Mineralogy and Microstructure of Lightweight Aggregates Produced from Washing Aggregate Sludge and Fly Ash

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INTRODUCTION.

Lightweight aggregates (LWAs) are granular, cohesionless, porous materials with a loose bulk density (ρb) not greater than 1.20 g/cm^3 or with a particle density not greater than 2.00 g/cm^3 (UNE-EN-13055-1, 2003).

Swamy and Lambert (1981) reported the importance of the microstructure for the main physical properties of artificial LWAs. Farran (1956) showed that the mineralogical composition of the aggregates is the main factor to consider in the study of concrete fracture, because the mineralogy of them fundamentally determines the adhesive behaviour between the cement paste and the aggregate.

The aim of this work is to establish the relationship between the values of the main physical properties, i.e. bloating index (BI), density, water absorption (WA$_{24h}$) and compressive strength (S) of the LWAs and their mineralogy and microstructure. The results of this study contribute to optimize the conditions for the manufacture of LWAs.

MATERIALS AND METHODS.

Different types of LWAs resulting from a previous study (González-Corrochano et al., 2009) have been selected. Aggregates of type 3.F(3) were manufactured with a 75:25 proportion (% wt) of washing aggregate sludge:fly ash (WS:FA), whereas types 3.F(2) were prepared using a 50:50 ratio. The heating temperatures (T$_{heating}$) were 1150ºC, 1175ºC, 1200ºC and 1225ºC for dwell times of 10 and 15 minutes. The sintering was carried out in a rotary kiln.

The first selected sample was type 3.F(3), heated at 1175ºC for 10 min (3.F(3)-1175-10), because it had the highest bloating index (BI=11.17%). 3.F(2), heated at 1200ºC for 15 min (3.F(2)-1200-15), was the second LWA selected, since the BI is also positive and its composition is different from the previous one. In order to compare the effect of temperature on the microstructure of these LWAs, 3.F(3)-1150-10 (sintered at a lower temperature than the first selected sample), and 3.F(2)-1175-15 and 3.F(2)-1225-15 (sintered at a lower and a higher temperature than the second selected LWA) were chosen.

The surface morphology of the fractured specimens was examined using a JEOL JSM-6400 scanning electron microscope (SEM) coupled with an energy-dispersive X-ray (EDX) analyzer. Electron microprobe analyses (EMPA) were also carried out using a JEOL JXA-8900 MWD/ED equipment. The bulk mineralogy (BM) was determined by X-ray diffraction (XRD) on an X'Pert Pro diffractometer, after grinding and homogenization of three entire pellets of each type to <53 µm.

RESULTS AND DISCUCCION.

LWAs Manufactured with 75% of Washing Aggregate Sludge and 25% of Fly Ash (type 3.F(3)).

Typical SEM micrographs of the LWAs studied are shown in Figures 1 and 2. 3.F(3)-1150-10 does not have a distinct external layer (Fig. 1) and there are no clear signs of expansion. However, at a higher temperature, 3.F(3)-1175-10 presents a dense external layer, which is well-differentiated (Fig. 2). Unlike the external layer, the internal material is vitrified and shows signs of bloating. Temperature gradients inside the molten aggregate during the heating process have been demonstrated by previous studies (Lo et al., 1999) and the mentioned structures could be the result of these heat gradients. The EDX spectra show that the external layers of 3F(3)-1175-10 are, in general, chemically homogeneous.
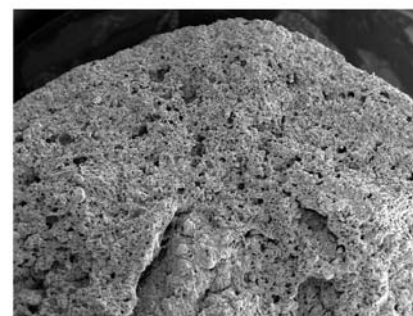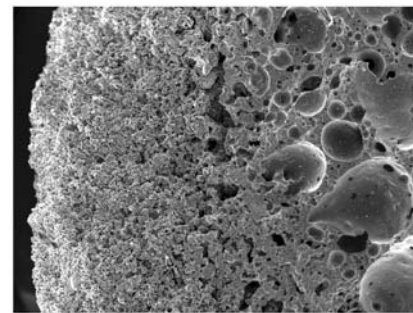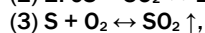

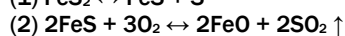fig 1. SEM micrograph of 3.F(3)-1150-10 (x20).

fig 2. SEM micrograph of 3.F(3)-1175-10 (x40).

The back-scattered electron (BSE) images obtained during the EMPA study show that, within 3.F(3)-1150-10 and within the external layer of 3.F(3)-1175-10, Fe oxides appear as rounded aggregates. The presence of varying amounts of pyrrhotite ($Fe_{1-x}S$), always located in the pore walls within the inner glassy core of the aggregates, is supported by the chemical analysis. González-Corrochano et al. (2009) reported traces of pyrite (FeS_2) in the fly ash. This mineral could release gas, causing bloating as a result of any of the following reactions (Utley et al., 1965):

(1) $FeS_2 \leftrightarrow FeS + S$
(2) $2FeS + 3O_2 \leftrightarrow 2FeO + 2SO_2 \uparrow$
(3) $S + O_2 \leftrightarrow SO_2 \uparrow$,

Therefore, pyrrhotite could be generated from the heating of pyrite according to reaction (1).

All the LWAs contain quartz (SiO_2), derived from the raw materials (WS and FA, González-Corrochano et al., 2009). Plagioclases (with mainly anorthitic composition, $CaAl_2Si_2O_8$) are also found in all the samples analysed. This is in agreement with the results from previous studies (Stoch et al., 1986) in which the formation of anorthite in ceramic wares begins in the temperature range 1000-1100ºC. The WS is formed by calcite ($CaCO_3$), which decomposes into $CaO(s)$ and $CO_2(g)$, and which could be consumed during the formation of anorthite at higher temperatures. Finally, pyroxene group minerals (ferroan diopside and augite) appear in all the types. Pyroxenes are neo-formed phases, since the raw materials did not contain them. A possible neo-formation mechanism would be substitutions of the Ca in the original structure of wollastonite ($CaSiO_3$) for Mg and Fe. Wollastonite could be formed by the reaction of calcite and quartz, accompanied by CO_2 release, at temperatures higher than 600-700ºC (Polettini et al., 2004). This neo-formation mechanism has been reported for raw materials containing quartz and calcite and lacking clay minerals, such as illite. In this study, the washing aggregate sludge is also composed of clay minerals; therefore, an alternative neo-formation mechanism must exist, such as reaction of the clay minerals with the calcium resulting from the decarbonation of calcite.

LWAs Manufactured with 50% of Washing Aggregate Sludge and 50% of Fly Ash (type 3.F(2)).

All the lightweight aggregates studied that were manufactured with this composition develop an external layer of variable thickness (100 µm-2000 µm), except for 3.F(2)-1150-10. *LWAs with an external shell, except 3.F(2)-1150-15, are also composed of an inner glassy material that presents signs of expansion, with pores of different sizes and not interconnected with one other.*

As in the case of LWAs with 25% of fly ash, the presence of Fe oxides, in the shells, and pyrrhotite, in the pore walls located in the glassy core, are observed.

All the LWAs manufactured with 50% of fly ash present quartz, hematite and plagioclases. Like quartz, hematite could be present in the LWAs as a relic of the raw materials (González-Corrochano et al., 2009). It has been reported that, at 370ºC-700ºC, hematite may result from the transformation of magnetite (Goyal et al., 2009); therefore, it is possible that a portion of the total hematite was neo-formed, from the magnetite in fly ash (González-Corrochano et al., 2009) .

Influence of the mineralogy and microstructure on the properties of the LWAs.

The lower BI values reflect a lower proportion of inner pores and a smaller pore size.

The presence of larger pores can be observed when the LWAs present a decrease in the density with temperature.

When a sintered-vitrified external layer is formed in the LWAs, WA_{24h} is not so related to the size, amount and/or type of pores in the interior, since water is blocked from going into them by the shell. However, when the external layer is not present, WA_{24h} values are dependent on the size and amount of each type of pore (open or closed).

Calcium feldspars and the consumption of quartz during the formation of a glassy phase improve the S values.

CONCLUSIONS.

From the mineralogy and microstructure study, we may conclude that:

● Most LWAs made with fly ash exhibit an external layer and isolated pores of different shapes and sizes.
● Vitrified pores are location sites for neo-formed crystalline phases such as pyrrhotite. In the non-vitrified material,

such as the external layers, the presence of Fe oxides is systematically observed.
● The main crystalline phases identified in the LWAs manufactured with washing aggregate sludge and fly ash are quartz, hematite and neo-formed phases from the plagioclase and pyroxene groups.
● The microstructure of the LWAs studied is related to the bloating index, dry particle density, water absorption and crushing strength values.
● The mineralogical composition of these LWAs is related to water absorption and crushing strength values.

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