Fundamental and industrial investigation on preparation of high acidity coefficient steel slag derived slag wool

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Steel slag is a by-product in steel production process with considerable volume and low utilization rate in China. This paper investigated the fundamental and industrial feasibility of preparation and properties of high acidity coefficient slag wool using steel slag and fly ash (FA) as raw materials. Slag samples with 30–50 wt % steel slag were modified by FA and viscosity of the modified melts were tested by rotating cylinder method. The slag samples were melted in cupola furnace and then produced into slag wool through melt spinning fiberization method. Modification of steel slag, viscosity of the modified melts and industrial parameters were systematically investigated. Produced slag wool were characterized by X-Ray diffraction, scanning electron microscope and differential thermal analysis. Properties (acidity coefficient, average diameter, shot content, thermal conductivity, etc.), leaching tests and radionuclides were tested according to Chinese national standards. High acidity coefficient slag wool produced by steel slag and FA exhibited properties superior to industrial rock wool. Steel slag and FA can be massively utilized and huge amount of natural resources can be correspondingly saved by substituting rock wool with the slag wool.

Key-words : Steel slag, Cupola furnace, Spinning fiberization method, High acidity coefficient, Slag wool

1. Introduction

Steel slag (SS) is a solid waste generated in steel production and generally can be categorized as basic oxygen furnace slag (BOFS), electric arc furnace slag (EAFS) and ladle refining slag according to the steelmaking process.¹ Potential toxicity caused by heavy metals and volume instability caused by hydration of free lime and magnesia restricted the utilization of steel slag.² Considerable volume of approximately 15% SS were produced in steel production process.³ In China, 808 million tons of crude steel were produced in 2016 and approximately 121.2 million tons SS were accordingly generated. The current utilization rate of SS is about 20% and the deposited SS (mainly BOFS) has been accumulated to more than 300 million tons in China, which occupies large amount of land and causes environmental pollution and waste of slag resources.¹,⁴–⁶ The Environmental Protection Tax Law of the People’s Republic of China executed from January 1, 2018 stimulates that discharged metallurgical slag will be subjected to environmental protection tax by 25 CNY per ton. Therefore, exploring an effective and profitable method for the massive utilization of SS is quite imperative.

Mineral wools play an important role in industrial and building thermal insulation due to their superb thermo-acoustic insulating and fire resistance properties.⁷–¹⁰ Acidity coefficient $M_k$ [mass ratio of $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/ (\text{CaO} + \text{MgO})$] is a specific parameter for evaluating the chemical durability of mineral wools. Rock wool with high $M_k \geq 1.6$ are mainly produced with natural resources (basalt, diabase, dolomite, etc.).¹¹ while slag wool with $1.1 \leq M_k \leq 1.5$ are mainly produced with industrial wastes. Slag wool have attracted extensive attention due to low cost and easy production among mineral wool products. Attempts have been extensively made to produce slag wool with different industrial wastes,¹² including blast furnace slag (BFS), copper slag, fly ash (FA), etc. Increasing acidity coefficient improves the chemical durability, water resistance and fire resistance properties of mineral wool products. In mineral wool industries, high acidity coefficient normally implies broad application, better quality and high profit. Saving natural resources by using industrial wastes and increasing the utilization rate of industrial wastes have significant social, economic and environmental benefits.¹³ Production of slag wool with steel slag and increasing the acidity coefficient of slag wool have barely been reported.

High acidity coefficient slag wool produced by SS should be investigated to substitute rock wool. This paper
aims to utilize SS and FA as raw materials for the production of high acidity coefficient slag wool. Modification of SS with FA, viscosity of the melts, industrial production parameters and properties of slag wool were presented and investigated.

2. Materials and methods

2.1 Materials

SS used in this investigation was supplied by an iron and steel enterprise in China. SS (mainly BOFS and EAFS) produced by the iron and steel enterprise was transported with slag ladle, poured into slag pit and then cooled with water. The cooled slag was then crushed, grinded, magnetic separated and stockpiled. Steel slag used in this investigation was the stockpiled slag. FA as the modification agent was used to adjust the acidity coefficient and chemical compositions of the slag. The chemical compositions of the SS, FA were determined by X-ray fluorescence spectrometer (XRF) (XRF-1800, SHIMADZU, Japan). Table 1 shows the main chemical compositions of SS and FA.

It can be seen that mainly CaO, SiO₂, Fe₂O₃, MgO and Al₂O₃ constitute SS and FA. FA has significantly affected the viscosity and acidity coefficient (Mₖ) of the melts due to high content of SiO₂ and Al₂O₃. Therefore, FA is chosen as the modification agent to modify steel slag.

2.2 Modification method

In mineral wool industry, acidity coefficient Mₖ was defined as mass ratio of (SiO₂ + Al₂O₃)/(CaO + MgO). The acidity coefficient Mₖ of SS was 0.4, while Mₖ of rock wool and slag wool have been stipulated at Mₖ ≥ 1.6 and 1.1 ≤ Mₖ ≤ 1.5 according to Chinese national standard GB/T 11835-2016 (Rock wool, slag wool and its products). Therefore, FA is chosen as the modification agent to modify steel slag.

2.3 Characterization

Chemical compositions of the raw materials were detected by XRF (XRF-1800, SHIMADZU, Japan). Phase identification of the slag wool fibres were determined by X-ray diffraction (XRD, M21 apparatus, Cu Kα radiation, MAC Science Co. Ltd., Japan). Thermal properties of the slag wool fibres were tested by differential thermal analysis (DTA, STA 409C, Netzsch) at heating rate of 10°C/min in air atmosphere and α-Al₂O₃ was used as reference. Microstructure of slag wool were observed by scanning electron microscope (SEM, ZeissEVO-18, Germany). Properties of slag wool (acidity coefficient, average diameter, shot content, thermal conductivity, etc.) were tested according to GB/T 5480-2008 (Test methods for mineral wool and its products). The burning behavior of slag wool was tested according to GB 8624-2012, Classification for burning behavior of building materials and products. Heavy metals contained in the produced slag wool were tested by leaching tests according to GB 5085.3-2007 (Identification standards for hazardous wastes - Identification for extraction toxicity).

The viscosity was tested by rotating cylinder method with RTW-10 developed by Northeastern University, China. Mo crucible containing 140 g slag was placed inside the furnace and 0.3 NL/min argon gas was used to avoid the oxidation of crucible and slag.

3. Results and discussion

3.1 Viscosity of modified melts

Viscosity of the slag melt is the predominant factor in the melt spinning fiberization method. Melt viscosity of 0.5–2.5 Pa·s is generally considered to be appropriate for the production of mineral wool fibers. Table 2 shows the viscosity of SS and FA proportion were listed in Table 2.

It can be seen from Table 2 that the increasing of steel slag proportion decreases Mₖ and the addition of FA significantly affected the Mₖ of the modified slag samples. SiO₂ and Al₂O₃ increase while CaO and MgO decrease with the increasing of FA due to the high SiO₂ and Al₂O₃ content in FA. Slag sample S1, S2, S3 and S4 can be categorized as rock wool with Mₖ exceeding 1.6 while S5 with Mₖ of 1.5 shall be classified as slag wool.

Table 1. Main chemical compositions of SS and FA (wt.%).

|          | SiO₂ | Al₂O₃ | CaO | MgO | Fe₂O₃ | MnO | TiO₂ |
|----------|------|-------|-----|-----|-------|-----|------|
| Steel slag | 15.40 | 2.33  | 52.84 | 8.66 | 19.21 | 2.36 | 0.81 |
| Fly ash   | 53.38 | 28.17 | 6.02 | 1.18 | 5.99  | 0.08 | 1.36 |

Table 2. Slag samples with different SS and FA proportion

| Sample | Mₖ (wt.%) | SS (wt.%) | Main chemical composition (wt.%) |
|--------|-----------|-----------|---------------------------------|
| S1     | 2.6       | 30.0      | 40.6 19.8 20.8 2.6 10.0 0.8 1.2 |
| S2     | 2.3       | 35.0      | 39.8 18.9 22.5 2.8 10.6 0.8 1.1 |
| S3     | 2.0       | 40.0      | 37.8 17.7 24.8 3.0 11.3 1.0 1.1 |
| S4     | 1.7       | 45.0      | 35.9 16.4 27.2 3.3 11.9 1.1 1.1 |
| S5     | 1.5       | 50.0      | 33.9 15.1 29.5 3.5 12.6 1.2 1.1 |
silicate anions. Increasing SiO₂ leads to strong development of the Si-O tetrahedral network interconnection by bridging oxygen while RO (e.g. CaO and MgO) decrease the polymerization degree of the slag structure by forming non-bridging oxygen (NBO). High content silica forms the main Si-O tetrahedron structure of the slag wool. Al₂O₃ enhances the glass network structure by forming Al-O tetrahedron as a glass forming oxide like silica and also improves the thermal resistance and chemical stability of the slag wool.¹⁸) RO decreases the viscosity and improves the fluidity of the melt as glass modifiers through depolymerizing Si-O tetrahedral network:

\[
RO = R^{2+} + O^{2-}
\]

\[
[Si₂O₆]^{6-} \text{(ring)} + O^{2-} = [Si₂O₁₀]^{8-} \text{(chain)}
\]

\[
[Si₂O₁₀]^{8-} \text{(chain)} + O^{2-} = [Si₂O₇]^{6-} \text{(dimer)} + [SiO₄]^{4-} \text{(monomer)}
\]

Increasing of RO would provide O²⁻ and then modify the complex silicate structure into simple and less polymerized [Si₂O₆]⁶⁻ (NBO = 3) and [SiO₄]⁴⁺ (NBO = 4).¹⁹) The viscosity of modified slag samples with the increasing of Mₖ from 1.5 to 2.6. S1 with high Mₖ of 2.6 and S5 with low Mₖ of 1.5 depicts relatively narrow temperature range compared to other samples, which is inappropriate for the industrial production process of slag wool. For S1 with 30 wt% SS, high temperature exceeding 1440°C was required to have the essential viscosity for industrial production process, which consumes more energy.

For slag wool produced by BFS, viscosity of the melt is relatively appropriate and stable in a broad temperature range when Mₖ at approximately 1.2. The viscosity of BFS type slag with low iron oxide (FeO and Fe₂O₃) is sensible to temperature and dramatic change caused by slight vibration of temperature deteriorate the viscosity stability of the slag.²⁰)

Fe³⁺ ions functioned as network modifier in octahedral symmetry.²¹) Iron oxide can break up the silicate anions by providing free oxygen ions according to the equations:²²)

\[
\begin{align*}
FeO &= Fe^{2+} + O^{2-} \\
Fe₂O₃ &= 2FeO^{+} + O^{2-} \\
2FeO^{+} &= 2Fe^{3+} + 2O^{2-}
\end{align*}
\]

O²⁻ provided by high content Fe₂O₃ in the modified slag samples depolymerized the Si-O tetrahedral network and decreased the viscosity of modified slag samples. Besides, coke/coal is the main energy source in cupola furnace and Fe₂O₃ could be reduced to FeO by direct reduction or indirect reduction, which significantly decreased the viscosity of the melts. High Mₖ SS modified by FA have the appropriate viscosity for the industrial production of mineral wool. A broad temperature range is desired in the industrial production of mineral wool with melt spinning fiberization method. Therefore, the optimized temperature is in the range of 1380–1500°C with 35–45 wt % steel slag proportion. Modified slag samples S2, S3 and S4 have appropriate viscosity for the industrial production in this temperature range.

### 3.2 Industrial experiment and analysis

Melt spinning fiberization on spinning wheel is the most commonly method used among the mineral wool production methods.²³) Pulverous steel slag and FA were pelletized into sphere with diameter 50–100 cm, while bulk steel slag with dimension between 50 × 50 × 50 and 100 × 100 × 100 cm³ can be directly used as raw materials. Coke was used as main heat source for the melting of the raw materials. Raw materials and coke were proportionally charged into the cupola furnace. Figure 2 shows the flow diagram of the production of slag wool with melt formed by steel slag and FA. Mineral wool melt was formed inside the cupola furnace and then tapped through the tap-hole into the feed channels above the spinning discs [Fig. 2(a)]. The melt with appropriate temperature was then spun into wool fibres with the spinning discs of four-roller centrifuge [Fig. 2(b)]. Different slag wool products were then produced with the fibres.

The tapping temperature of the melt should be kept approximately 1550°C due to a 50–100°C temperature drop from the tap-hole of the cupola furnace to the spinning discs of the centrifuge. The melt forms thin radial film due to viscosity. The co-effect of inertial force, viscous force and surface tension force convert the melt film into fibres.²⁴) High speed airflow coaxially to the discs blows the fibres into the collection chamber to produce slag wool products. Normally, a fraction of the unconverted melt remains in the form of solidified shots (particles with diameter ≥ 0.25 mm), leading to the incomplete fiberization and deterioration of the quality of the slag wool products. The practical spinning speed for disc1 to disc4 are 3000–4000, 4000–5000, 4500–6000, 4500–6000 t/min, respectively. In industrial production process, modified slag sample S1–S5 were successfully produced into slag wool according to the aforementioned conditions.
3.3 Characterization of slag wool

The melt was spun into slag wool with melt spinning fiberization method. Phase identification of the slag wool were determined by XRD and XRD spectra of the slag wool is shown in Fig. 3. The amorphous curve without apparent crystalline peak illustrates the vitreous structure of the slag wool. The slag wool fibres were fast cooled during the high-speed spinning fiberization process and thus the amorphous phase can be obtained. The amorphous structure contributes to the excellent acoustic and thermal insulation properties of the slag wool.

Slag wool can be produced from modified slag samples with 30–50 wt % SS proportion. Average diameter of slag wool fibres and shot content of slag wool were shown in Fig. 4. The average diameter of slag wool fibres decreases from 6.4 to 4.6 μm as the SS proportion increases from 30 to 50 wt %, while shot content stables in the range of 4.5–5.5%. Average diameter of slag wool fibres decreases with the increasing of acidity coefficient. Average diameter of ≤6.0 μm and shot content of ≤7.0 were stipulated according to Chinese national standard GB/T 11835-2016 (Rock wool, slag wool and its products for thermal insulation). Low viscosity melt tend to produce slag wool fibres with small diameter while the shot content might correspondingly increase due to the decreasing of viscous force. S1 with average diameter of 6.4 is not qualified according to GB/T 11835-2016. S2–S4 with steel slag proportion of 35–45 wt % were considered to be appropriate for the production of high acidity coefficient slag wool.

S1–S5 slag wool exhibited similar apparent morphology and micromorphology despite the differences of average diameter and shot content. Photograph and SEM images of S4 slag wool are shown in Figs. 5 and 6, respectively. Figure 5 depicted yellowish-brown color and highly interweaved fibres with black shots attached or wrapped. The yellowish-brown color of the slag wool is caused by high Fe₂O₃ content and the color slightly depended with
the increasing of SS proportion. The fibres were produced into slag wool products (slab, lamella, etc.) for the industrial applications after spraying binders and water repellent. Figure 6(a) shows porous structure formed by intensively interweaved fibres and trace amounts of small black shots attached to or wrapped by the fibres, which explains the preeminent thermo-acoustic insulation properties of the slag wool products. Figure 6(b) shows smooth surface without surface defects (crackles, holes, etc.) of the fibres, which improves the mechanical properties and chemical stability of the slag wool products.

The thermal properties of slag wool were investigated by DTA. DTA curve of slag wool from room temperature to 1300°C in air atmosphere is shown in Fig. 7. Exothermic peak corresponds to the crystallization temperature while endothermic peak represents the melting temperature of the slag wool. The exothermic peaks indicate that the crystallization temperature of 900, 910, 915, 917 and 918°C for S1 to S5 slag wool, respectively. Endothermic peaks at approximately 1215°C indicating the melting temperature of the slag wool. The crystallization temperature and melting temperature of industrial rock wool investigated by Alves et al.2) are 830 and 1160°C, respectively. Crystallization behavior deteriorates the properties of the slag wool and the crystallization temperature should be the upper limit temperature for the industrial application. Gualtieri et al.9) reported that rock wool can be melted with maximum firing temperature of 1100°C while the melting temperature of the investigated slag wool are approximately 1215°C. Besides, low thermal conductivity (70 ± 2°C) of approximately 0.036 W/(m·K) and grade A burning behavior of the investigated slag wool also meet the requirements of Chinese national standards. The investigated high \( M_k \) slag wool exhibited thermal properties superior to rock wool and can be applied as substitute for industrial rock wool.

### 3.4 Application feasibility and benefits

Slag wool products are mainly applied as industrial, building and ship thermal insulation materials. Potential toxicity caused by heavy metals should be seriously considered. Table 3 shows the leaching tests of possible heavy metals in slag wool samples. It can be seen that only minimal heavy metals were detected by leaching tests. The slag wool produced by SS and FA show scarcely any potential toxicity of heavy metals. The internal exposure index and external exposure index of slag wool produced by SS and FA are 0.1 and 0.2, which can satisfy the requirement of Chinese national standard GB 6566-2010 (Limits of radionuclides in building materials). These results indicate that slag wool produced by SS and FA is environmentally acceptable.

Recently, demand for rock wool has increased with an average annual growth over 15% in China and the annual output of rock wool was approximately 252.5 million tons in 2016. Approximately 101.0 million tons SS and 151.5 tons FA can be consumed if substituting rock wool with high acidity coefficient slag wool (e.g. \( M_k \) 2.0 with 40 wt% SS and 60 wt% FA). European countries mainly use rock wool as the high grade thermal insulation and fire-resistant materials while most of the mineral wool products in China are actually inferior quality slag wool produced

| Element | Detected value (mg/L) | Standard value (mg/L) |
|---------|-----------------------|----------------------|
| Cd      | <0.003                | ≥1                   |
| Pb      | <0.050                | ≤5                   |
| As      | <0.010                | ≤5                   |
| Cr(VI)  | <0.004                | ≤5                   |

Table 3. Leaching tests of possible heavy metals in slag wool.
by BFS. Production of slag wool with high $M_k$ and properties similar or even better than rock wool by SS and FA promoted the massive and profitable utilization of SS and FA. Huge amount natural resources can be correspondingly saved by substituting rock wool. Steel slag and FA can be utilized and natural environment acceptable with properties superior to visco-Newtonian melts exhibit appropriate viscosity. Porous structure and amorphous phase improve thermo-acoustic insulation properties while smooth surface improve chemical stability. Average diameter decrease as steel slag ratio increase. Crystallization temperature of 900–918°C is the upper limit temperature. High $M_k$ slag wool exhibited thermal conductivity of 0.036 W/(m·K) and grade A burning behavior. High $M_k$ slag wool is environmentally acceptable with properties superior to rock wool. Steel slag and FA can be utilized and natural resources can be correspondingly saved by substituting rock wool with high $M_k$ slag wool.

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