Cement & Concrete Composites 34 (2012) 400–407

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

# Effect of granulometry on cementitious properties of ladle furnace slag

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ARTICLE INFO

*Article history:*
Received 28 May 2010
Received in revised form 24 November 2011
Accepted 24 November 2011
Available online 8 December 2011

*Keywords:*
Ladle furnace slag
Mortar
Granulometry
Cementitious properties

ABSTRACT

Ladle furnace slag (LFS), a by-product of the steel making process, was tested for its potential use as a supplementary cementing material. The material used for the tests was screened or ground, producing three samples of different fineness, and the granulometry of these LFS samples was also tested by particle size analysis. Their chemical and mineralogical composition was assessed by chemical analysis, X-ray diffraction and thermogravimetric analysis. Finally, in order to determine the cementitious and pozzolanic character of LFS in relation to its granulometry, slag–lime and slag–cement mortars were produced and tested in compression. The results show that although LFS is a weak supplementary cementing material, it shows some self-cementing and pozzolanic properties that can be enhanced by screening or grinding the raw material. Even though different levels of fineness and granulometry can be reached with each method, generally, grinding seems to improve LFS binding properties more than sieving.

## 1. Introduction

The melting of scrap for the production of steel in a basic oxygen furnace (BOF) or an electric arc furnace (EAF) is common practice in many countries [1]. This process produces steel slag as a by-product, which is used in many countries as construction aggregate [2,3]. At a later stage of the production process, flux is added in order to refine the steel coming out of the furnace and a second by-product is produced, named ladle furnace slag (LFS). Steel slag utilization is of pertinent importance for the sustainability of the steel industries as by-product disposal is an acknowledged environmental burden and recent legislation provides extra financial incentives for their utilization, mainly through taxation and fines. Thus, although LFS is produced at lower volumes compared to steel slag, its utilization is also very significant for the steel industries. LFS shows a different chemical composition compared to steel slag, with significantly lower content in ferrous oxides and increased fineness [4,5]. The chemical compositions of both steel slag and LFS vary depending on the batch synthesis, due to the fact that in scrap melting production is carried out in batches, as opposed to the continuous process of blast furnace steel making. Furthermore, local conditions, different manufacturing practices, and scrap metal variations could also affect significantly the chemical composition of the produced slag [6,7].

Typically, LFS is mostly constituted of calcium oxides, as well as silica, magnesium and aluminum oxides [8]. Compared to EAF slag which is largely inert, the increased fineness and weak cementitious properties of LFS have suggested its potential use as a supplementary cementing material [9,10]. Research has shown that it does show some latent hydraulic and pozzolanic properties and that it could be used as an alternative binder for low-strength applications [11–14]. In order to increase final strength, researchers have suggested several ways of processing the raw material such as re-melting [10], use of activators [15] or screening [4,16].

It is generally acknowledged that the presence of free lime and magnesia in LFS could cause problems in restrained structural members due to delayed expansion phenomena [17]. Suggested procedures for the control of expansion problems include rapid cooling of LFS [7], weathering in outdoor conditions for a period of at least 6 months [18,19], its use in ternary systems with siliceous material and cement [15], and mixing with inert material [20]. Other alternatives concern the use of LFS in unrestrained construction applications, such as earthworks and soil stabilization [21].

The above-mentioned research has shown that it is possible to successfully introduce LFS as a binder in civil engineering applications, when material-specific parameters are taken into account. In this report, LFS of low free Cao and MgO contents, subjected to weathering in outdoor conditions for a period of 1 year, was tested as a supplementary cementing material for low-strength applications. The purpose of this work was to assess the influence of fineness obtained by sieving or grinding on the cementitious and pozzolanic properties of LFS.

## 2. Materials and methods

Since freshly produced LFS has grain sizes up to 500–1000 μm or even more, sieving and grinding were considered as ways of

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doi:10.1016/j.cemconcomp.2011.11.015

increasing its fineness. Although sieving seems easy and economic, it also suggests rejection of the largest fraction of the raw material. Grinding, on the other hand, could include all the available material but also increase cost significantly, especially if very high fineness is to be reached. For the needs of this experimental program, it was decided to produce two LFS samples by sieving through the 100 μm and 45 μm sieves (named LFS100 and LFS45, respectively) and also to produce a third LFS sample by grinding the weathered LFS. The ground sample was measured to have 21% retained material at the 45 μm sieve (LFS21%). These three LFS samples of different granulometry were tested for their chemical, mineralogical and mechanical properties.

### 2.1. LFS material characterization

A chemical analysis was carried out on each of the samples (Table 1), while their granulometry was measured by laser particle size analysis, using a Mastersizer 2000 instrument (Fig. 1). In addition, DTA–TG thermogravimetric thermal analysis (TA Instruments SDT 2960) and X-ray diffraction (Philips PW1840) were used to determine their mineralogical characteristics (Figs. 2 and 3, respectively). Free lime was determined by deducting the amount of $Ca(OH)_2$ determined by the DTA–TG analysis from the amount of $CaO_f$ determined according to the relevant European Standard EN 451-1 [22], while reactive silica was determined according to the EN 197-1:2000 [23]. The apparent specific density of LFS was also measured according to ASTM C188-95 [24].

The presence of reactive $SiO_2$ and $Ca(OH)_2$ in LFS implies that it may show both self-cementing and pozzolanic properties as a binder [25]. In a preliminary effort to investigate the self-cementing capacity of LFS, a slag-paste was produced by mixing water with net LFS (LFS100) at a 1:2 ratio. After curing at 20 °C and 95% RH, the hardened paste compressive strength was measured at 7 and 28 days. Also, scanning electron microscopy (using a JEOL JSM 5840A instrument), energy dispersive spectroscopy (using ISIS 300 software), DTA–TG analysis and X-ray diffraction analysis were used to determine the latent hydraulic character of LFS (Figs. 4–6, Table 2).

### 2.2. Laboratory mortar mixtures

Since LFS might be considered as a Type II (pozzolanic or latent hydraulic) addition according to EN 206-1:2000 [26], each sample was used to produce lime-based and cement-based mortars in order to test its cementitious capacity in different systems. Thus, three series of lime-based and three series of cement-based mortar mixtures were produced in the laboratory, according to Table 3. The lime–slag mortar mixtures were prepared using hydrated lime powder and standard sand having a lime:slag:sand:water ratio of 1:2.4:9:1.6, following the mixing requirements of ASTM C593-83 [27]. Cylindrical specimens 50 mm in diameter and 100 mm in height were cast, cured at 20 °C and 95% RH and tested for compressive strength at 7, 28 and 200 days. The workability of the mixtures was recorded by flow table expansion (Table 3). Also, DTA–TG analysis was carried out at 28 and 200 days for each of the slag–lime mortars (Fig. 7).

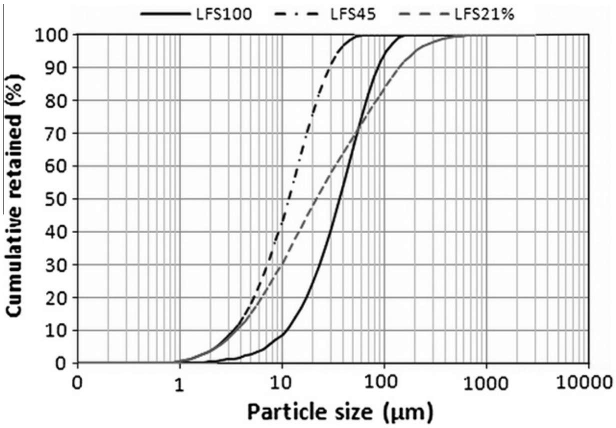

**Fig. 1.** Particle size analysis of LFS samples.

The materials other than LFS used for the cement-based mixtures were cement type I42.5N and standard sand. Workability was measured by flow table expansion and the water requirement for a constant workability of 160 ± 10 mm was also recorded. The slag–cement mortar mixtures were prepared using 20% LFS as cement replacement and a starting water/binder ratio of 0.484, modified by ±5% according to the requirements of ASTM C311-02 [28] in order to reach adequate workability (Table 3). 40 × 40 × 160 mm specimens were cast from each mixture, cured at 20 °C and 95% RH and tested for compressive strength at 7 and 28 days.

## 3. Results and discussion

### 3.1. Granulometry, mineralogical composition and characterization of LFS

When considering volume fraction below 45 μm, it seems, as expected, that sieving through the 45 μm sieve gave finer material; 43.62% below 10 μm, compared to 8.83% for LFS100 and 30.5% for LFS21%. Also specific surface was considerably higher for LFS45; 0.849 $m^2/g$, compared to 0.282 $m^2/g$ for LFS100 and 0.660 $m^2/g$ for LFS21%. The grinding process gave a material (LFS21%) of grain size distribution comparable to LFS100, but coarser than LFS45. Both specific surface and volume fraction below 10 μm – which are parameters considered to influence the cementitious character of binders [29] – were higher for LFS21% when compared to LFS100 and lower when compared to LFS45.

Apparent specific density did not vary much between the three samples; the values found were equal to 2560–2590 $kg/m^3$. Chemical composition also does not change much with fineness; only reactive $SiO_2$ content increased slightly and magnesium oxide content decreased with grinding. These changes, however, are favorable and could contribute to improved pozzolanic activity and reduction of long-term expansion of the ground slag [25,30]. Ferrous oxides, sulfates and, most importantly, free lime contents were very low and should not impose any problems when using

**Table 1**
Chemical composition (wt.%) of the three LFS samples.[a]

| Sample | CaO | $CaO_{free}$ | $SiO_2$ | $SiO_{2,reactive}$ | $Al_2O_3$ | MgO | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| LFS100 | 55.6 | 0.6 | 23.0 | 17.9 | 1.3 | 6.7 | 1.7 | 0.3 | 0.4 | 0.43 |
| LFS45 | 55.9 | 0.9 | 23.2 | 18.0 | 1.3 | 6.8 | 1.6 | 0.3 | 0.5 | 0.20 |
| LFS21% | 55.7 | 0.8 | 26.1 | 20.5 | 2.0 | 4.3 | 1.5 | 0.2 | 0.9 | 0.25 |

[a] LFS100:LF slag sieved at 100 μm; LFS45:LF slag sieved at 45 μm; LFS21%:LF slag ground until 21% retained at 45 μm.

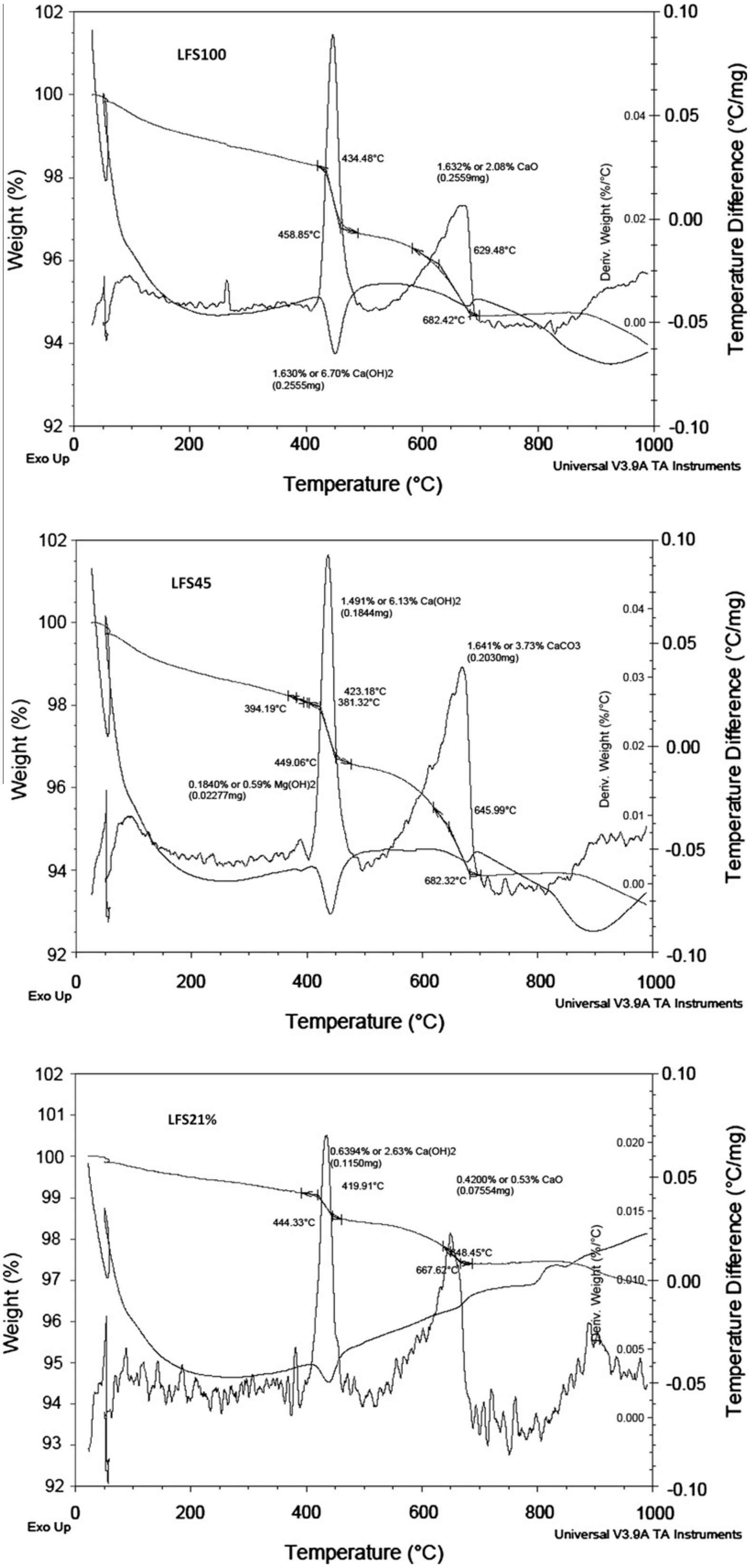

**Fig. 2.** DTA–TG analysis of LFS samples.

any of the LFS samples as a binder, since the European Standards [31] propose free lime content below 2.5% to ensure reduced risk of expansion.

DTA–TG thermal analyses are shown in Fig. 2, while XRD patterns of the three LFS samples are shown in Fig. 3. Regarding the mineralogical composition, the main mineral identified on all slag

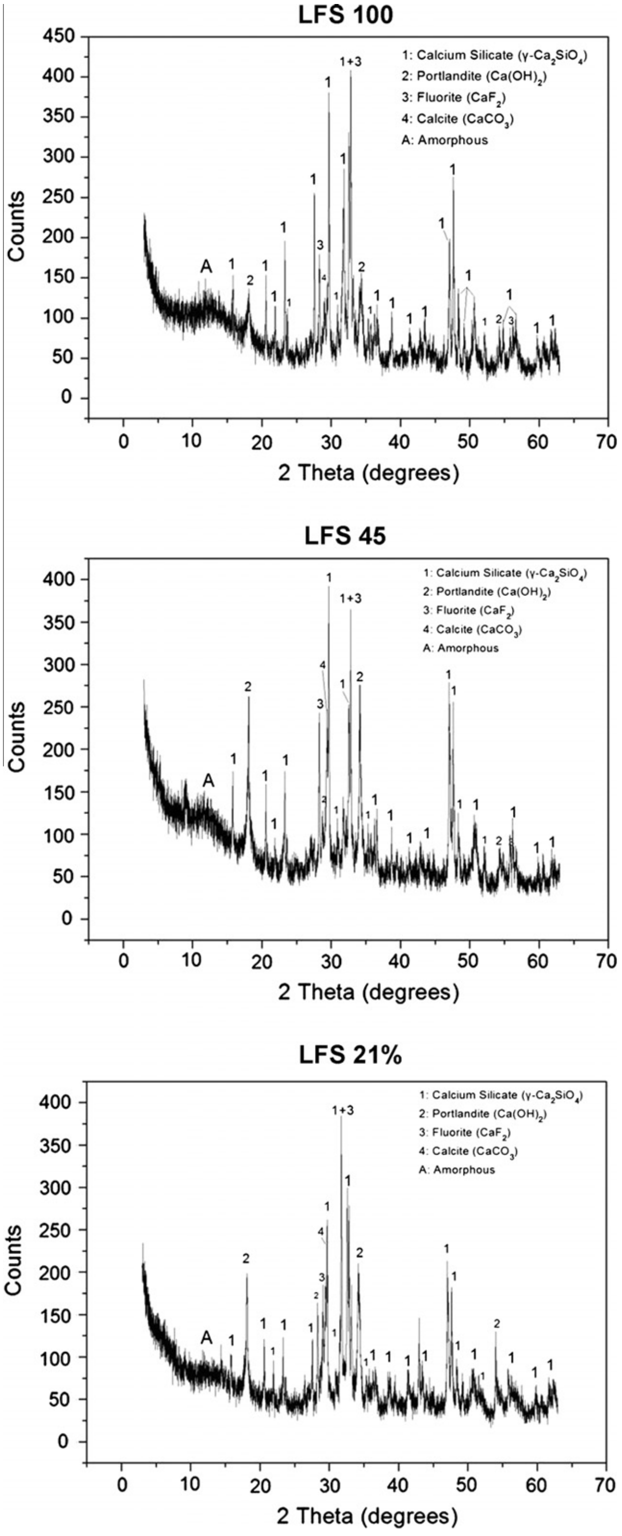

**Fig. 3.** XRD patterns of LFS samples.

samples was dicalcium silicate as well as minor quantities of portlandite, fluorite, calcite and amorphous material, as also verified by Shi [4]. Dicalcium silicate exists in the molten slag – that reaches temperatures of approximately 1600 °C – in the form of α-$C_2S$ which, on cooling, transforms to β-$C_2S$ and subsequently to γ-$C_2S$. The latter is a stable form of calcium orthosilicate, which does not possess hydraulic properties and is found in cement and slags [32]. It could be said from Fig. 3, but not based on quantitative analysis, that the content of minerals and amorphous material may differ in sieved and ground slag samples.

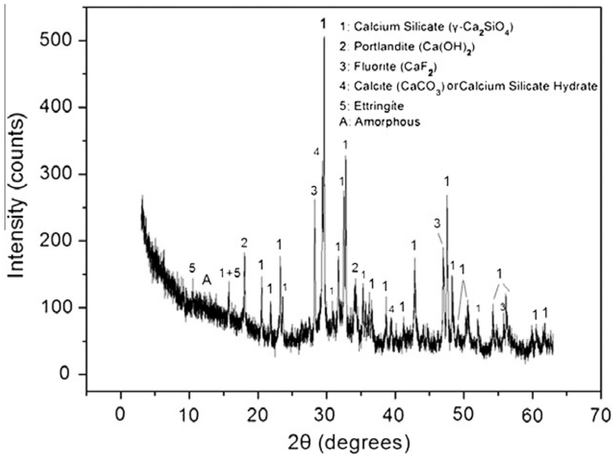

**Fig. 4.** XRD analysis on 28-day net-LFS hardened paste.

Portlandite was detected by thermal analysis, where sieved samples showed similar contents (around 6%) while ground slag showed reduced content (2.63%). The detected $Mg(OH)_2$ is low (0.50% for LFS45 and 0.11% for LFS21%), while calcium carbonate ranges from 3.71% for LFS100 to 3.73% for LFS45 and 0.95% for the ground sample.

The hardened slag paste showed self-cementing capabilities, producing a 7-day compressive strength of 0.87 MPa and a 28-day compressive strength of 2.88 MPa. X-ray diffraction analysis (Fig. 4), scanning electron microscopy (Fig. 5) and energy dispersive spectroscopy (EDS) was carried out on hardened slag paste at 28 days. Region A in Fig. 5, followed by the EDS analysis results (Table 2) show an area with possible presence of ettringite in low amounts, while regions B and C in Fig. 5, which focus on hardened binder, also followed by EDS analysis (Table 2) show the possibility of C–S–H compounds formation in low amounts. DTA–TG analysis at 7 and 28 days shows a decrease of portlandite content (from 7.11% to 5.92%) during the wet curing, which could be attributed to the C–S–H compound formation by pozzolanic reaction (Fig. 6).

### *3.2. Strength development of slag–lime and slag–cement mortars*

The mixtures with hydrated lime (as described in Table 3) are used to assess the pozzolanic properties of the material. The compressive strength of these mixtures is shown in Fig. 8. The results showed that sieved LFS is a weak pozzolan that develops low early strength (LFS100 and LFS45 both show 7-day strength less than 1 MPa). Strength gain is improved slightly at 28-days and reaches almost 2 MPa for LFS45, but is still relatively low, in comparison to the requirements of ASTM C593-83 (5.5 MPa 28-day compressive strength). Regarding ground slag LFS21%, 7-day strength increased twofold compared to that of sieved slag mortars, while 28-day strength is also significantly improved (2.5 MPa). Although calcite formation is a possible reason for strength gain, the strength increase rate, as well as the wet curing regime does not explain the ultimate strength gain. The slow pozzolanic reaction enables all slag–lime mortars to develop enhanced strength over the long term. Ground slag develops a 200-day strength of 5.11 MPa, while sieved slag mortars develop a 200-day strength of about 3 MPa. The DTA–TG analysis performed on slag–lime mortars showed considerable $Ca(OH)_2$ availability for all mortars at 28 days. Under wet curing, $Ca(OH)_2$ reduced continuously and had disappeared

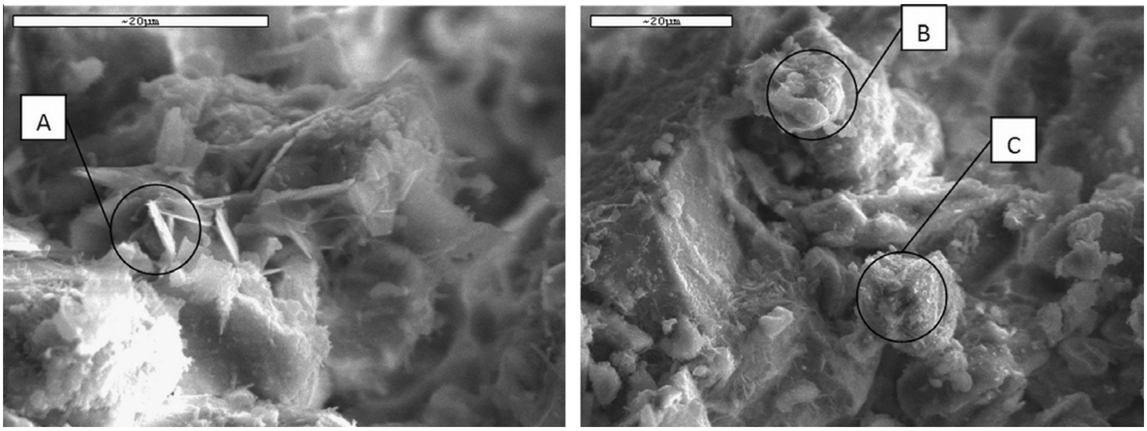

**Fig. 5.** SEM photographs of 7-day net-LFS hardened paste showing possible ettringite and calcium silicate hydrate formation (Bar = 20 μm).

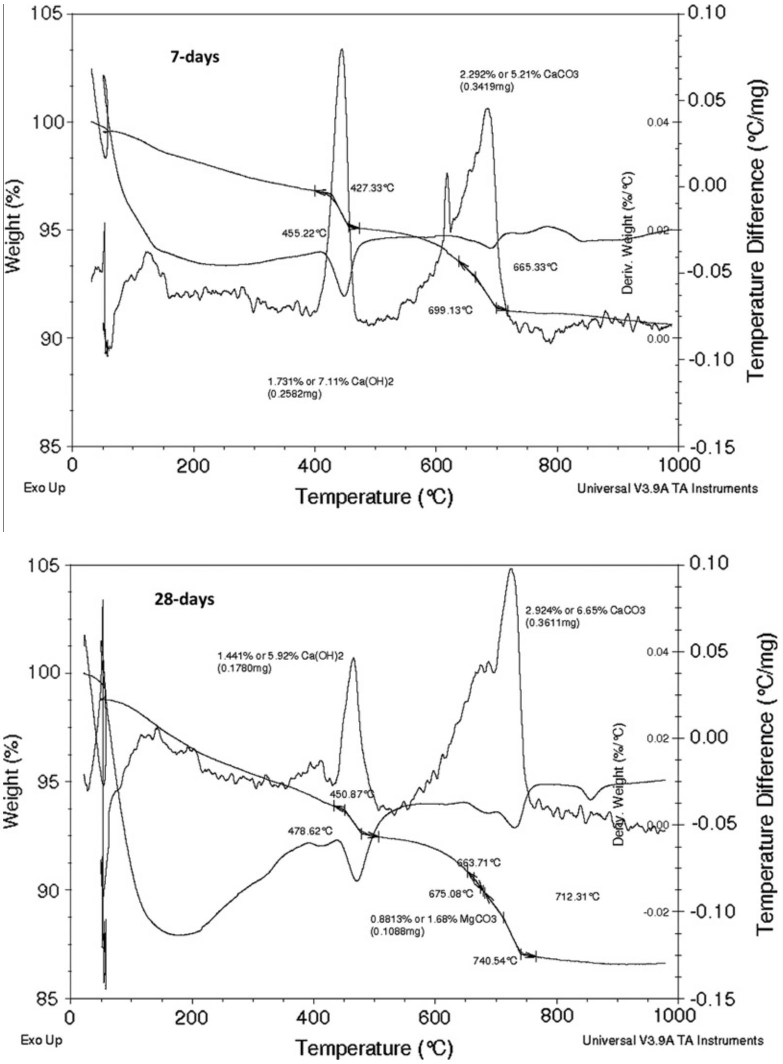

**Fig. 6.** Net-LFS hardened paste DTA–TG analyses at different ages.

when measured by thermal analysis at 200 days, contributing to strength development (Fig. 7).

The cementitious properties of ladle furnace slag were also tested with the slag–cement mortars. The 7-day and 28-day of the compressive strength of the mortars prepared according to Table 3 are shown in Fig. 9. The rate of strength development was

**Table 2**
EDS analysis results (wt.%) on 7-day net LFS slag paste.

| Position (Fig. 5) | O | Mg | Al | Si | S | Ca | Fe |
|---|---|---|---|---|---|---|---|
| A | 65.00 | 0.26 | 2.30 | 7.82 | 1.95 | 22.65 | 0.14 |
| B | 62.31 | 0.63 | 3.79 | 7.23 | 0.91 | 22.90 | 1.70 |
| C | 66.60 | 0.49 | 0.95 | 9.15 | 0.65 | 21.69 | 0.42 |

**Table 3**
Composition of the LFS mixtures.

| Mixture | SL100 | SL45 | SL21% | REF | SC100 | SC45 | SC21% |
|---|---|---|---|---|---|---|---|
| CEM I42.5N (g) | – | – | – | 500 | 400 | 400 | 400 |
| Lime (g) | 150 | 150 | 150 | – | – | – | – |
| LFS100 (g) | 360 | – | – | – | 100 | – | – |
| LFS45 (g) | – | 360 | – | – | – | 100 | – |
| LFS21% (g) | – | – | 360 | – | – | – | 100 |
| Standard sand (g) | 1350 | 1350 | 1350 | 1350 | 1350 | 1350 | 1350 |
| Water (g) | 240 | 240 | 240 | 242 | 252 | 242 | 238 |
| Flow table expansion (mm) | 110 | 110 | 115 | 165 | 165 | 170 | 165 |
| Fresh mortar unit weight (kg/m$^3$) | 2135 | 2127 | 2147 | 2315 | 2260 | 2280 | 2282 |

similar for all mixtures, although mixture with ground slag SC21% mixture is the closest to the reference mixture, since it developed 93.8% and 93.3% of the reference mixture compressive strength at 7 and 28 days, respectively. The SC45 mixture developed 86.4% and 87.1% of the reference mixture compressive strength at 7 and 28 days, respectively, while the SC100 mixture had 77.2% and 75.9% of the reference strength, accordingly. Since all percentages are above 75% – a threshold value set both by ASTM C618-03 [33] and EN 450-1:2005 [31] – it can be said that LFS shows the potential to be used as a supplementary cementing material. Moreover, the results for the slag–cement mortars confirm that using finer slag increases mechanical strength and also that grinding can increase strength further.

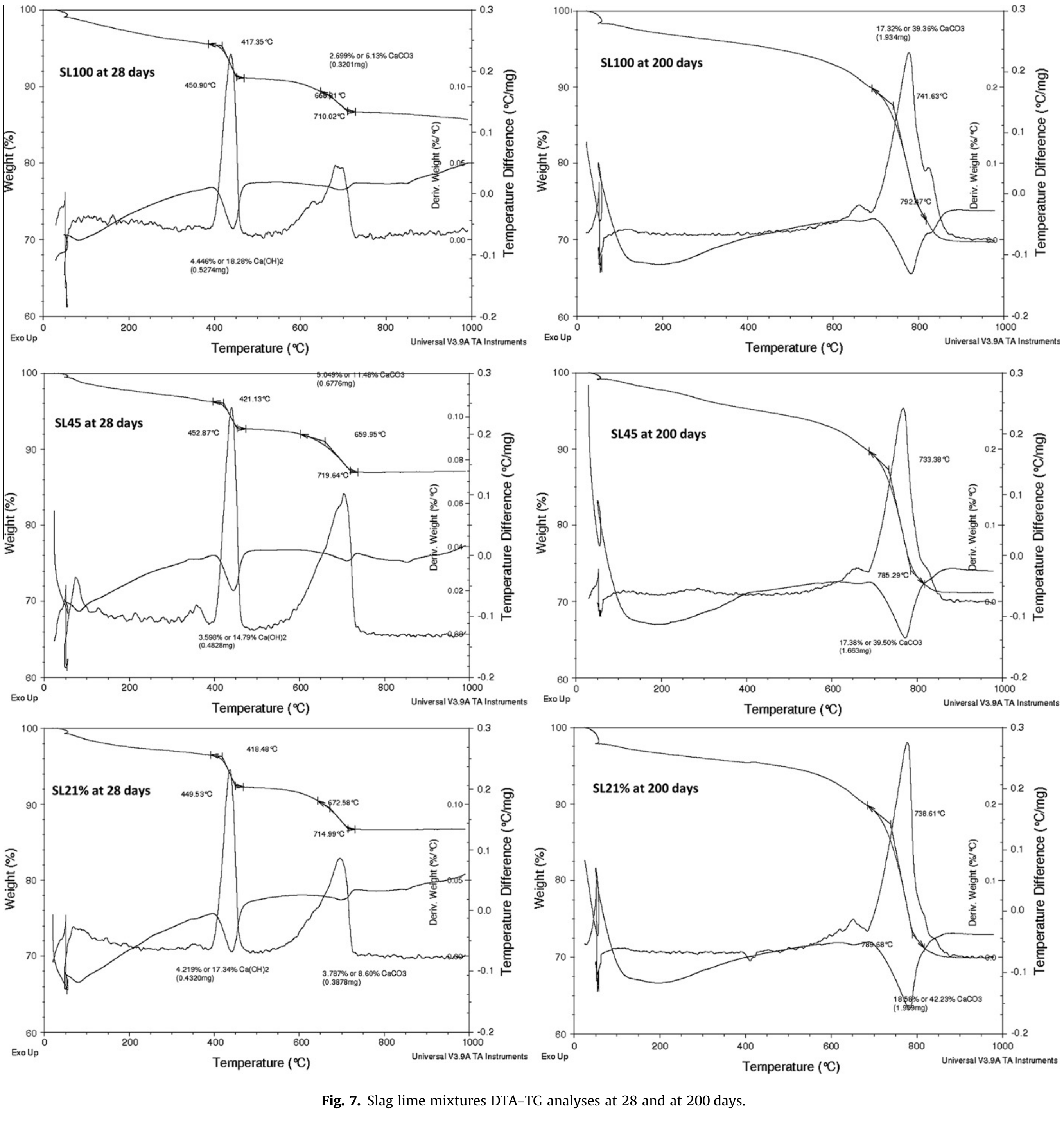

**Fig. 7.** Slag lime mixtures DTA–TG analyses at 28 and at 200 days.

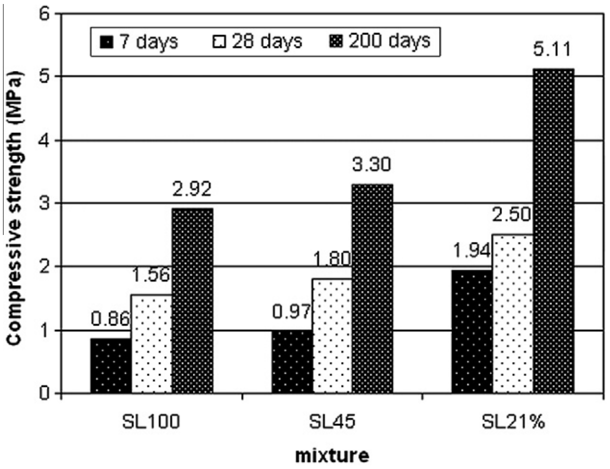

**Fig. 8.** Strength development of slag–lime mortars (lime:slag:sand ratio of 1:2.4:9 – average of six specimens).

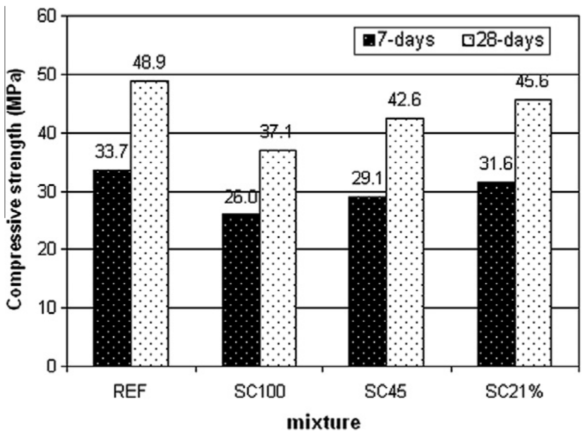

**Fig. 9.** Strength development of slag–cement mortars (slag:cement:sand ratio of 0.2:0.8:2.7 – average of six specimens).

## 4. Conclusions

Sieving and grinding were used as ways to enhance the cementitious properties of ladle furnace slag (LFS) for use either with lime or cement. Grinding did not seem to affect significantly either the chemical or the mineralogical composition of LFS. Although sieved slag had higher specific surface, grinding produced a more uniform granulometry. Also, free CaO or free MgO content did not increase by the process of grinding, while reactive $SiO_2$ was slightly higher for ground slag.

Dicalcium silicate was identified as the main mineral in all slag samples and portlandite, fluorite and calcite were identified as minor constituents. The presence of portlandite in slag suggested potential self-cementing capacity which was verified by strength development in hardened slag paste. X-ray diffraction, microscopy and spectroscopy measurements in the hardened slag paste identified the possibility of C–S–H formation which could account for the latent hydraulic properties of LFS. The presence of reactive silica in LFS also suggested pozzolanic activity which was tested by measuring the strength development of slag–lime mortars according to the relevant standards. The slag–lime mortars, after wet curing, developed 28-day strengths of 1.56–1.94 MPa and 200-day strength of 2.92–5.11 MPa, which confirm the weak pozzolanic character of LFS.

The mortar strength results showed that although sieving can give very fine material with increased specific surface, ground LFS developed higher strength levels. This can be attributed to the increase of the reactive constituents in the ground material due to the process of grain crushing. Regarding strength development, ground LFS at 20% cement replacement rate developed 93.3% of the strength of the reference mortar, which shows that its use with cement could be viable.

Ladle furnace slag could be characterized as a supplementary cementing material of low early strength, which shows some latent hydraulic and pozzolanic properties. The strength levels achieved would allow its use in masonry mortars as prescribed in Eurocode 6 (EN 1996-1-1) [34], as well as several low-strength cement and concrete applications. Increasing LFS fineness can improve its performance, while grinding seems to enhance mechanical properties more than sieving. Ground LFS could provide a low-cost alternative supplementary cementing material contributing to increased by-product utilization in construction.

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