO/MgO in the slag. As f-CaO/MgO is hydrated, $Ca(OH)_2$/$Mg(OH)_2$ forms and expands in volume, which causes the collapse of BOF slag. In this situation, the f-CaO/MgO of BOF slag has reacted so that the BOF slag becomes more stable. Consequently, various strategies have been applied for reducing f-CaO/MgO in BOF slag by using post-treatments of slag with hydration-based methods (e.g. steam aging). However, the compositional inhomogeneity of BOF slag renders the hydration-based methods of failures. Since the inclusion of f-CaO/MgO and dolomite in slag (see Scheme 1) cannot be reached easily by water, the hydration-based methods are ineffective in removing f-CaO/MgO completely. Therefore, the hot stage slag modification was developed. The HBM technique demonstrates its functions for removing the factors of volumetric expansion caused by f-CaO/MgO. The principle of the HBM operation is shown in Scheme 2. Generally, silica is injected into molten slag to react with f-CaO/MgO. In addition to silica, 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. Depending on the basicity of BOF slag, 10-15% of silica was injected into the molten slag for the modification. 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 min. For a successful modification, the volumetric expansion should be less than 0.4% by our QC examination. By this QC examination, the success rate of BOF slag modification was merely 27% in the early stages (shown in Fig.3) of the HBM operation. A lot of experimental parameters have been tried for increasing the success rate. Finally it was found that the factors associated with "temperature" and "viscosity" are critical for achieving a successful modification of BOF slag. With the parameters that have been optimized, presently, the success rate of modification is steadily higher than 96%.



Scheme 1. The compositional inhomogeneity of BOF slag shows minerals (e.g. f-CaO/MgO, dolomite and C3S) are included in the slag. Only f-CaO/MgO that is exposed on the surface of slag can be hydrated by water and stabilized. Therefore, hydration-based methods are not practical for stabilizing BOF slag.



Scheme 2. The concept of the HBM technique. By blowing oxygen into the molten slag, this oxidation reaction of FeO occurs, which generates heat for maintaining the temperature of molten slag.

In fact, a successful modification can significantly diminish the amount of embedded f-CaO/MgO and dolomite in the slag, such that the inclusion of white minerals (generally, f-CaO/MgO and dolomite) in slag become less apparent. This phenomenon is clearly represented in Figs 4a and 4b, respectively. In Figure 4a, white minerals embedded in BOF slag are observed. In contrast, there is no apparent inclusion of white minerals observed in the modified BOF slag (Fig.4b).

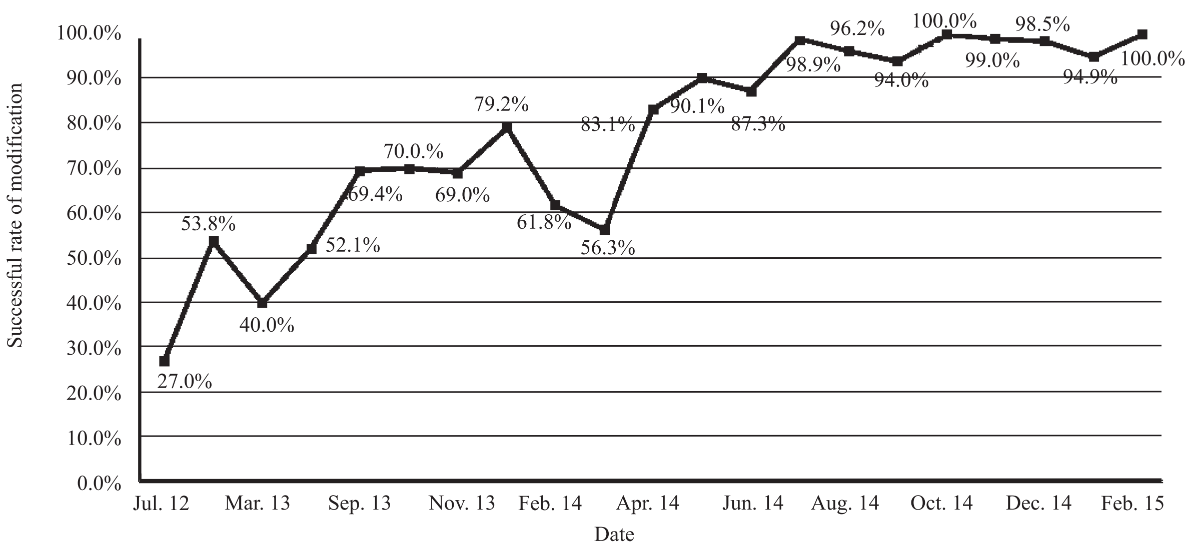


Fig.3. The success rate of the modification increased significantly from July 2012 to February 2015 by refining several experimental parameters.

(a)

(b)

Fig.4. The pictures of the BOF slag (a) without HBM and (b) with HBM treatment.

The BOF and modified BOF slag were analyzed by Powder X-Ray Diffractometer (PXRD), respectively, to identify the compositional difference between them. As PXRD profiles (Fig.5) show, the mineral phases of the BOF and modified BOF slag are similar except that no f-CaO (denoted by stars) is obtained in modified BOF slag. This result is consistent with the chemical analytical result of modified BOF slag (data not shown). Also, the measurements of residual expansion of the modified BOF slag reveal that the slag has been stabilized completely (i.e. the residual expansion is nearly zero). On the basis of the analytical data, it is believed that the HBM technique can effectively diminish expansion factors of BOF slag.

Many attempts were made for the utilization of modified BOF slag. At present, the modified BOF slag was used as a raw material for making pavement / grass bricks (Fig.6a), concrete materials, AC (Asphalt Concrete) road construction and railway ballast at CSC. Pavement and grass bricks with distinct sizes (Fig.6b) can be made for the uses of sidewalk and parking, respectively. To find an appropriate substitution level of modified BOF slag for pavement making, pavement bricks with different percentages of modified BOF slag

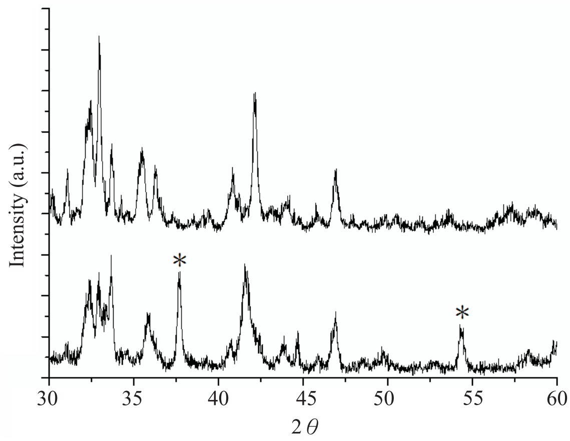


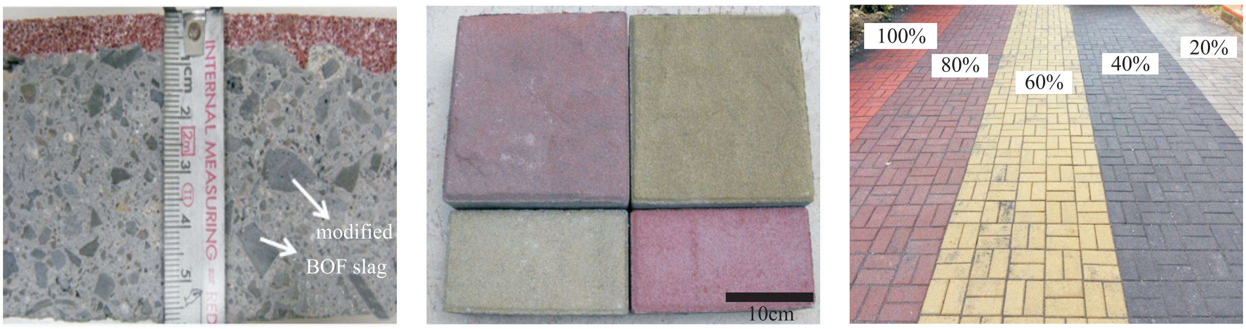
Fig.5. The XRD pattern profiles of BOF (bottom) and modified BOF slag (top), respectively. The stars denote the phase of f-CaO.

(from 20-100 wt.%), labeled by different colors were made (Fig.6c). It was found that the compressive strength of the modified BOF slag-based bricks is generally higher than 70 MPa (Table 1), which shows a better mechanical property than the ones without substitution by modified BOF slag. The pavement bricks have been paved outdoors to evaluate their stability. At present, no volumetric expansion and breakages were found in the pavement bricks (Fig.6c) after 15 months of outdoor experiments.

Besides pavement bricks, revetment blocks (size: $50\times50\times25$ cm^3) which consist of ca. 40 wt.% of modified BOF slag were made. Also, tetrapods (10 t/unit) were produced in the same manner. The concrete products are now placed outdoors to evaluate their stability (Figs 7a and 7b, respectively). Up to now, the concrete products still exhibit their volumetric stability after 8 months of outdoor experiments. More attention will be paid to the observation of revetment blocks and tetrapods, in particular, during the typhoon and plum rain seasons this summer in Taiwan. In addition to the aforementioned applications, modified BOF slag was utilized for substituting natural aggregates in AC roads (Fig.8a) and railway ballast (for torpedo car uses at CSC, Fig.8b). In the preliminary examination, good qualities of these modified BOF slag-based products were shown. Besides conventional uses of modified BOF slag, the development of high value-added products such as ceramic tiles is in progress. With the help of the HBM technique, volumetric expansion problems of BOF slag is solved, which shows promises for utilization and reuse of BOF slag.

Table 1 Better compressive strength is displayed, as natural aggregates of the pavement bricks are replaced by modified BOF slag

Modified BOF slag Substitution percentage (%)	0	20	40	60	80	100
Compressive strength (MPa)	69	78	74	76	72	80



(a) (b) (c)

Fig.6. (a) The modified BOF slag is utilized as a raw material for making bricks, (b) The pavement/grass bricks with a variety of colors and sizes can be made by using modified BOF slag as a raw material, (c) Pavement bricks with different levels of modified BOF slag substitute paved outdoors demonstrate good volumetric stability.

(a) (b)

Fig.7. (a) The revetment blocks (size: 50×50×25 cm^3) and (b) Tetrapods (10 t/unit) made of 40 wt.% of modified BOF slag are now placed outdoors for field tests.

(a) (b)

Fig.8. (a) The road with the length of 1.2 km was paved by modified BOF slag-based AC in Tainan city of Taiwan, (b) Modified BOF slag was utilized in the railway ballast of torpedo car at CSC.

4. CONCLUSION

In comparison to other post-treatment approaches of BOF slag, it has been proven that only the HBM technique can effectively reduce the residual expansion of slag. The HBM Station was developed and established by CSC in 2012. Through refining several experimental parameters during HBM operation, the success rate of modification is steadily higher than 96%. With the high success rate of modification, the production and the quality of modified BOF slag rises so that different applications of modified BOF slag can be achieved. These applications include modified BOF slag-based pavement/grass bricks, concrete products (revetment blocks and tetrapods), AC road and railway ballast (for the uses of torpedo car at CSC). Up to now, the modified BOF slag-based products have been placed outdoor for a period of 8-15 months. Still, good stability is exhibited. Further examinations and careful observations would be done on the modified BOF slag-based products to evaluate the quality of modified BOF slag. Furthermore, novel applications of modified BOF slag are currently being developed.

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