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Characteristics and cementitious properties of ladle slag fines from steel production

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Abstract

Ladle slag is a by-product from further refining molten steel after coming out of a basic oxygen furnace (BOF) or an electric arc furnace (EAF). Air-cooled ladle slag has a very large portion of fine particles due to the conversion of β-C_2S to γ-C_2S during the cooling process. X-ray diffraction (XRD) analysis of three ladle slag fine samples passing 100, 200 and 325 mesh indicates that the major mineral in ladle slag fines is γ-C_2S, which does not show cementitious property in water. Experimental results have indicated that ladle slag fines show significant cementitious property in the presence of an alkaline activator. The finer the ladle slag is, the better the cementitious property of the slag is.

Keywords: Ladle slag; Mineralogical composition; Cementitious property; X-ray diffraction; Activator

1. Introduction

Steel slag is a by-product from either the conversion of iron to steel in a basic oxygen furnace (BOF), or the melting of scrap to make steel in an electric arc furnace (EAF). The chemical composition of steel slag is highly variable, thus, the mineral composition of steel slag also varies. Olivine, merwinite, C_3S, β-C_2S, C_4AF, C_2F, RO phase (CaO–FeO–MnO–MgO solid solution) and free-CaO are common minerals in steel slag. Steel slag is used as asphalt concrete aggregate in most countries that have steel plants. High free-CaO content in steel slag may cause volume expansion problems. The Ministry of Transportation of Ontario, Canada banned the use of steel slag in asphalt concrete several years ago due to the expansion problem.

The presence of C_3S, β-C_2S, C_4AF and C_2F endorses steel slag cementitious properties. It is generally agreed that the cementitious properties of steel slag increases with its basicity. However, free-CaO content also increases with the basicity of steel slag. The C_3S and β-C_2S contents in steel slag are much lower than those in Portland cement. Thus, steel slag can be regarded as a weak Portland cement clinker [1]. Steel slag exhibits very good cementitious property under the action of chemical activators [2]. Also, cement containing steel slag has much better corrosion resistance than conventional Portland cement [3].

To further refine the steel after coming out of the BOF or EAF, fluxes are added to the molten steel while in a ladle. The slag from this process is usually called ladle slag. The chemical composition of ladle slag is significantly different from that of steel furnace slag in that the former has a very low FeO content, a higher Al_2O_3 content. The difference in chemical composition results in different mineral composition. Ladle slag has a CaO/SiO_2 ratio of around 2 and consists mainly of C_2S.

C_2S exists in four well-established polymorphs: α, α′, 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 [4]. Since the major mineral in ladle slag is C_2S, ladle slag from a slow cooling process has a very high percentage of fine powder, which makes materials handling more difficult and makes it unsuitable for use as aggregates. For example, the limit for less than 200 mesh is about 5% for asphalt concrete aggregate in most places, while the fines less than 200 mesh in ladle slag can be up to 20–35%.

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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	Total
LS100	57.0	26.8	5.2	3.2	3.0	1.7	1.60	1.0	0.3	0.2	100.0
LS200	56.6	26.9	4.3	3.9	3.9	2.4	1.0	0.5	0.3	0.3	100.1
LS325	55.9	26.4	4.7	4.2	4.4	2.3	1.0	0.5	0.3	0.3	100.0

In this study, characteristics and cementitious properties of ladle slag with different finesses from an EAF production was investigated. The purpose of the work is to explore potential applications for ladle slag fines in cement and concrete production.

2. Experimentation

2.1. Raw materials

The ladle slag in this study was from an EAF steel production. Three slag fine samples designated as LS100, LS200 and LS325 were obtained by screening to pass #100, #200 and #325 sieves, and were analysed for their chemical composition, as listed in Table 1. The three samples have very similar chemical composition regardless of differences in their finenesses. However, their CaO content slightly decreases with the fineness, and their MgO, F and SO_3 contents slightly increase with the fineness of slag samples.

A commercial ASTM Type I Portland cement (PC) was used as reference cement. A ground pelletized blast furnace slag (BFS) was used to blend with ladle slag to make a blended cement. Their chemical composition and some physical properties are show in Table 2. Chemical reagent Na_2SiO_3 was used a chemical activator to activate the potential cementitious property of the ladle slag.

2.2. Powder X-ray diffraction (XRD) analysis of ladle slag fines

Ladle slag fines were ground to powder with a manual mortar for Powder XRD analysis using a Philips PW 1139 Diffractometer. Minerals in ladle slag were identified by a computer from the characteristic peak database of the Powder Diffraction File of the Joint Committee on Powder Diffraction Standards.

2.3. Chemical activation of cementitious property of ladle slag fines

Since ladle slag fines contain a high content of free CaO, they cannot be used to replace Portland cement due to potential soundness problems. In this study, 40% of ground blast furnace slag by mass was blended with 60% of those ladle slag fines samples to make blended cements. Cementitious property of such a blended cement was evaluated by using Na_2SiO_3 as an activator. Na_2SiO_3 was dissolved into mixing water then added into the blended cement. One part ladle slag-based cementing material or Portland cement was mixed with 2.75 parts standard Ottawa sand and sufficient mixing water to produce mortars with specified flowability. The water requirement for ladle slag-based cementing material ratio was found to be 0.58 instead of 0.485 that is specified for Portland cement. Then these mortars were cast into $5 \times 5 \times 5$ cm ($2 \times 2 \times 2$ in.) cubic moulds and cured in a moist chamber with a relative humidity over than 95%. After in moulds for 3 days, these cubes were demoulded and then cured in sealed plastic bags. At 3, 7 and 28 days, three cubes were tested in compression and presented results are averages of the three replicates.

3. Experimental results and discussion

3.1. Mineral composition of ladle slag

XRD patterns of the three ladle slag samples are shown in Fig. 1. The identified minerals and their quantity are summarized in Table 3, which include C_3S, β-C_2S, $54CaO{\cdot}MgO{\cdot}Al_2O_3{\cdot}16SiO_2$, $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$, γ-C_2S, $3CaO{\cdot}MgO{\cdot}3SiO_2$, $CaMg(CO_3)_2$, CaF_2 and $Ca(OH)_2$. The three slag samples have very similar XRD patterns and γ-C_2S is the major phase in all three samples. The only difference is that LS200 sample contains more C_3S and $54CaO{\cdot}MgO{\cdot}Al_2O_3{\cdot}16SiO_2$ than samples LS100 and LS325. $54CaO{\cdot}MgO{\cdot}Al_2O_3{\cdot}16SiO_2$ and C_3S have the same structure but in the former compound where two moles of SiO_2 are replaced by one mole of MgO and one mole of Al_2O_3, respectively.

Although free CaO is always present in ladle slag, it could not be clearly identified by XRD here. This may be due to the content of CaO, which is not sensitive to XRD. However, $Ca(OH)_2$ was identified in all the three samples.

Table 2
Chemical composition (mass %) and some physical properties of Portland cement (PC) and blast furnace slag (BFS)

Item	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	Total	Density (kg/m^3)	Blaine fineness (m^2/kg)
PC	20.7	3.7	3.0	62.9	4.2	2.6	0.1	0.6	0.3	98.1	3140	340
BFS	35.3	9.9	0.6	34.7	14.6	4.0	0.3	0.4	0	99.8	2920	495

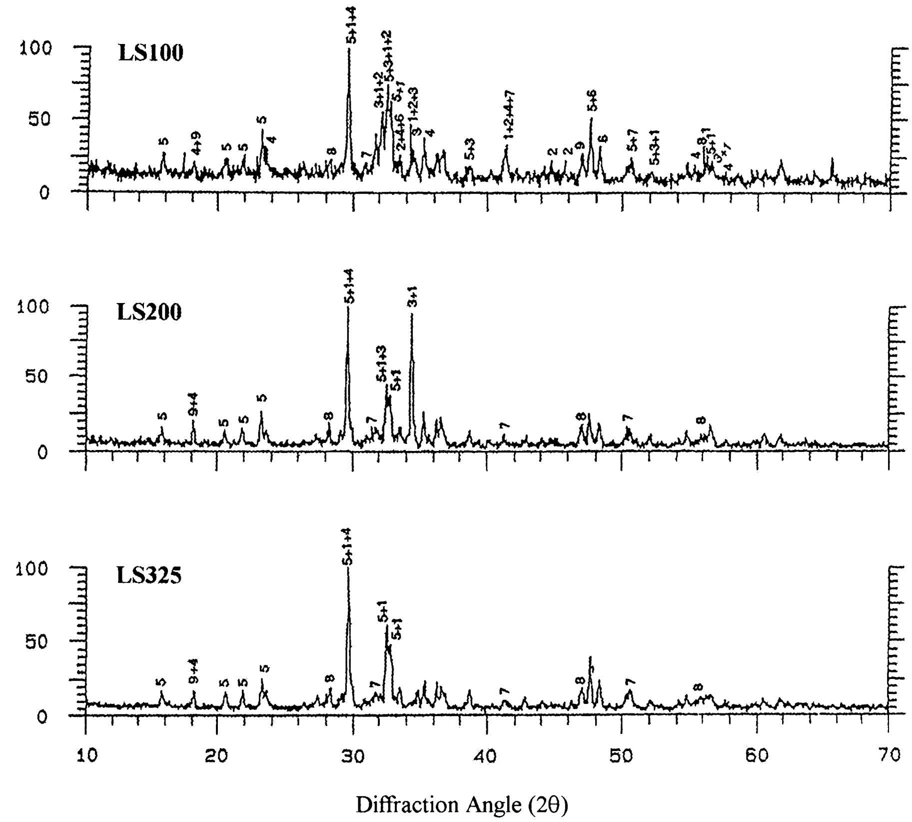

Fig. 1. XRD patterns of ladle slag samples.

Based on the chemical analysis in Table 1, C_2S should be the major mineral in the ladle slag. β-C_2S exists at temperatures over 1000 °C. Since the molten ladle slag was poured onto ground and cooled down slowly, β-C_2S converts to γ-C_2S when the temperature drops down about 960 °C. Since β-C_2S and γ-C_2S have different crystal structure and density, 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.

Among the identified minerals, only C_3S, β-C_2S and $54CaO{\cdot}MgO{\cdot}Al_2O_3{\cdot}16SiO_2$ can exhibit cementitious property under normal hydration conditions. However, their quantities are very small, it can be expected that the cementitious property of these ladle slag fines is very weak under normal hydration conditions.

Table 3
Identified minerals in ladle slag fines

No.	Mineral compound	Quantity of minerals in ladle slag fines		
		LS100	LS200	LS325
1	$3CaO{\cdot}SiO_2$	minor	minor	minor
2	β-$2CaO{\cdot}SiO_2$	minor	trace	trace
3	$54CaO{\cdot}MgO{\cdot}Al_2O_3{\cdot}16SiO_2$	trace	minor	trace
4	$11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$	trace	trace	trace
5	γ-$2CaO{\cdot}SiO_2$	major	major	major
6	$3CaO{\cdot}MgO{\cdot}3SiO_2$	trace	trace	trace
7	$CaMg(CO_3)_2$	trace	trace	trace
8	CaF_2	trace	trace	trace
9	$Ca(OH)_2$	trace	trace	trace

3.2. Cementitious property of ladle slag in the presence of chemical activators

When ladle slag fines are mixed with water, they exhibit little cementitious property. Fig. 2 shows the mortar strength

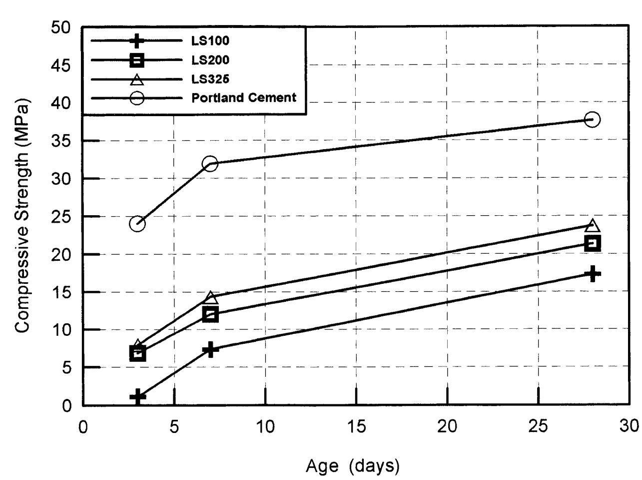

Fig. 2. Strength development of ladle slag-based cement mortars.

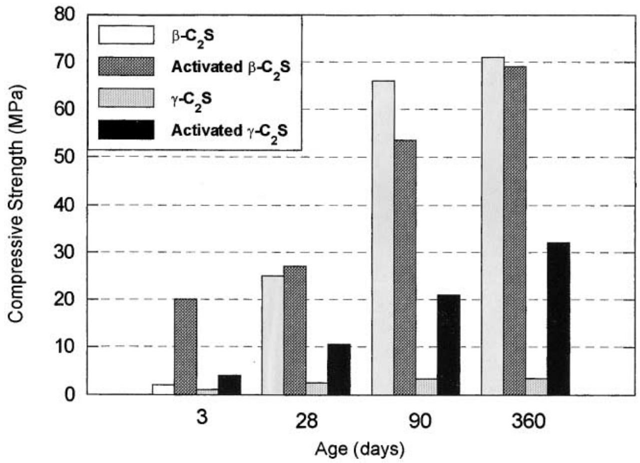

Fig. 3. Effect of chemical activator on strength development of β-C_2S and γ-C_2S minerals[6].

of ladle slag based cementing materials with ground blast furnace slag and a chemical activator cured at room temperature. Blast furnace slag itself exhibits very high strength under the action of proper chemical activators [5]. One obvious feature of these results is that the strength increases with the fineness of ladle slag. Although, there are some differences in mineral composition of these sample, for example, β-C_2S is a minor component in LS100 and 54CaO·MgO·Al_2O_3·16SiO_2 is a minor component in LS200, the differences in mineral composition do not seem to have an obvious effect on strength as the fineness does. The other obvious feature is that these ladle slag based cementing materials showed very low strength at 3 days, but they had faster strength gain rate than the reference Portland cement.

It is well-known that β-C_2S hydrates and gains strength slowly, and γ-C_2S is an inert mineral under normal hydration conditions. It is reported that the potential cementitious property of both β-C_2S and γ-C_2S can be significantly increased by chemical activators under room temperature curing conditions. Fig. 3 is the strength development of β-C_2S, activated β-C_2S, γ-C_2S and activated γ-C_2S, β-C_2S has a low early strength but a high later strength. Activation of β-C_2S can significantly increase its early strength and does not show an obvious effect on later strength. γ-C_2S shows little cementing properties itself. The activation of γ-C_2 S increases its early and later strength significantly, however, its strength is still lower than that of the activated β-C_2S.

4. Conclusions

The major mineral in ladle slag fines is γ-C_2S regardless of their fineness. The other identified minerals include C_3S, β-C_2S, 54CaO·MgO·Al_2O_3·16SiO_2, 11CaO·7Al_2O_3·CaF_2, γ-C_2S, 3CaO·MgO·3SiO_2, $CaMg(CO_3)_2$, CaF_2 and $Ca(OH)_2$.

Since the quantity of cementitious minerals such as C_3S, β-C_2S, and 54CaO·MgO·Al_2O_3·16SiO_2 is very limited, the cementitious property of ladle slag fines is very weak under normal hydration conditions. Ladle slag fines show significant cementitious property in the presence of a chemical activator at room temperature. The potential cementitious property of ladle slag fines significantly increases with their fineness regardless of some differences in their mineral composition.

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