# Production of Lightweight Aggregates from Coal Gasification Fly Ash and Slag

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## INTRODUCTION

The Integrated Gasification in Combined Cycle (IGCC) power plant of ELCOGAS S.A. in Puertollano, Ciudad Real, (Spain) is the first IGCC power plant implanted in Spain and the second one in Europe as result of an European Community project of the THERMIE program.[1] It has been designed to produce electricity by the gasification of a mixture of coal and petroleum coke. Gasification process convert the solid combustible mixture into a gas that is subsequently depured to separate sulphur and dust particles. The cleaned gas composed by 60% CO, 22% $H_2$, 10% $N_2$, 4%$H_2O$ and 4% $CO_2$, is then burned with high efficiency in a combined cycle electricity-generating unit.[2]

The gasification of the combustible takes place at 1450ºC and 25 atm. of pressure reducing atmosphere to get the optimum partial pressure of oxygen to yield CO as synthesis gas. In these conditions, the inorganic fraction of the coal is fully melted and the resulting melt acquire a high capacity of gases solution[3].The melt cooled and solidified by quenching in a water dump give rise to a vitreous slag. The fly ash comes from small drops of melt and volatile compounds which are carried up by the ascending gases. The mixture of gases is cooled in a refrigerating system where fly ash solidify at temperatures from 950 to 400 ºC. Latterly, the fly ash is separated and recovered from the filters in the gas cleaning unit.
ELCOGAS fly ash is a grey powder of very small particle size, with an average particle diameter below 3µm. Chemical and physical properties of IGCC fly ash from Puertollano plant has been previously studied[4]. Fly ash composition is not very different to that of the combustible ash, incremented in volatile oxides content. As a consequence of the low $pO_2$ at which fuel is burned, reducing forms of oxides and sulphides are found in these wastes' composition. Pozzolanic activity of this fly ash and its suitability to be used as concrete additive has been yet assessed, [5] being at present recycled for that use.

The slag from Puertollano plant has been characterised [6,7] and several applications have been investigated as grog material in manufacture of construction bricks[8,9] and synthesis of glassceramics. [10]

The vitreous slag and fly ash wastes produced in Puertollano IGCC power plant exhibit expanding properties when are heat treated at high temperatures in oxidizing conditions due to a degassing of the glassy phase in the form of bubbles that are released to the viscous liquid phase at temperatures near the softening point. This foaming process is simultaneous to the devitrification for crystalline phases growth, and the consequence of both processes is the conversion of the slag and the fly ash in a porous lightweight ceramic or glass-ceramic material being mullite, hercynite and anorthite the main developed crystalline phases in the fly ash and Mullite in the slag.

Two different ways of synthesizing lightweight aggregates (LWA) from waste materials are reported in several publications; the first one, consisting on the incorporation of a gas former waste to the mixture of clay that is conformed in spherical form and heat treated at high temperatures around 1100-1200ºC [11,12] . The voids are generated by the combustion or gasification of the waste included in the mass of the aggregate. A second way arises from waste glass that is milled at very fine particle size and mixed with foaming additives such as silicon carbide or calcium carbonate[13, 14]. In both cases, a viscous liquid phase formation prior to the gas forming reaction is the mechanism of retention of bubbles inside the aggregates giving as a result the expansive foaming of the particulates.
The coal gasification wastes here considered may be used as foaming agent as well as glassy matter to produce LWA.

This paper reports the result of the investigation to produce LWA by taking advantage of the foaming reaction of ELCOGAS IGCC power plant residues using 100% of the these gasification wastes.

## EXPERIMENTAL DETAILS

The fly ash (FA) and slag (SL) here considered come from gasification process in ELCOGAS plant in Puertollano (Spain). Chemical analysis was done by X ray fluorescence (XRF) and infrarred spectroscopy (IR); mineralogical analysis by X -ray diffraction (XRD). The thermal properties has been analysed by Differential Thermal Analysis (DTA) run at a heating rate of 10ºC/min, in platinum crucibles using calcined powdered aluminium oxide as reference. Slag samples were in milled to particle size below 300 μm and the fly ash were analysed in powder as received.

The expansion was measured by means of a Hot-Stage Microscope (HSM). The samples were examined as cylindrical specimens of 2mm diameter, 4 mm of height, made of as received fly ash and milled slag as fine powder of particle size <50 μm. Images of the specimens and data of the variation of the specimen height were taken at fixed intervals of temperature. The sintering curve displays the variation of the specimen

height in percentage related to the initial height taken as 100%. Consequently shrinkage is measured as values below 100% and expansion as values over 100%.
The lightweight aggregates were manufactured as follows: The mixture of fly ash or fly ash/slag was handily moulded in spherical shape with a 20-22 % of distilled water, and dried at 110ºC. Then, the spheres of different sizes were introduced in a preheated oven at the expansion temperatures of 1150, 1175 and 1200ºC for 10-15 minutes.

Two mixtures were tested, LWAFA: made of 100% fly ash and LWA-SLFA made of a 50% mixture of slag milled at particle size < 300μm and fly ash.

The thermal treatment for expansion was performed in two different ways:

- A single step of direct expansion at 1175ºC, giving the aggregates **#LWA-FA1**.
- Two steps of heating at 700 and 1175ºC giving the aggregates **#LWAFA2** and **#LWA-SLFA**.

The aggregates **LWA-FA2** obtained at 1175ºC and and **LWA-SLFA** at 1150ºC were characterised and analysed according to the specifications of the European standard EN-13055-1: ”Lightweight aggregates for concrete, mortar and grout”. The result of these analysis was compared to the values given by the producer of a commercial LWA.

The volume expansion of the aggregates was measured by the percentage of volume increment of the particles, where the volume was calculated considering an average diameter of the particle. The density of the aggregates was tested by helium picnometry in two different forms: as bulk particle and as powder (particle size < 50μm) in order to have the bulk and real density values respectively.

The leaching tests were done according to the standards EN-12457 and EN-1744-3 with distilled water in different conditions as it is explained in Table 6 : The leachates were analyzed by ICP-MS in the laboratory of the Jaume Almera Institut (CSIC), Barcelona.

An ecotoxicity test was done in order to evaluate the capability of these LWA made from fly ash to be used as growing substrate for gardening or agriculture. A Microtox test was carried out in the Laboratory of Environmental Engineering and Management of the Technical University of Crete.

## RESULT AND DISCUSSION

### 1 Characterisation of Elcogas fly ash and slag

Table 1 gives the chemical analysis of the ELCOGAS IGCC slag and fly ash. The high content of glass former oxides (>80% $SiO_2$ + $Al_2O_3$) and low level of modifying or fluxing oxides in its composition are the main reason for the high viscosity of the melted fly ash and slag.

| % | Slag | Fly ash |
|---|---|---|
| $SiO_2$ | 55.12 | 56.47 |
| $Al_2O_3$ | 28.20 | 24.13 |
| $Fe_2O_3$ | 5.77 | 3.99 |
| MnO | 0.05 | 0.03 |
| MgO | 0.93 | 0.68 |
| CaO | 6.04 | 3.64 |
| $Na_2O$ | 0.40 | 0.70 |
| $K_2O$ | 2.38 | 4.05 |
| $TiO_2$ | 0.76 | 0.54 |
| LOI | 0.34 | 5.78 |
| C | 0.38 | 4.95 |
| S | 0.51 | 1.39 |

*Table 1 Chemical composition of slag and fly ash from Puertollano IGCC power plant*

The mineralogical composition of Puertollano fly ash and slag (Fig 1) show their mainly amorphous/vitreous character. However, some very small diffraction peaks were detected in the fly ash, which correspond to sulphide crystalline phases: galene (PbS), sphalerite (ZnS) and pyrrotite (FeS).

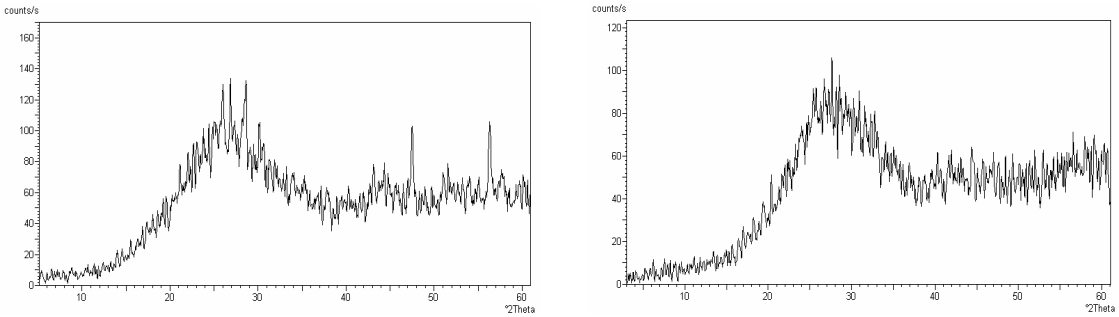



*Fig. 1 XRD patterns. left: IGCC fly ash; right: IGCC slag.*

Fig. 2 show the DTA curves of both IGCC wastes. The fly ash trace depicts a first small exothermic peak observed at 540|C, due to the sulphides oxidation. A large exothermic is produced by ferrous oxidation at 720ºC, temperature of hematite ($Fe_2O_3$) formation. A small and broad exothermic effect is detected up from 1000ºC which is caused by the crystallization of mullite, hercynite and anorthite, the main crystalline phases as assessed by XRD analysis.

The DTA trace of the slag displays a similar tendency, with an exothermic effect due to ferrous oxidation to hematite at temperatures around 700ºC and a second exothermic peak appearing at higher temperatures, due to the crystallization of mullite and anorthite. The intensity of the peak at 700ºC for the slag is lower than fly ash, which can explained by the finer particle size of the fly ash.

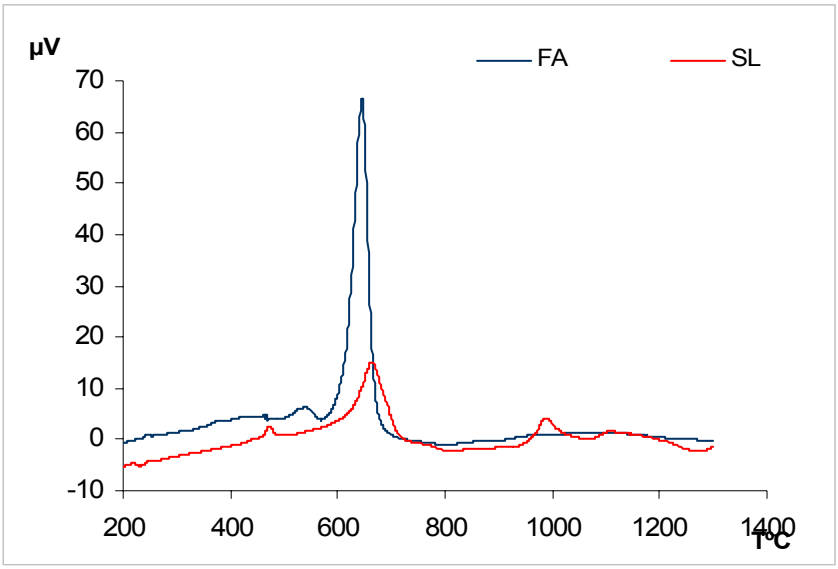



*Fig.2 DTA traces of IGCC Fly ash. (●)and IGCC Slag(○)*

The expanding capacity of the ELCOGAS fly ash and slag was followed by Hot Stage Microscopy through the variation of the specimen height during the heating at increasing temperatures.

The sintering curve obtained by HSM (Fig.3) show different traces to that of vitreous materials which only display a descendent slope from initial shrinkage to the melting temperature. Here, after the initial shrinkage at temperatures up from 900ºC the specimen height remains constant during an interval of 100ºC approximately, followed by and increase of height at temperatures over 1130ºC for the fly ash and 1240ºC for the slag sample. Maximum values of height increase are 20-25%, reached by fly ash between 1200 and 1350 ºC, and by slag at 1300-1350ºC.
Several specimen images recorded during heating are shown in Fig. 4, where the changes in the specimen dimensions can be observed.

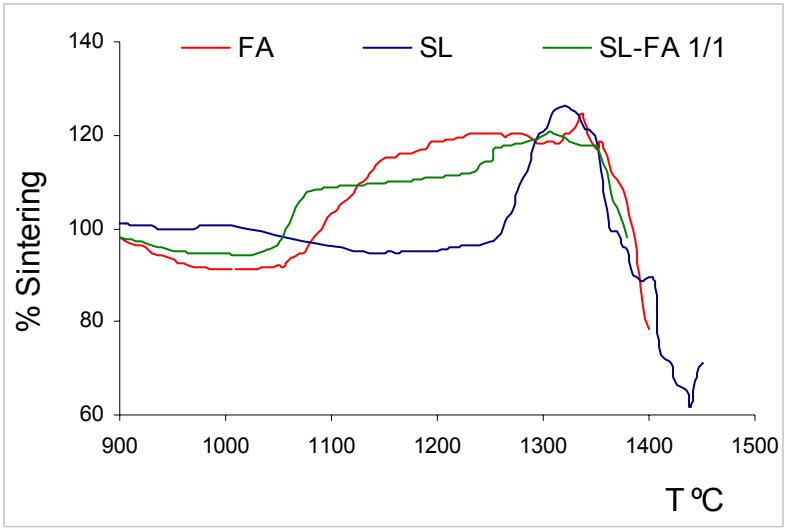



*Fig 3 Sintering curve by HSM. Fly ash, Slag and mixture 1/1 .*

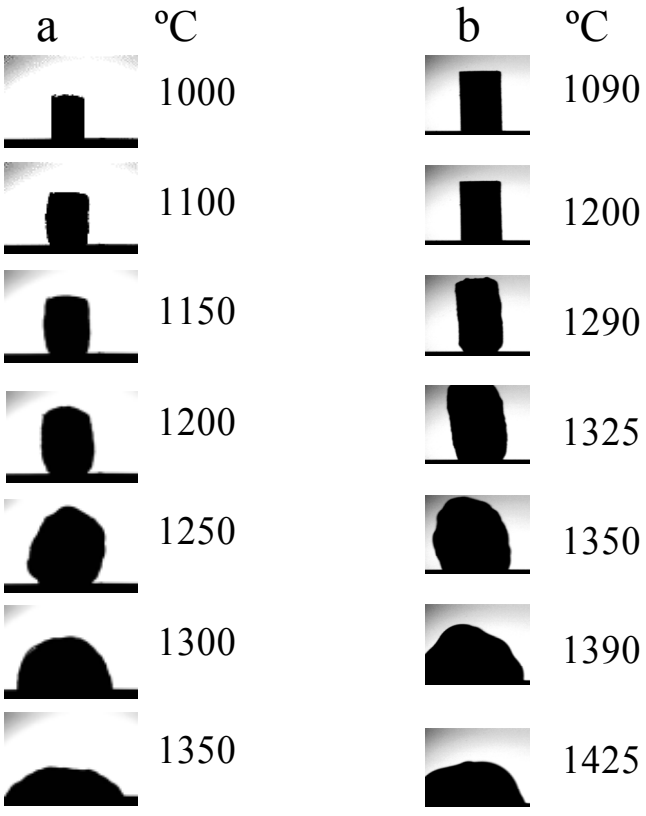



*Fig 4 Hot stage microscopy images. a)Fly ash; b) Slag.*

Table 2 shows the range of temperature and percentage of expansion measured by HSM for the fly ash, the slag and a mixture 1/1 of them:

| Mixture LWA | Fly ash and Slag content % | Expansion Temperature (HSM) ºC | Expansion (HSM) % |
|---|---|---|---|
| FA | FA100 | 1130-1190 | 10-18 |
| SL | SL-100 | 1275-1300 | 10-23 |
| LWA-SLFA 1 | SL50, FA50 | 1075-1230 | 7-17 |

*Table 2 Temperature and percentage of linear expansion*

## 2- Synthesis and characterisation of Lightweight aggregates

Fig.5 shows the external view of the LWA-FA aggregates at different stages of heating and the different inner part of the LWA aggregates obtained in one or two steps of heating can be observed in Fig. 6. As it can be seen, the direct heating for expansion leads to a less oxidized aggregate of larger pore size. A SEM image of a LWA show in detail the fracture face and the surface of a LWA-FA2 particle at 1175ºC.

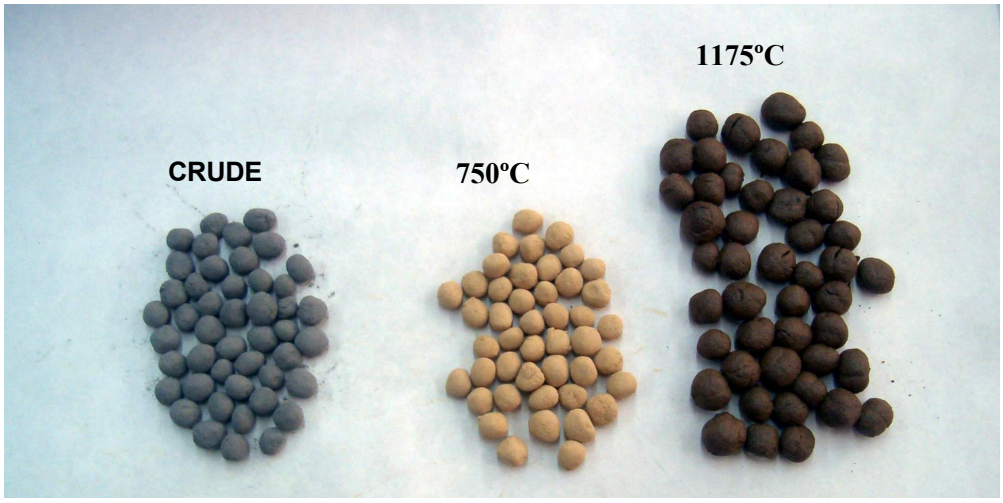
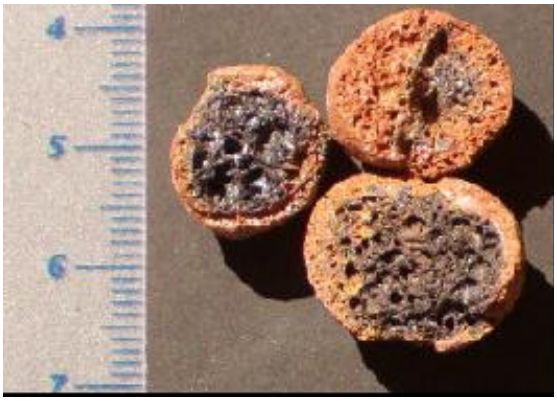



*Fig 5 External view of particles of fly ash before and after being transformed into LWA*



LWA- FA1: one step of heating

*LWA- FA2 Two steps of heating*

*Fig 6 Inner view of LWA particles.*

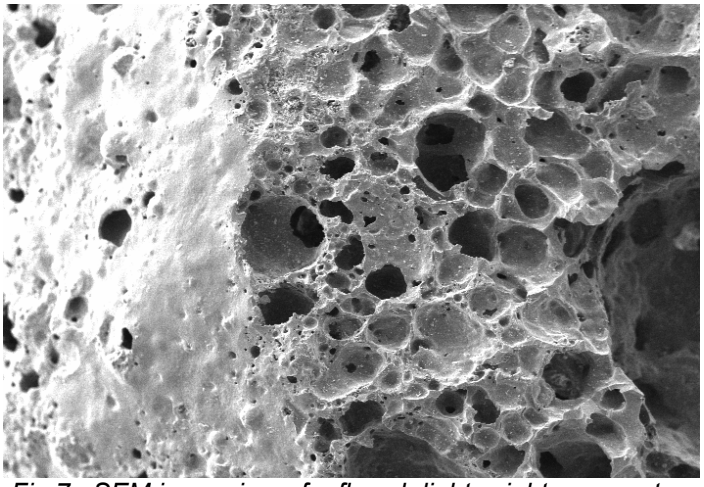


*Fig 7 SEM inner view of a fly ash lightweight aggregate*

- Expansion of the aggregates

The evolution of the expansion with temperature was determine by measuring the volume increment of the aggregates after the different thermal treatments at 1150ºC, 1175ºc and 1200ºC.
As it can be deduced from the traces of Fig 8 the higher expansive effect is achieved by LWA particles at temperatures above 1175ºC and initial diameter > 8 mm, due to a lower surface/volume ratio of the spheres over this size.

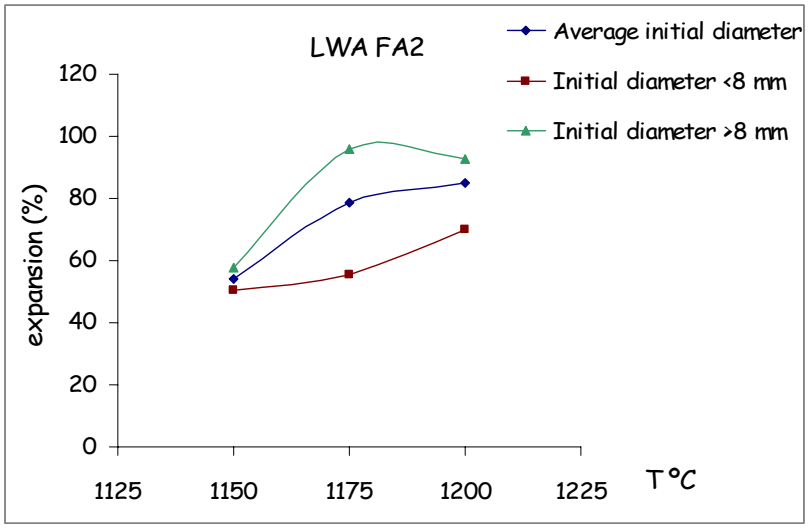



*Fig.8 Volume expansion vs temperature of heating*

- Variation of the density and water absorption with the expansion temperature

Density measures were performed by Helium pycnometry in three different ways, as powder sample, as entire particles and the same entire particles after being coated with an organic glaze. The particles were thermal treated first at 750ºC for 10 min and then introduced in a second preheated furnace at expansion temperatures from 900| to 1200ºC in steps of 25 ºC, for 15 min.
As it can be seen from the plots of density vs temperature of heating, (Fig. 9a,) the values of density of the powdered sample are quite regular, with values between 2.69 and 2.75 Kg/l. In contrast the evolution of density with temperature of the bulk samples show a different pattern. The fly ash density decreases from a value of 2.74, close to that obtained on the powdered sample at 900ºC, followed by a progressive descend of density due to the release of bubbles until the minimum value of 0.90 kg/l at 1075 ºC. At higher temperatures, the growing values of density seem to indicate a change from close to open porosity in the fly ash specimens. That increase of bulk density is not observed when measured the coated particle.
Water absorption of the fly ash particles (Fig9b) gives the lower values for the specimens obtained at 975-1050ºC, corresponding to closed porosity, increasing at higher temperatures to the maximum value at 1150ºC. The further decrease in absorption at 1175º-1200ºC may be due to the closure of surface voids by a less viscous liquid phase.

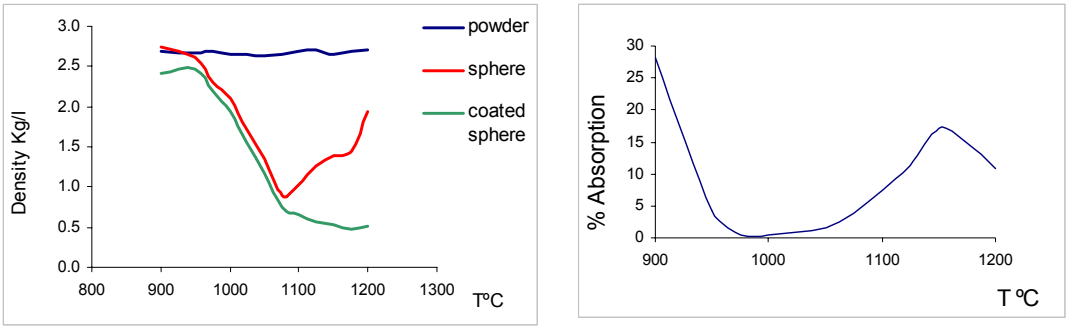



Fig. 9 Evolution of density and water absorption of fly ash particles with the temperature of expansion

- Comparative analysis of Fly ash based LWA and commercial aggregates

The aggregates LWA-FA2 obtained at 1175ºC in two steps of heating were characterised and analysed according to the specifications of the European standard EN-13055-1: ”Lightweight aggregates for concrete, mortar and grout”. The result of several analysis was compared to the values given by the producer of a commercial LWA.

The mineralogy analysis of the LWA-FA2 particles exhibit a higher content of glassy phase and some crystallization peaks of mullite, hercynite and anorthite, that grow in a devitrification process during the heat treatments. A different pattern is observed for commercial LWA, where a lower content of glassy phase and peaks of quartz, spinel, magnetite and cristobalite are detected.

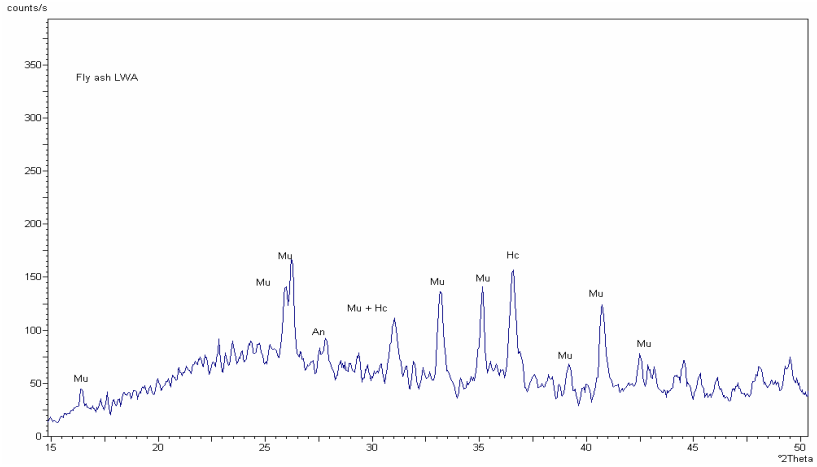



*Fig 10 Diffraction pattern of fly ash based LWA*

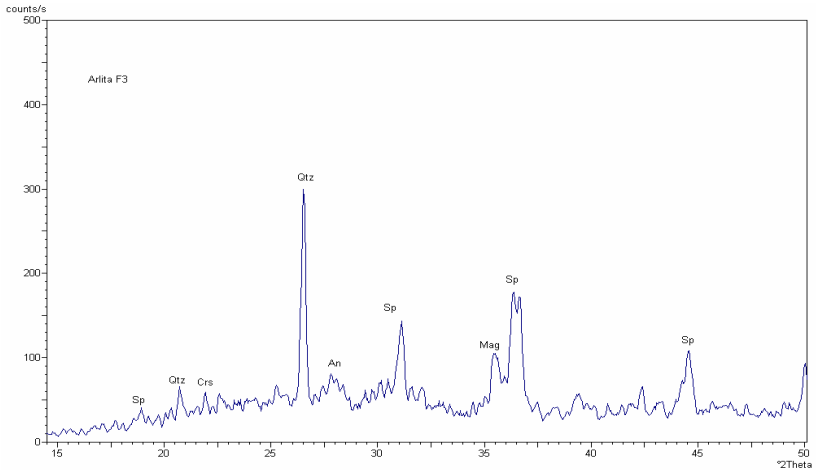



*Fig 11 Diffraction pattern of commercial LWA*

The European standard EN- 13055-1 establish a series of parameters for LWA to be determined, but no restrictive values are defined.

| EN-13055-2003 | Units | Standard method | COMERCIAL LWA | LWA-FA2 | LWA-SLFA |
|---|---|---|---|---|---|
| Chlorides | % $Cl^-$ | EN 1744-1: 1998 | n.d. | 0.016 | 0.014 |
| Total sulphur | %S | EN 1744-1: 1998 | n.d. | 0.56 | 0.42 |
| Particle shape | | - | spherical | spherical | spherical |
| Particle size | mm | EN 933-1 | 7-16 | 7-16 | 7-16 |
| Bulk Density | $Kg/m^3$ | EN 1097-3 | 325 ± 50 | 356 | 370 |
| Water absorption | % dried mass | EN 1097-6 | 23 ± 3 | 11.2 | 7.5 |
| Freezing-thawing resistance | % weight loss | EN 13055 (Anex C) | 1,86 | 0.6 | 0.51 |

*Table 3 Results of some of the analysis specify in standard EN-13055-1*

- Leaching tests of LWA made of fly ash #129.

The leaching tests were done according to the standards EN-12457 and EN-1744-3 with distilled water in different conditions as is explained in Table 4 .

| LEACHATE | LEACHING PROCEDURE |
|---|---|
| L1 | Two steps baked particles (LWA-FA2) fractured in pieces between 2 and 5 mm, L/S 10/1, room temperature, stirred 24 h (EN-12457) |
| L2 | One step baked particles (LWA-FA1) fractured in pieces between 2 and 5 L/S 10/1, room temperature, stirred 24 h (EN-12457) |
| L3 | Bulk particles of LWA L/S 40/1, room temperature, stirring 24 h (EN-1744-3) |

*Table 4 Procedures of leaching of LWA made of 100% fly ash*

The result show that all the samples give in general a low release of heavy metals.

| mg/l | L1 | L.2 | L3 | mg/l | L1 | L.2 | L3 |
|---|---|---|---|---|---|---|---|
| **Al** | 0.5252 | < 0.100 | < 0.100 | **Zn** | 0.05 | 0.011 | 0.41 |
| **Ca** | 14 | 30 | 46 | **Ga** | 0.01 | 0.00 | 0.00 |
| **Fe** | 0.0879 | < 0.100 | < 0.100 | **Ge** | 0.02 | 0.03 | 0.00 |
| **K** | 2.7 | 4.5 | 2.9 | **As** | 0.05 | 0.09 | 0.00 |
| **Mg** | 1.1 | 5.4 | 13.7 | **Se** | 0.00 | 0.00 | 0.00 |
| **Mn** | 0.0042 | 0.0193 | 0.0019 | **Sr** | 0.05 | 0.11 | 0.23 |
| **Na** | 5 | 11 | 21 | **Y** | 0.0 | 0.0 | 0.0 |
| **P** | < 0.100 | < 0.100 | < 0.100 | **Zr** | 0.0 | 0.0 | 0.0 |
| **S** | 4.5 | 18.8 | 15.5 | **Mo** | 0.1 | 0.1 | 0.0 |
| **Li** | 0.1 | 0.4 | 0.0 | **Cd** | 0.0 | 0.0 | 0.0 |
| **Be** | 0.0 | 0.0 | 0.0 | **Sn** | 0.0 | 0.0 | 0.0 |
| **B** | 1.03 | 0.52 | 0.04 | **Sb** | 0.0 | 0.1 | 0.0 |
| **Sc** | 0.0 | 0.0 | 0.0 | **Cs** | 0.0 | 0.0 | 0.0 |
| **Ti** | 0.0 | 0.0 | 0.0 | **Ba** | 0.1 | 0.0 | 0.1 |
| **V** | 0.6 | 0.1 | 0.0 | **W** | 0.0 | 0.0 | 0.0 |
| **Cr** | 0.0 | 0.0 | 0.0 | **Tl** | 0.0 | 0.0 | 0.0 |
| **Co** | 0.0 | 0.0 | 0.0 | **Pb** | 0.0 | 0.0 | 0.0 |
| **Ni** | 0.016 | 0.388 | 0.031 | **Bi** | 0.0 | 0.0 | 0.0 |
| **Cu** | 0.0 | 0.0 | 0.0 | | | | |

*Table 5 Chemical composition of leachates from LWA*

- Ecotoxicity Test

An ecotoxicity test was carried out in order to evaluate the capability of these LWA made of fly ash to be used as growing substrate for gardening or agriculture.
A Microtox test was carried out in the Laboratory of Environmental Engineering and Management of the Technical University of Crete. The solutions to grow the photo-

bacterium Vibrio Fisheri were obtained by leaching the two types of LWA made with 100% of fly ash¨LWA-FA1 and LWA-FA2 in water.
The conditions of leaching were: L/S 10/1, 3 days, no stirring and temperature of 25ºC. The same procedure was followed with the raw fly ash and slag. The result given in table 6 show that only a slight ecotoxicity is detected for raw fly ash after 15 minutes of growth.

| Sample | | 5 minutes | 15 minutes |
|---|---|---|---|
| LWA-FA1 | Entire LWA particles | No ecotoxicity | No ecotoxicity |
| LWA-FA2 | | No ecotoxicity | No ecotoxicity |

*Table 6 Microtox toxicity ($EC_{50}$)*

## CONCLUSIONS

The fly ash and slag generated in the integrated gasification in combined cycle (IGCC) power plant of ELCOGAS power plant has been proved to be recycled as lightweight aggregates (LWA) by taking advantage of the singular behavior of the IGCC fly ash at high temperatures, with release of gases and subsequent bubble formation and expansion caused by these bubbles.

The test using 100% of IGCC wastes have been performed and the best conditions to obtain the aggregates are: two steps of thermal treatmemt, first at 750º for 10-15 minutes and second the expansion step at 1150º-1175ºC for 10-15 min to give rise to porous lightweight aggregates, with values of bulk density, water absorption, freeze resistance and mechanical properties similar to a commercial LWA, having also a good internal and external appearance.

Gradual values of density and water absorption can be modulated by controling the expansion temperature.

No leaching of harzadous elements have been detected and the trace elements vaues are below the range of inert materials for landfill disposal as is establised in the european normative[15]. Microtoxicity of leachates of the aggregates made of fly ash have also been proved to be harmless.

## ADKNOWLEDGES

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