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Cementitious properties of ladle slag fines under autoclave curing conditions

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Abstract

Ladle slag fines consist mainly of γ-C_2S, which does not show cementitious property in water, but can exhibit significant cementitious property in the presence of alkaline activators at room temperatures. This study deals with the hydraulic reactivity of ladle slag fines under autoclaving conditions. The results indicate that ladle slag fines cannot be used as cementing material alone because of the presence of free lime in ladle slag. The combination of a ladle slag fine and a siliceous material, such as silica flour (ground quartz), can eliminate the soundness problem and give very high strength. The introduction of a small amount of Portland cement or hydrated lime into ladle slag fine–silica flour system can increase strength significantly. Lime is more effective than Portland cement due to the presence of Al in Portland cement. The autoclaving temperature should be higher than 175 °C and the time for constant temperature does not need to be more than 4 h to achieve satisfactory strength. Finally, seven batches of experiments are designed to plot isostrength contours for ladle slag fine–cement–silica flour and ladle slag fine–hydrated lime–silica flour ternary systems.

Keywords: Ladle slag; Steel slag; Autoclave curing; Composition; Strength

1. Introduction

To further refine the steel after coming out of a basic oxygen furnace or an electric arc furnace, calcium aluminate or CaF_2 is added to the molten steel as a flux for further refining while in a ladle. The slag from this process is called *ladle slag*. When CaF_2-based fluxes are used, the ladle slag consists mainly of CaO and SiO_2 with a CaO/SiO_2 ratio of around 2. This means that the main mineral in the slag is C_2S. C_2S exists in five well-established polymorphs: α, α_H', α_L', β, and γ. On cooling from elevated temperatures, α-C_2S transforms to β-C_2S at 630 °C, then transforms to γ-C_2S at lower temperature. The conversion of β-C_2S to γ-C_2S is accompanied by an increase in volume of nearly 10% and results in the shattering of the crystals into dust because of their different crystal structures and densities [1]. Thus, ladle slag is sometimes called *falling slag*. The fines less than 200 mesh in ladle slag can be up to 20–35%, which causes difficulties during materials handling and management.

In a previous study [2], X-ray diffraction analysis of three ladle slag fine samples passing 100, 200, and 325 mesh indicated that the major mineral in ladle slag fine is γ-C_2S, which does not show cementitious property in water. However, they exhibit significant cementitious property in the presence of alkaline activators at room temperatures. The finer the ladle slag is, the better the cementitious property of the slag is. Since ladle slag contains free lime, it cannot be used as a Portland cement replacement alone. This study deals with the cementitious properties of ladle slag under autoclave conditions. The purpose of the work is to find applications for ladle slag fines in production of construction products.

2. Experimentation

2.1. Raw materials

The ladle slag fines in this study were from an electric arc furnace steel production using CaF_2-based fluxes. Four ladle

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Table 1
Chemical analysis of ladle slag samples (%)

Slag sample	CaO	SiO_2	Al_2O_3	MgO	F	SO_3	Fe_2O_3	MnO	TiO_2	ZrO_2
LS100	57.0	26.8	5.2	3.2	3.0	1.7	1.59	1.0	0.3	0.2
LS325	55.9	26.4	4.7	4.2	4.4	2.3	1.0	0.5	0.3	0.3

slag fines were obtained by screening to pass #16, #50, #100, and #325 ASTM standard sieves, respectively. The ladle slag fines used here were the same for the previous study [2]. The chemical composition of the slag fines passing #100 and #325 sieves is shown in Table 1. The ladle slag consists mainly of CaO and SiO_2. The fineness of the slag does not show an obvious effect on the chemical and mineral composition of these slag fines.

The other raw materials used in this study include a commercial ASTM Type I Portland cement, silica flour (ground quartz) passing 50 μm, a commercial hydrated high-calcium lime, and an ASTM Class F coal fly ash.

2.2. Preparation and curing of specimens

Since ladle slag fines contain a very high content of free CaO, it cannot be used to replace Portland cement due to potential soundness problems. In this study, siliceous materials such as silica flour (ground quartz) and coal fly ash were used together with ladle slag fines. Portland cement and hydrated lime were used to improve the strength of the systems. The mixing proportions of these materials will be given in relevant paragraphs.

The dry materials were blended first then mixed with water. The mixtures were filled into a steel mould with a diameter of 2.5 cm, then compacted the mixture with a piston with a pressure of 20 MPa for approximately 10 s. Enough material was filled into the mould so the height of the compacted specimen is around 4 cm. After compaction, the cylinder sample was pushed out of the mould. After 3–4 h of still time, these cylinders were placed in an autoclave for curing. The temperature of the autoclave was increased to desired temperatures at a rate of 30 °C/h, held for 4 h at the desired temperature, then was cooled down naturally by turning off the autoclave heaters.

2.3. Testing of specimens

After the specimens were cooled down to room temperature, their densities and compressive strength were measured. The presented result is an average of three specimens.

3. Experimental results

3.1. Ladle slag–silica flour/fly ash systems

As expected, compacted cylinders made with 100% ladle slag fines cracked during autoclaving (No. 1 in Table 2) due to free lime in the ladle slag fines as identified in the previous study. Since ladle slag has a CaO/SiO_2 ratio around 2, mixtures were designed with some siliceous materials to consume the free lime and some lime in γ-C_2S to form CSH with a lower C/S ratio. Two formulations were designed, autoclaved, and tested as shown in Table 2. The ladle slag fines used passed #100 mesh sieve. Another batch, which consists of 50% Portland cement and 50% silica flour and is typically used in autoclaved concrete block manufacture, was used as a reference. It can be seen that the composition of 80% ladle slag fines and 20% silica flour gave a compressive strength of 23 MPa, which is significantly lower than that of the typical commercial production formulation for autoclaved concrete blocks (76.2 MPa), but much higher than that of the composition of 80% ladle slag fines and 20% fly ash (5.3 MPa). This means that the use of fly ash is not suitable for use together with the ladle slag fines under the current hydrothermal conditions.

Table 2
Mixing proportions and compressive strength of autoclaved ladle slag–silica flour/fly ash cylinders

No.	Formulation	Compressive strength (MPa)
1	100% ladle slag fines	cracked during autoclaving
2	80% ladle slag fines + 20% silica flour	23.0
3	80% ladle slag fines + 20% fly ash	5.3
4	50% Portland cement + 50% silica flour	76.2

3.2. Ladle slag–Portland cement/lime–silica flour system

To improve the strength of ladle slag fine-based material, a small percentage of silica flour was replaced with Portland cement or hydrated lime (Table 3). The other materials used were the same as above. It can be seen that a replacement of 7% silica flour with Portland cement increased the strength from 23 to 34.3 MPa. There is no measurable difference between the use of Portland cement or hydrated lime in these formulations.

3.3. Effect of the fineness of ladle slag fines on strength

The results described above indicate that the use of small amount of cement or hydrated lime is very helpful in

Table 3
Mixing proportions and compressive strength of autoclaved ladle slag–Portland cement/lime–silica flour cylinders

No.	Formulation	Compressive strength (MPa)
5	80% ladle slag fines + 7% Portland cement + 13% silica flour	34.3
6	80% ladle slag fines + 7% hydrated lime + 13% silica flour	36.2

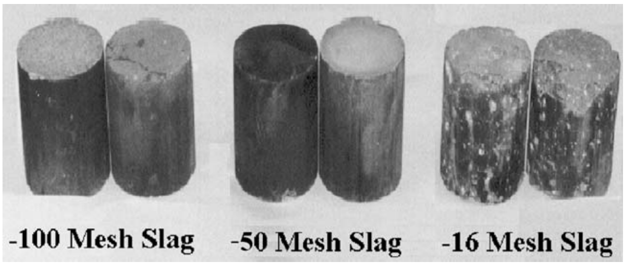

Fig. 1. Appearance of specimens made with ladle slag fines with different finenesses after autoclaving.

improve the strength of the ladle slag–based materials. It is critical to know how the sizes of slag particle affect the soundness and strength of ladle slag-based materials. Four ladle slag fines with passing #16 to #50, #100, and #325 mesh sieve were tested. The composition of the mixture consisted of 50% ladle slag fines, 25% silica flour, and 25% Portland cement. The preparation, curing, and testing of the specimens were the same as described above. After autoclaving, it was noticed that all the specimens looked intact but those ones containing ladle slag fines passing #16 mesh cracked and showed many pop-outs (Fig. 1).

Table 4 is a comparison of the specimens made with −50, −100, and −325 mesh ladle slag fines. It can be seen that the strength of the batch made with −50 mesh ladle slag fines is 42.1 MPa, which is significantly lower than the other two batches made with −100 and −325 mesh ladle slag fines. However, there is no difference between the batches made with ladle slag finesses passing 100 and 325 mesh, which exhibited compressive strength of 59.4 and 61.2 MPa, respectively.

3.4. Effect of curing temperature and time on compressive strength

Different curing temperatures, and the times for constant temperatures were also investigated to see how they affect the compressive strength of the cylinders. The results in Table 5 indicated that, for a given 4 h of constant temperature time, the strength of the material cured with a constant temperature of 150 °C (34.3 MPa) is obviously lower than that cured with a constant temperature of 175 °C (59.4 MPa). Increasing the constant temperature from 175 to 200 °C did not show an obvious effect on the strength of the specimens. The increase of the time for constant curing temperature from 4 to 8 h at both 175 and 200 °C only slightly increased the strength of the specimens.

Table 4
Effect of the fineness of ladle slag fines on strength of the material consisting of 50% ladle slag fine + 25% Portland cement + 25% silica flour

No.	Ladle slag fine	Compressive strength (MPa)
7	−50 mesh	42.1
8	−100 mesh	59.4
9	−325 mesh	61.2

Table 5
Effect of curing temperature and time on compressive strength of the material consisting of 50% ladle slag fine + 25% Portland cement + 25% silica flour

No.	Curing temperature (°C)	Curing time (h)	Compressive strength (MPa)
10	150	4	34.3
11	175	4	59.4
12		8	61.2
13	200	4	60.8
14		8	63.5

3.5. Optimization of ladle slag–Portland cement–silica flour system

The results described above indicated that the use of Portland cement and hydrated lime could have a significant effect on strength. A seven-batch factoral design method, as described in early publications [3–5], was used to investigate how the three components—ladle slag fine (X_1), Portland cement (X_2), and silica flour (X_3) affect the strength (S) of the system

$$S = A_1X_1 + A_2X_2 + A_3X_3 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3 + A_{123}X_1X_2X_3$$

where A_1, A_2, A_3, A_{12}, A_{13}, A_{23}, and A_{123} are constants. It is generally agreed that this methodology can predict of strength for a ternary system very well with the least amount of batches of experiments [3–5].

The composition and compressive strength of the seven batches are listed in Table 6. A software called Surfer was used to do the regression and to plot the isostrength contours in a ternary diagram, as shown in Fig. 2. The highest strength of the ladle slag–silica flour–Portland cement

Table 6
Composition and compressive strength of ladle slag fines–cement–silica flour system cured at 175 °C for 4 h

No.	Composition (%)			Compressive strength (MPa)
	Ladle slag (−100 mesh) (X_1)	Cement (X_2)	Silica flour (X_3)	
15	80	0	20	5.3
16	50	50	0	29.1
17	0	50	50	66.1
18	0	80	20	63.9
19	33.33	33.33	33.33	63.2
20	50	25	25	58.7
21	65	20	15	54.2

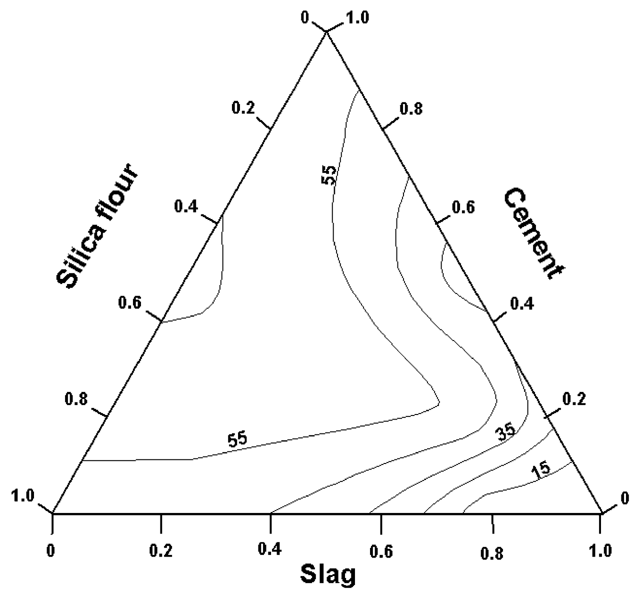

Fig. 2. Isostrength contours of ladle slag fines (−100 mesh)–cement–silica flour system cured for 4 h at 175 °C.

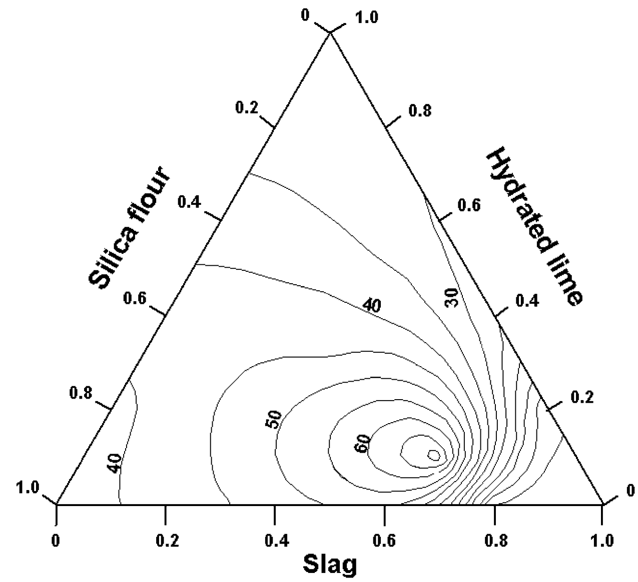

Fig. 3. Isostrength curves of ladle slag fines (−100 mesh)–hydrated lime–silica flour system cured at 175 °C for 8 h.

system is lower than that of the silica flour–Portland cement system. However, the introduction of small portion of Portland cement is very helpful to the strength of the ladle slag–silica flour. Also, the use of up to 33% slag did not show an obvious effect on the strength of the silica flour–Portland cement system.

3.6. Optimization of ladle slag–hydrated lime–silica flour system

The seven-batch factoral design was also used for the ladle slag–hydrated lime–silica flour system. The composition and compressive strength after autoclaving of the seven batches are listed in Table 7. The results were analyzed and plotted in the same way as above. The isostrength contours of the system are plotted in Fig. 3. For this system, the optimum composition is very obvious: approximately 70% ladle slag, 20% silica flour, and 10% hydrated lime, which give a compressive strength around 70 MPa.

Table 7
Composition and compressive strength of ladle slag fines–hydrated lime–silica flour system cured at 175 °C for 4 h

No.	Composition (%)			Compressive strength (MPa)
	Ladle slag (−100 mesh) (X_1)	Hydrated lime (X_2)	Silica flour (X_3)	
22	80	0	20	5.3
23	80	20	0	4.8
24	0	40	60	41.5
25	0	20	80	38.4
26	33.33	33.3	33.33	43.4
27	50	20	30	57.1
28	65	10	25	72.4

4. Discussions

Fig. 4 shows the hydration products of $CaO–SiO_2–H_2O$ system at different temperatures. It can be seen that a system

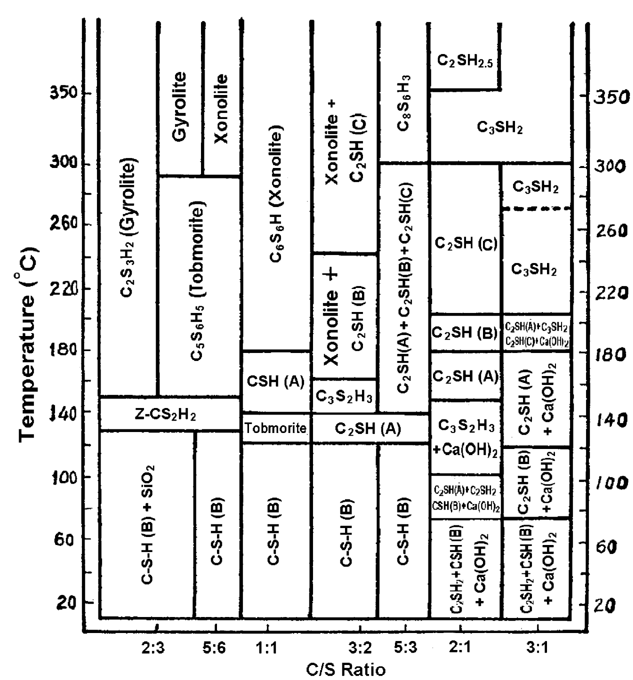

Fig. 4. Hydration products of $CaO–SiO_2–H_2O$ system at different temperatures [9].

with a CaO/SiO_2 ratio of around two forms mainly C_2SH although three polymorphs A, B, and C can form depending on temperatures. All forms of C_2SH has very low strength compared with the CSH with a low C/S ratio, such as CSH(B), tobermorite, xonotlite, etc., formed under hydrothermal conditions. Of course, the starting raw materials affect the reaction rates and even the nature of reaction products.

The hydration of γ-C_2S in water is very slow and its main hydration product is CSH(B) under 120 °C [6]. At 120 °C, γ-C_2S hydrates extremely slowly in water, but can convert into C_2SH(A) completely within 3 days even in the presence of a very small quantity of C_2SH(A). At above 150 °C, γ-C_2S hydrates very quickly and forms C_2SH(C). However, the main hydration products of β-C_2S or Portland cement at 150 °C is C_2SH(A), which is a coarse crystal prism and exhibits very low strength [7,8]. Although C_2SH(C) has a morphology of irregular particle and is very different from that of C_2SH(A), they have very similar specific surface area and mechanical properties [9].

The calcining temperature can have a great effect on the particle size and hydraulic reactivity of β-C_2S or γ-C_2S [10]. A mixture of 35–40% γ-C_2S and 60–65% β-C_2S formed at 1100 °C has a typical size of 1–3 μm while the one formed at 1450 °C has a typical size of 40–45 μm. Thus, the former exhibited significantly higher hydraulic reactivity and higher strength than latter.

The addition of a proper amount of ground quartz into β-C_2S or γ-C_2S can change its hydration product and increase its strength very significantly. Laboratory results [10] indicated that a mixture of β-C_2S and γ-C_2S, which was formed at 1100 °C, exhibited a strength of around 40 MPa under hydrothermal condition. The addition of 20% ground quartz increases the strength to approximately 110 MPa. The addition of CaO can further increase the strength of the system. A mixture consisting of 30% mixed C_2S, 20% CaO, and 50% ground quartz showed a strength of approximately 130 MPa. A measurement of hydration product in the hydrated system indicated that the use of CaO obviously increased the amount of hydration products in the system. This means that presence of CaO does accelerate the hydration of C_2S.

In this study, specimens made with 100% of ladle slag cracked during autoclaving curing due to the presence of free lime in the slag. As 20% slag is replaced with silica flour, it solves the cracking problem, but the specimen showed a strength of only 23 MPa. However, when a small portion of lime or Portland cement is introduced into ladle slag–silica flour system, it increases the strength of the specimens very significantly. When lime is used, the optimum composition consists of approximately 70% ladle slag, 20% silica flour, and 10% hydrated lime, and gives a compressive strength around 70 MPa. When Portland cement is used, it seems that the highest strength of the ladle slag–silica flour–Portland cement system is lower than the highest strength of the silica flour–Portland cement system. However, the introduction of small portion of Portland cement is very helpful to the strength of the ladle slag–silica flour. Also, the use of up to 33% slag did not show an obvious effect on the strength of the silica flour–Portland cement system. Thus, the results from this study are completely in agreement with these previous studies.

The use of fly ash, instead of silica flour, resulted in a very low strength. This may be attributed to the chemical and mineral composition of fly ash. Several studies have confirmed that the use of amorphous ingredients results in a lower reaction degree and a lower crystallized degree of reaction products compared with the use of crystalline ingredients [11,12], which can be attributed to the nuclei effect of the crystalline ingredients during the formation of the reaction products.

The other reason may be attributed to the presence of Al_2O_3 in the fly ash, which affects the structure and nature of hydration products. For $CaO–SiO_2–H_2O$, tobmorite will be the main hydration product under the hydrothermal conditions used in this study. The presence of a small amount of Al results in the formation of Al-substituted tobmorite [13,14], but the amount of Al_2O_3 was limited to the solid solution limit ($Al/(Si+Al)<0.16$). As the Al concentration increases, hydrogarnet forms. It will become the dominant phase when $Al/(Si+Al)\geq0.2$ [15] and the only phase when $Al/(Si+Al)\geq0.24$ [16]. It was found that the $CaO–SiO_2–H_2O$ system with $Al/(Si+Al)=0.05$ exhibited the highest strength; the further increase of Al content decrease the strength of the system and hydrogarnet-dominated system showed significantly lower strength than tobmorite-dominated system [16]. Thus, the use of fly ash is not suitable for the production of high strength autoclaved products.

The use of Portland cement, instead of CaO, does not give strengths as high as CaO. This may be attributed to the presence of Al_2O_3 in Portland cement, as described as above.

5. Conclusions

The γ-C_2S-based ladle slag fines could show excellent cementitious under hydrothermal conditions. Compacted cylinders made with 100% ladle slag fines cracked during autoclaving due to the presence of free lime in the ladle slag fines. The combination of ladle slag fine and siliceous materials, such as silica flour (ground quartz) or coal fly ash, can solve the soundness problem when the ladle slag fines pass #50 mesh sieve. Use of silica flour gives much higher strength than fly ash.

The introduction of Portland cement or hydrated lime into ladle slag fine–silica flour system can increase strength very significantly. The autoclaving temperature should be higher than 175 °C and the time for constant temperature does not need to be more than 4 h to achieve satisfactory strength. However, the use of Portland cement is not as effective as lime due to the presence of Al in Portland cement.

A 7-batch study using factoral design method indicated that, in the ladle slag–silica flour-hydrated lime system, the optimum composition consisted of approximately 70% ladle slag, 20% silica flour, and 10% hydrated lime. In the ladle slag–silica flour–Portland cement system, a mixture of 50% Portland cement and 50% silica flour gave the highest strength. However, the use of up to 33% did not show an obvious effect on the strength of the system.

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