Effect of Pre-calcination of Lead-zinc Tailings on the Activation of Blast Furnace Slag

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Abstract. *Blast furnace slag and lead-zinc tailings (LZTs) are solid wastes from the iron-making and mining industries, respectively. In order to reuse these solid wastes, the LZTs were pre-calcined at different temperatures and then explored whether it is capable of being the activator of slag. The effects of pre-calcination on the phase composition of LZTs were elucidated by XRD. The compressive strength of LZTs-activated slag pastes was investigated, and the mineral composition and microstructure of the pastes were detected by XRD and SEM. The results imply that with the elevating of heating temperature from 500 °C to 1000 °C, the dolomite in LZTs decompose into CaO and MgO, and the oxidation of pyrite resulted in the formation of Fe_2O_3 and gaseous SO_3, then SO_3 reacted with a part of formed CaO to produce $CaSO_4$. The resulting $CaSO_4$ and CaO can become the sulfate activator and alkaline activator of slag, respectively. The LZTs-activated slag pastes prepared with the LZTs preheated at 800 °C exhibit the highest strength at 90 d, which yield 24 MPa. The hydration products of LZTs-activated slag were ettringite and calcium silicate hydrates (C-S-H gel). Large amounts of dense C-S-H gel bond together, connecting most of the ettringite networks into a whole, thus forming a dense structure and effectively improving the strength of LZTs-activated slag. The outcome of this study provides a potential disposing or reusing approach of the large amounts of LZTs.*

Keywords: *Lead-zinc tailings, Ground granulated blast furnace slag, Pre-calcination, Ettringite, Compressive strength.*

1 Introduction

The high content of amorphous calcium-aluminate-silicate glass phase endows the ground granulated blast furnace slag (GGBFS) with potential hydraulicity. GGBFS could be activated by alkali to prepare alkali-activated slag materials (AAS), or stimulated by gypsum in the presence of cement clinker or lime (Kühl and Schleicher 1952), known as super sulfated cement.

However, the high cost and potential pollution of the activators of AAS and super sulfated cement limits the application of GGBFS. Interests have been paid for a long time on the feasibility of using wastes as a substitution of alkali or gypsum. Many studies indicate that a wide series of solid wastes containing alkali or sulfate are capable of activating the cementitious property of slag (Chaunsali and Peethamparan 2013, Murmu and Singh 2015).

Lead-zinc tailings (LZTs) refer to the residue of lead-zinc ore treated by specific means of separation and purification. The mineral compositions of LZTs are generally composed of dolomite, sulfide and quartz, which are difficult to be directly utilized. It is proposed that pre-calcination might be a proper way to convert LZTs to an alternative activator of GGBFS. During heating, the sulfides in LZTs may transform to sulfate to play as the activator. Meanwhile, the main component dolomite might be decomposed into magnesium oxide and calcium oxide (Olszak-Humienik and Jablonski 2014), which provides the basic components as alkaline

activators of slag.

Therefore, the effect of calcination on the phase evolution of LZTs and the possibility of pre-calcined LZTs as alternative activator of GGBFS are investigated in this study. The mineral composition of pre-calcined LZTs and LZTs-activated slag were analyzed by X-ray diffraction (XRD). The compressive strength of a series of LZTs-activated slag pastes was evaluated. This work might shed more light on the disposal of the large amount of LZTs and GGBFS.

2 Materials and methods

The LZTs used in this study were obtained from a lead-zinc mining area in Guangxi, China. The LZTs were dried in an electric blast drying at 105 ±5 °C oven to constant weight and ground by an SM-500 ball mill for 30 min so that they could pass through the 200-mesh standard sieve. And a type of S95-grade GGBFS was used as the pozzolanic raw material, which is supplied by Longze Water Purification Material Co., Ltd., Gongyi City, Henan Province, China. The LZTs were fired at different temperatures ranging from 100 °C to 1000 °C for 1 h. According to the formulas in Table 1, LZTs, GGBFS and water were weighed and mixed evenly. The mixtures were immediately cast into $20 \times 20 \times 20$ mm^3 cubic molds and covered with plastic film to prevent water evaporation. After 48 h curing in the molds at room temperature of 25 ± 5 °C, all the paste specimens were demolded and cured in water at room temperature of 25 ± 5 °C for varied durations.

Table 1. The formula of LZTs-activated slag paste samples using LZTs pre-calcined at different temperatures.

Sample mark	LZTs	LZTs: GGBFS	W/C
A0	Unheated		
A600	600 °C*1 h		
A700	700 °C*1 h	3: 7	0.52
A800	800 °C*1 h		
A900	900 °C*1 h		

The compressive strength of LZTs-activated slag was tested via using a computer-controlled pressure testing machine (WHY-300/10, Shanghai Hualong) with loading rate of 0.5 mm/min. Five samples were set as a batch for measurement and the average value of their compressive strength was calculated as the final results. The X-ray diffractometer of Rigaku Ultima IV of Japan was used to characterize the phase assemblage of raw materials and LZTs-activated GGBFS with Cu Kα radiation at 40 kV and 40 mA. The XRD patterns were obtained with a 2θ range of 5~80° at 0.02° step size, and the scanning rate is 10°/min.

3 Results and discussion

3.1 Phase transformation of LZTs during calcination

The XRD patterns of LZTs pre-calcined at 100~1000 °C are plotted in Figure 1. As shown in Figure 1(a), the mineral phases of LZTs without calcination are mainly dolomite ($CaMg(CO_3)_2$), baryte ($BaSO_4$), pyrite (FeS_2) and quartz (SiO_2). The main mineral composition does not change significantly when the LZTs are heated to 100 °C, 200 °C and 300 °C for 1 h. However, when

the LZTs are heated to 400 °C for 1 h, pyrite almost disappears while hematite (Fe_2O_3) appeared, indicating that Fe_2O_3 forms by the reaction of FeS_2 with oxygen (Bhargava et al. 2009).

When LZTs are heated to 500 °C for 1 h, a small amount of anhydrite ($CaSO_4$), periclase (MgO) and calcite ($CaCO_3$) are observed while FeS_2 completely disappears. The generation of MgO and $CaCO_3$ is caused by the decomposition of dolomite at about 500 °C. Actually, it has been reported that at about 500 °C, dolomite would decompose into MgO and $CaCO_3$, and $CaCO_3$ would further decompose slightly to generate a small amount of CaO and CO_2 (Olszak-Humienik and Jablonski 2014). However, it is noteworthy that the peaks of anhydrite ($CaSO_4$) are shown in the XRD pattern instead of the peaks of CaO. It is deduced that under the condition of heating, the thermally decomposition of sulfur-containing compounds or oxidation of the sulfides results in the formation of gaseous SO_2, then the subsequent oxidation of SO_2 to SO_3 leads to the reaction of the latter with the basic oxides in the LZTs, thereby forming $CaSO_4$ (Gregurek et al. 2015). Moreover, the lime formed by the decomposition of $CaCO_3$ is not well crystallized. This explains the absence of CaO in XRD patterns.
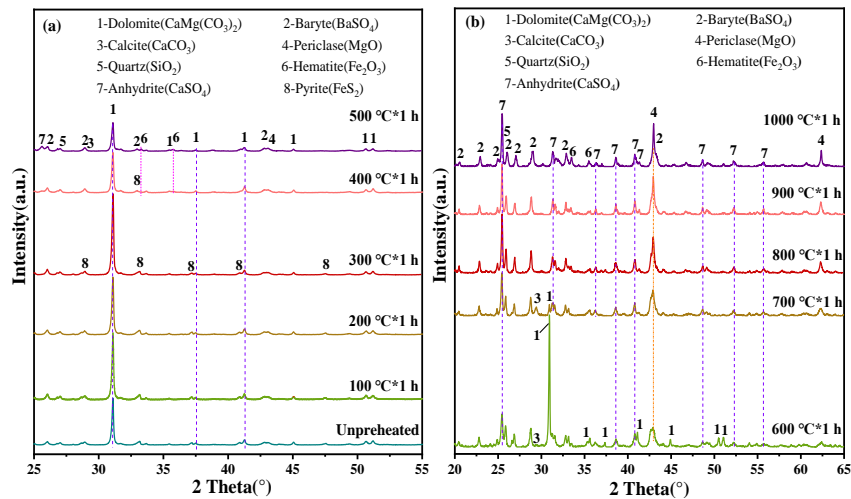

Figure 1. XRD patterns of LZTs pre-calcined at 100~1000 °C (a: 100~500 °C; b: 600~1000 °C).

As the temperature rises to 600 °C and above (Figure 1(b)), the dolomite continues to disintegrate into MgO and $CaCO_3$, the latter of which gradually decomposes to CaO. The generated CaO keeps on reacting with SO_3, so more $CaSO_4$ is produced. A significant reduction in the peaks relevant to the dolomite phase can been seen at 700 °C, while the increase of the peaks corresponding to $CaSO_4$, MgO and $CaCO_3$ are observed. The results reveal that the decomposition rate of dolomite is greatly improved at 700 °C. When the LZTs are heated at 800 °C for 1 h, dolomite and $CaCO_3$ completely decompose while a large amount of $CaSO_4$ is generated simultaneously until all the SO_3 is absorbed and solidified. When further heated to 900 and 1000 °C, the main mineral phases of LZTs are not much different from those at 800 °C. The above results imply that the sulfide in LZTs oxidizes and dolomite decomposes during heating. And $CaSO_4$ is further generated by the combination of SO_3 and CaO, which could serve as the sulfate activator of GGBFS.

3.2 LZTs-activated slag

In order to investigate the actual activation effect of pre-calcined LZTs on GGBFS, the LZTs preheated at 600~900 °C were respectively mixed with slag with a constant weight ratio of 3: 7, while the unheated LZTs blended slag was taken as the control group (Table 1). The compressive strengths of GGBFS pastes blended with LZTs calcined at different temperatures after curing for 3 d, 7 d, 28 d and 90 d were measured. As seen from Figure 2, LZTs-slag pastes prepared from LZTs without preheating does not show any strength. The LZTs pre-calcined at 600 °C exhibit the activation effect on the GGBFS that the pastes (A600) show a compressive strength of about 4 MPa after 3 d curing. With the prolonging of curing duration, the compressive strength gradually increases to 12 MPa at 90 d. Pastes prepared by slag and LZTs calcined at 700 °C show higher mechanical property than A600. Although the strength of A700 at 3 d is a bit higher than A600, the compressive strength at 7 d and 28 d of A700 is almost twice as much as that of A600.
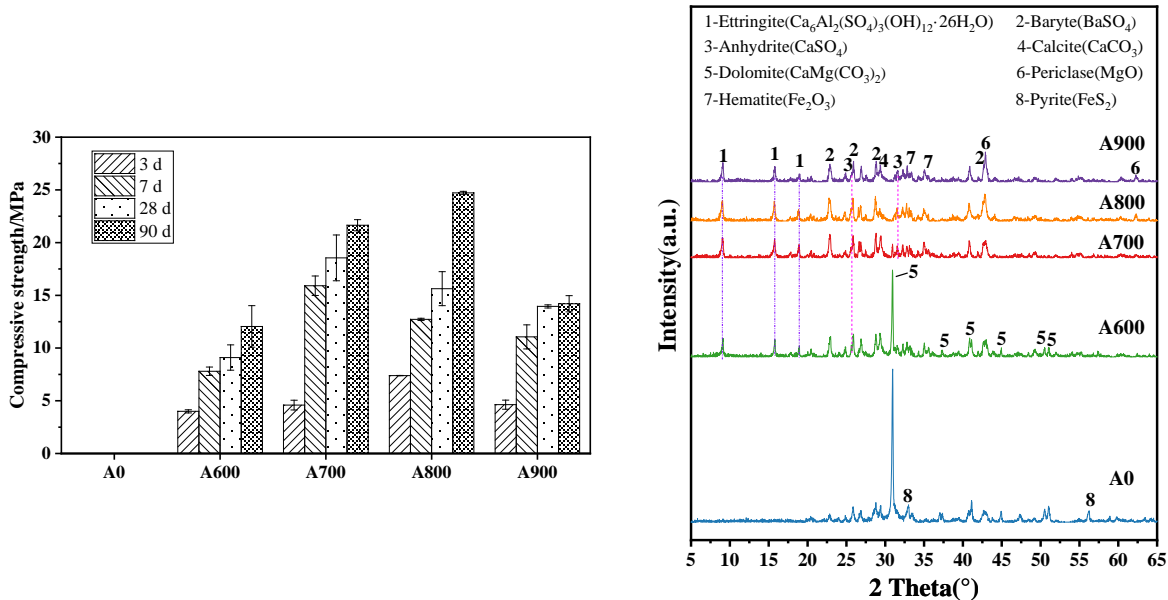
Figure 2. Compressive strength of LZTs (700 °C)-activated slag pastes samples prepared with different LZTs/GGBFS ratios after 3 d, 7 d, 28 d and 90 d curing (L-%: the proportion of LZTs in the sample).

Figure 3. XRD patterns of LZTs-activated slag paste samples prepared with LZTs preheated at different temperatures (LZTs: GGBFS=3: 7; cured for 28 d).

Compared with A700, A800 pastes has slightly higher early strength (3 d), but the strength at 7 d and 28 d is lower. This is because that LZTs calcined at 800 °C has more alkali than at 700 °C, which is conducive to the early strength of the slag. With the pre-calcination temperature elevating to 900 °C, the compressive strength of LZTs-activated slag (A900) decreases. The compressive strength evolution indicates that pastes A700 and A800 show obviously better mechanical property than A600 and A900. According to the previous results of the XRD diffraction patterns (Figure 1), it is due to the increase of dolomite decomposition rate at 700 °C and 800 °C, which provides a large amount of activator, that the strength of LZTs-activated slag is significantly improved than sample A600. The phases of LZTs are not much

different between heating at 900 ℃ and 800 ℃. However, the elevated calcination temperature leads to the better crystallinity of the $CaSO_4$ and CaO, which is deteriorating their activation ability on the GGBFS. Therefore, sample A900 shows a decreased compressive strength compared with A800.

In order to reveal the cementing mechanism of LZTs-activated slag, XRD patterns of LZTs-activated slag paste samples prepared with LZTs preheated at different temperatures cured for 28 d were obtained and shown in Figure 3. It can be seen that the main mineral phases of the A0 sample are still dolomite, pyrite, etc., which are not much different from the LZTs without preheating. It indicates that the LZTs without preheating have basically not reacted with the slag, thus the LZTs-activated slag paste samples prepared by unpretreated LZTs does not show any strength in the previous strength results. However, $CaSO_4$ (2θ=25.59°, 31.30°, etc.), MgO (2θ=42.94° and 62.32°) and ettringite (AFt, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$) ($2\theta$=9.26°, 15.95° and 19.09°) are both observed in samples A600~A900, indicating that the hydration reaction is carried out between the pretreated LZTs and slag. $CaSO_4$ and MgO in the pre-calcined LZTs are used as sulfate activator and alkaline activator of slag. Under the excitation effect of alkali, the slag is gradually decomposed, and the dissolved calcium, silicon, and aluminum ions from slag react with sulfate ions to form calcium silicate hydrates (C-S-H gel), calcium aluminate hydrates (C-A-H gel) and ettringite (Angulski da Luz and Hooton 2015). This hydration principle is as same as that of super sulfate cement and the reactions are shown in Eq. 6 to Eq. 9:

$$Ca(OH)_2+SiO_2 \rightarrow C\text{-}S\text{-}H(gel) \tag{6}$$
$$Ca(OH)_2+Al_2O_3 \rightarrow C\text{-}A\text{-}H(gel) \tag{7}$$
$$C\text{-}A\text{-}H(gel)+CaSO_4+H_2O \rightarrow AFt \tag{8}$$
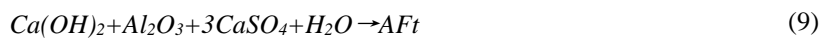$$Ca(OH)_2+Al_2O_3+3CaSO_4+H_2O \rightarrow AFt \tag{9}$$

Figure 4 displays the SEM images of sample A800 cured for 28 d. As can be seen in the figure, much ettringite is generated with a slenderer shape. Large amounts of needle or rod-shaped crystals grow and extend to about 5~6 μm long and fill in the pore space. The ettringite grows gradually to form a continuous and dense spatial network structure, which fills the pores and contributes to the strength of LZTs-activated slag. In addition, a small amount of C-S-H cements the ettringite together, which enhances the compactness of the system. The formation of a dense structure can effectively improve the strength of LZTs-activated slag at the later stage of hydration.
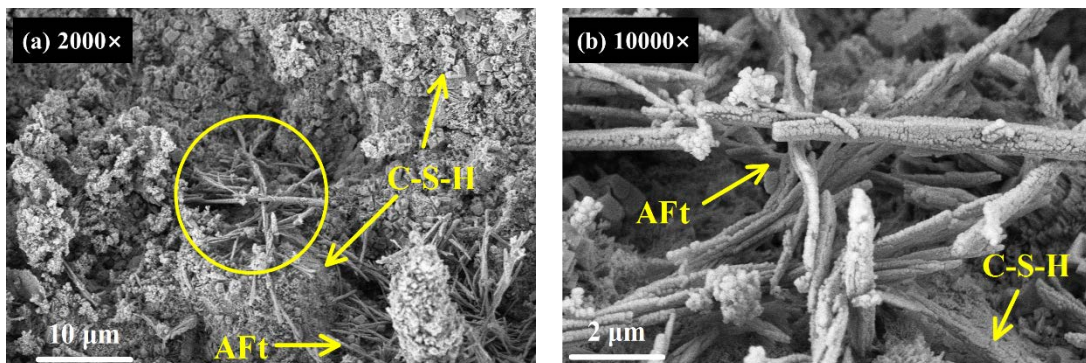

Figure 4. SEM images of sample A800 (28 d).

4 Conclusion

In this paper, the phases evolution of LZTs pre-calcined at 500~1000 °C for 1 h was evaluated, and the activation effect of pre-calcined LZTs on the cementitious property of GGBFS was investigated. The main conclusions are drawn as follows:

After pre-calcination at temperature above 500 °C, the dolomite in LZTs begin to decompose into CaO and MgO. And the oxidation of pyrite during heating results in the formation of Fe_2O_3 and SO_3, and SO_3 reacts immediately with the formed alkali oxides in the LZTs to produce $CaSO_4$. At 800 °C, the dolomite decomposes completely so the maximum amount of $CaSO_4$ and alkali oxides is generated.

The $CaSO_4$ and alkali oxides generated during preheating of LZTs can be used as sulfate activator and alkaline activator of slag. The LZTs-activated slag pastes prepared with the LZTs preheated at 800 °C exhibit the highest strength at 90 d, which yield 24 MPa.

The hydration products of LZTs-activated slag are mainly ettringite and hydrated calcium silicate (C-S-H gel). Ettringite grows in a staggered accumulation, which plays a key role on the early strength. C-S-H gel grows and bonds together, connecting the ettringite networks, thus forming a dense structure which supplies the strength at the later age.

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