The Effect of the Particle Size Differentiation of Lignite Fly Ash On Cement Industry Applications

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ABSTRACT

The chemical and mineralogical composition of lignite fly ash (FA) varies as a function of the prevalent conditions in both the processes of power production and lignite mining. The differentiation of the qualitative and quantitative composition of the Greek calcareous lignite fly ash, as a function of its particle size distribution, is verified in this paper. According to the results of the conducted research, a fine-grained fraction of considerable amount presents properties that obstruct the sustainable exploitation of lignite fly ash in cement industry applications. On the other hand, the same grain fraction (because of its hydraulic properties) can be utilized in other sort of applications, based on different criteria. The coarse-grained fraction (which reflects a low proportion to the total fly ash output) presents the same undesired characteristics as well. However, the intermediate grain fraction [75-150μm] presents the highly desired properties in the field of the utilization of fly ash as pozzolanic additive in the production process of cement. In addition, the mechanism of the formation of the intermediate grain fraction strongly prevents the factors that cause the variation of its quality. It is therefore the optimum part of the whole amount of lignite fly ash, to be utilized as additive in cement manufacturing. The outcomes of this paper will hopefully contribute to the crucial goal of the expansion of the utilization of lignite fly ash in Greek cement industry by proposing a more effective way of using this material, basically by taking advantage of its fundamental chemical and mineralogical properties.

INTRODUCTION

During the pulverization of lignite, its grains are fractured in a way that leads to the enrichment of specific components in particular FA particles. The chemical and mineralogical composition of the inorganic fraction included in the organic part of the fuel (inherent ash) is substantially different from that of the inorganic fraction that comes

along with the fuel after the mining process (extraneous ash). The main mass of the FA particles consist of non-volatile compounds. Actually, the volatiles can either condensate in them, or form finer FA particles that are not trapped by the electrostatic precipitators.[1, 2] The coperphilic (Goldschmidt) trace elements participate in that process by being enriched in the finer particles. Rather, the lithophilic (Goldschmidt) trace elements are intensely presented in the coarse-grained fraction. Other components, with a diameter of approximately 0.1μm, are incorporated in the so-called pockets of the fuel, and are then able to coalescence and consequently form coarser particles.[3] The different chemical and mineralogical composition of the various lignite FA particles can sufficiently explain the occurrence of certain phenomena in the every day power production process (erosion and corrosion of the metallic surfaces of boilers)[4] as well as provide effective solutions for the expansion of the FA utilization in Greece.[5]

Lignite FA is the main industrial by-product of lignite-fired power plants, utilized as additive for the manufacture of different types of CEM II (according to EN 197-1) under various proportions to the final product. According to the ASTM standards, fly ash is classified based on the extent of its major elements (Si, Al, Fe and Ca) as Class N, F and C. Greece annually produces over 13 million tones (mainly C Class) of lignite fly ash. Unfortunately, not more than 15% of this amount is afterwards used. The transportation cost of FA and the variation of its quality are mainly the factors that restrain the utilization of this material in the production process of cement industry.[6-8]

MATERIALS AND METHODS

The fly ash samples (with composition typical of the average annual FA output) were selected from the electrostatic precipitators of the lignite-fired power plant of Amynteon-Filotas in Northern Greece. The chemical and mineralogical composition of the different lignite fly ash grain fractions was defined by means of XRF and XRD respectively. STIM and RBS methods were applied for the determination of particle size and matrix composition, while PIXE was used for the quantitative analysis of minor and trace elements. The Loss on Ignition tests were carried out by Thermogravimetric Analysis (TGA). The different FA grain fractions were subjected to N_2 adsorption using BET Method in order to determine their specific surface area (SSA). The values of the critical temperatures for the physical and chemical conversions were derived by oxidizing atmosphere tests and the specific gravity by the implementation of SG-ASTM C642.

RESULTS AND DISCUSSION

Chemical composition and loss on ignition (LOI) of the FA fractions

Figure 1 illustrates the variation of the major and minor chemical compounds in the different lignite FA fractions. It is crystal clear that the non-participation of the FA fraction with particles finer than 50μm in the cement production process effectively reduces the concentration the non-desired chemical compounds: SO_3 and CaO. Therefore, the discard of this FA fraction: a) advantages the specifications for the utilization of FA b) results in the enhancement of the mechanical properties of the final

cement products and c) economizes on the production process by the avoidance of the transportation of useless material.
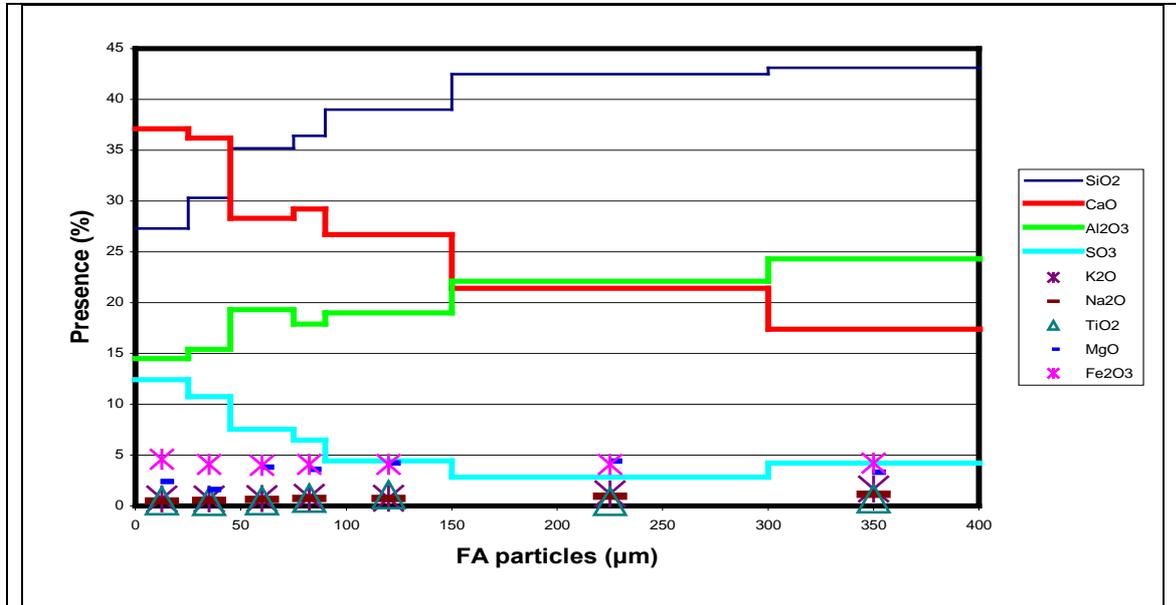

Figure 1. Differentiation of the chemical composition of FA as a function of its particle size distribution

Table 1 shows the values of the percentage weight loss throughout the heating of the different FA grain fractions at the given temperatures:

Grain Fraction (μm)	800ºC	950ºC	1050ºC	1150ºC	1250ºC	δ 950/1250ºC
< 25	1.5	1.1	1.5	9.3	9.7	8.6
25-45	1.4	0.9	1.0	2.7	7.6	6.7
45-75	1.3	0.8	-	2.2	4.4	3.6
75-90	1.2	0.8	0.8	1.3	3.6	1.8
90-150	1.5	1.4	1.6	2.6	3.0	1.6
150-300	4.62	3.7	3.8	4.6	4.6	0.9
> 300	12.9	10.9	11.2	12.0	12.4	1.5

Table 1. Weight loss (%) of the various FA grain fractions

LOI values steadily decrease from the FA fraction with particles smaller than 25µm up to the FA fraction with grain size [75-90] µm. The grain fraction of particles finer than 90µm is completely incinerated. In this fraction, LOI is attributed to the weight loss caused by the thermal disruption of its components (mainly carbonate salts of Ca). Beginning from the grain fraction of 90-150µm, the presence of the unburned lignite gradually increases and peaks in the coarse-grained particles. The gradual increase of LOI is connected with the existing unburned lignite in coarser particles.

The intense presence of CaO in the fine-grained fractions (along with their high specific surface area) leads to their high desulphurization capacity and consequently the high concentration of SO_3 in these particles (mainly with diameter <45µm). This fact, in addition to the limited time of their exposure in high temperatures, results in the bigger weight loss of the aforementioned FA particles at high temperatures, where the endothermic processes are more likely to take place under the release of SO_X. Figure 2 describes the alteration of weight loss of the different FA grain fractions throughout the thermal testing at [950-1250] ºC, as a function of the mean size of the particles, also comparing with the initial percentage presence of SO_3. On the scale of temperatures from 900ºC to 1200 ºC, for the given chemical composition of lignite fly ash, the evolution of the following sequence of reactions is possible: formation of $5CaO \cdot 3Al_2O_3$, $2CaO \cdot 3Al_2O3$, disruption of the product, completion of the formation of $XCaO \cdot SiO_2$, $CaO \cdot 2SiO_2$ (with the participation of $CaSO_4$) and configuration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $3CaO \cdot Al_2O_3$ (with the participation of $CaSO_4$ and of aluminosilicate ingredients). The evolution of these reactions demands active reactants that take for granted the conversion of crystalline to amorphous, which is favorable at the temperatures developed in the coarse-grained fractions. At higher temperatures the disruption of $CaSO_4$ takes place.
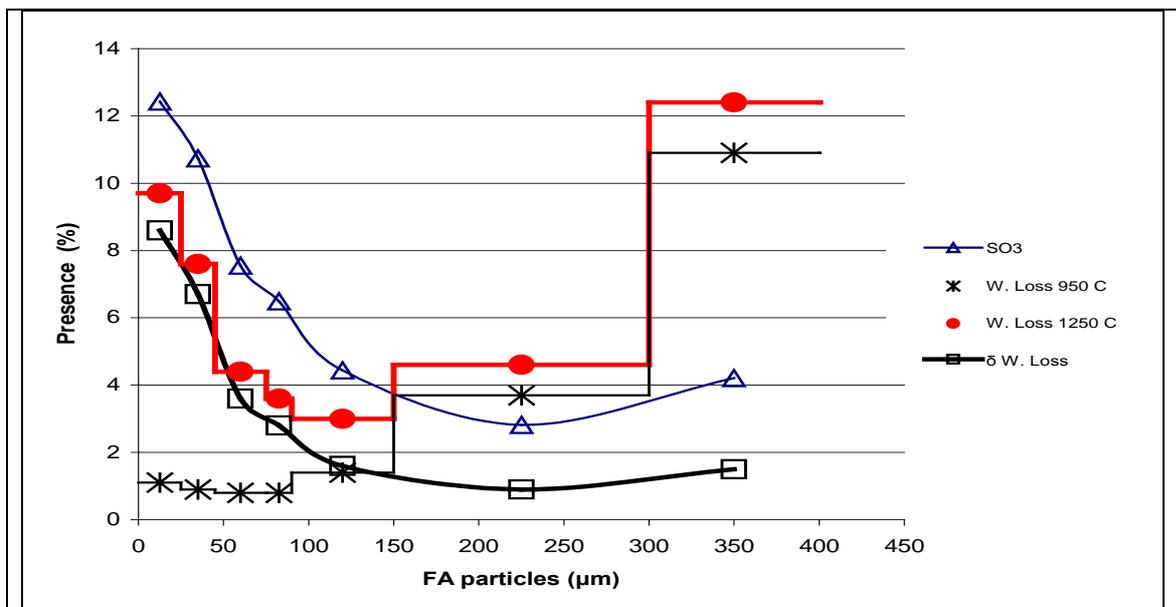

Figure 2. Weight Loss (at 950ºC and 1250ºC) and SO_3 in the different FA grain fractions

The discard of the FA fraction with particles finer than 100μm results in: a) the reduction of the percentage Loss On Ignition (LOI) of the additive material (FA) (high LOI in the additives should be definitely avoided in the production process of concrete because it dramatically increases the demands of water) b) the enhancement of the energy content, taking advantage of the unburned lignite that is included in the fraction and c) the enhancement of the pozzolanic properties of the additive material (FA).

The weight loss at high temperatures (>1150°C) is bigger for the fine-grained FA particles and decreases proportionally to the increase of the mean diameter of the particles (<90μm). At lower temperatures (<1150°C), the FA fractions demonstrate (on a smaller scale) the similar behavior. During the heating at the temperature range of [950-1250] °C (a strongly endothermic procedure) the additional loss of weight varies proportionally to the presence of SO_3 and decreases with the increase of the mean diameter of the incinerated particles.

Specific Surface Area (SSA) and Specific Gravity (SG) of the FA fractions

Table 2 shows the values of specific surface area and specific gravity of the several lignite FA fractions:

Grain Fraction (μm)	SSA (m^2/g)	SG (g/cm)
< 25	4.90	0.55
25-45	3.64	0.58
45-75	3.20	0.67
75-90	2.79	0.77
90-150	3.62	0.75
150-300	5.46	0.69
>300	6.85	0.57

Table 2. Specific gravity and specific surface area of the different FA grain fractions

As expected, in the incinerated FA grain fraction [<90μm], the SSA decreases with the increase of the mean diameter of the particles. In the FA grain fractions with particles coarser than 90μm, the SSA rises proportionally to the increase of the mean diameter of FA particles and their LOI. The rise of the SSA values is attributed to the porosity of the unburned lignite particles that is formed after the volatiles release in the boiler, during the power production process.

The SG values in the totally incinerated fractions [<100μm] do not contradict with the respective SSA measures, since the lowest SG value refers to the finest grain fraction and the highest to the grain fraction [75-90] μm. The better pozzolanic properties, the significant amorphous phase as well as the economical transportation, «suggest» the selective utilization of the grain fraction [50-100] μm. (High specific gravity values of FA make the transportation cost of the material drop)

Figure 3 describes the differentiation of the specific surface area, specific gravity and loss on ignition of FA as a function of the mean size of its particles.
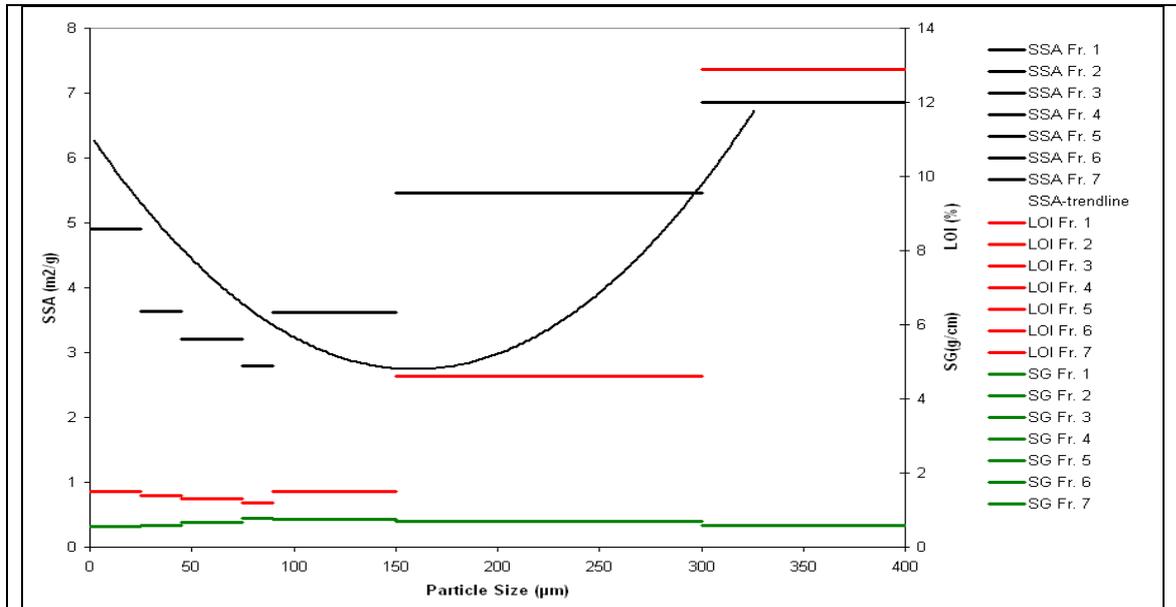
Figure 3. Specific Surface Area, Specific Gravity and Loss on Ignition as a function of the diameter of the FA particles

Critical temperatures for the physical and chemical conversions of the FA fractions

Table 3 presents the values of Initial Deformation Temperature (I.D.), Spherical Temperature (S.T.), Hemispherical Temperature (H.T.) and Fusion Temperature (F.T.) of the various lignite FA grain fractions:

Grain Fraction (µm)	Initial Deformation (I.D.) (ºC)	Spherical Temperature (S.T.) (ºC)	Hemispherical Temperature (H.T.) (ºC)	Fusion Temperature (F.T.) (ºC)
< 25	1198	1273	1303	1347
25-45	1188	1232	1253	1305
45-75	1162	1168	1178	1218
75-90	1162	1169	1176	1212
90-150	1171	1184	1204	1268
150-300	1194	1220	1249	1345
> 300	1198	1218	1257	-

Table 3. Critical temperatures for the physical and chemical conversions of the various FA grain fractions

For the incinerated FA fractions [<90μm], the values of the critical temperatures [(I.D.), (S.T.), (H.T.) and (F.T.)] decrease as the mean diameter of the particles increases. In the same fraction, the increase of particle size results in the decrease of the change of I.D. and F.T. that is attributed to the reducing crystalline phase. The differentiation of the critical temperatures of FA as a function of its particle size distribution is reasonable because of the various residence times of the different fractions in the boiler facilities, which is the result of the range of their density and specific surface area. Figure 4 illustrates the differentiation of the temperatures for the physical and chemical conversions of the FA grain fractions, collating the points of Initial Deformation, Spherical Temperature and Hemispherical Temperature (as a function of the mean size of the particles) with the residence time of particles in the combustion chamber.
The curves that describe the changes in the critical temperature values, as a function of the mean size of the FA particles, converge on the temperature of 1140ºC and the particle size of 90μm. It should be mentioned that this point of temperature is the Initial Deformation Temperature of lignite fly ash.
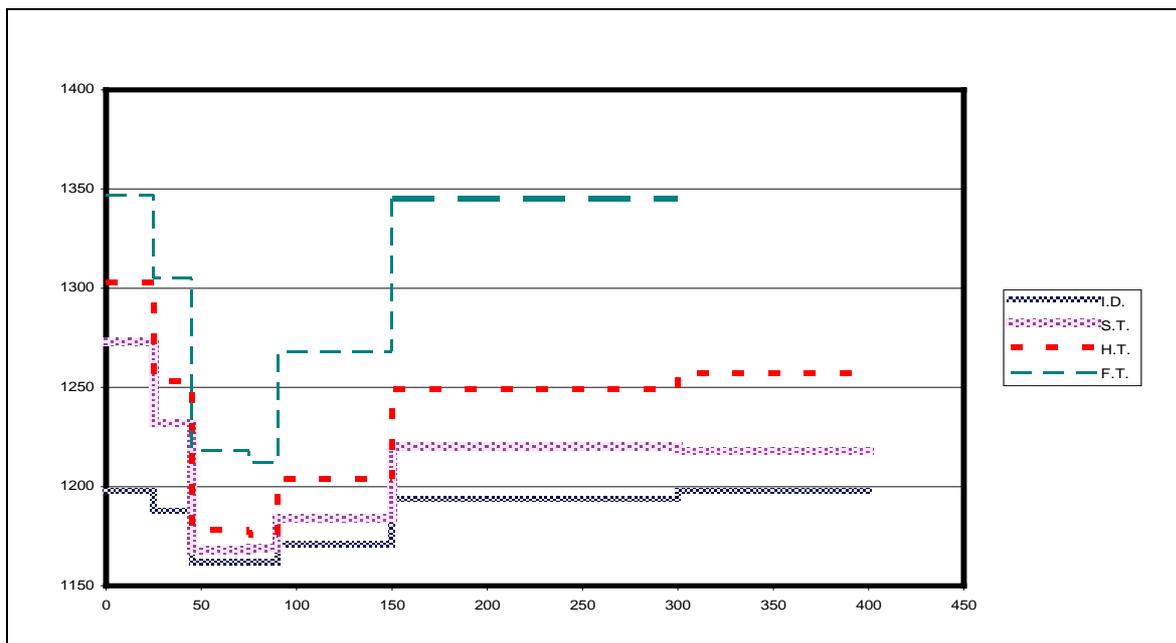

Figure 4. Critical temperatures for the physical and chemical formation of FA as a function of its particle size distribution

Overall characteristics of the different FA grain fractions

Grain Fraction [<75] μm:

The low density of this grain fraction limits the residence time of its particles in the combustion chamber and results in their insignificant exposure at high temperatures and in the subsequent obstruction of the endothermic reactions. However, the co-transfer of particles and flue gases, along with the high SSA values of this grain fraction, favor the reactions between their ingredients. The substantial presence of CaO in the fine-grained fractions is reasonable because of the -easy to crumble- limestone minerals that occur in the feedcoal (lignite). Additionally, the thermal disruption of $CaCO_3$ explains the significant occurrence of free lime (CaO_f). The experimental weight loss is attributed to the non-disrupted (because of the limited available time) part of the limestone. The considerable percentage presence of SO_3 is explained by: a) the initial occurrence of plaster in the inorganic part of feedcoal and b) the formation of $CaSO_4$ because of the desulphurization action of $CaCO_3$ and CaO during the co-transfer of the FA grain fraction and the flue gases. The insignificant thermal exposure of this grain fraction is also evident from its significant crystalline phase as well as the high values of conversion temperatures (I.D., F.T., S.T. and H.T.). As expected, the active silicon shows a lower percentage presence, while the concentrations of SiO_2 and Al_2O_3 (components of the -difficult to crumble- minerals of lignite) are lower in respect with the coarser particles.

The presence of calcareous ingredients in this fraction makes the hydraulic properties of (hydrated) mixtures develop. Therefore, the non-utilization of the «as received» grain fraction [<75] μm in cement industry applications is suggested. In fact the discard of this fraction results in the saving of an important amount of energy, thus decreasing both the production cost and the environmental disturbance caused by cement industry. On the other hand, the low density and the significantly high specific surface area of the fine FA particles render them suitable materials for road construction and soil recondition applications.

Grain Fraction [75-150] μm:

Because of the high density of its particles, this fraction presents the bigger residence time, not only in the areas of high temperatures (combustion chamber), but also in the whole boiler facilities. The chemical compounds of these particles exposure at high temperatures and they consequently undergo endothermic conversions. As a result: a) this FA fraction demonstrates the lowest values of weight loss and b) its components react and form easily melted compounds. Afterwards the $CaSO_4$ is disrupted, under the simultaneous formation of calcium-silicate compounds, reaction that leads to the release of SO_3. Therefore, this fraction presents the lowest weight loss values during its heating at the different points of temperature. Under the intense external conditions, the converting crystal compounds give rise to the glass phase, while there is not enough time available for their effective crystallization. The little specific surface area of this fraction is attributed to the aforementioned softening and fusion of its particles.

The grain fraction [75-150] μm is that with the higher energy content, with the concentrated aluminum-silicate and calcium-silicate ingredients in glass phase, with the insignificant occurrence of crystalline phase and with the higher percentage presence of SiO_2 and active Si. Reasonably, this FA fraction has obtained the higher pozzolanic properties. Moreover, the non-occurrence of free lime (fCaO) along with the low SO_3

and LOI values, render this fraction suitable for participation in the stage of clinker grinding, during the production process of cement industry. However, the low SSA values of this fraction and the demand for crumbling the surface glass (in order to improve the existing pozzolanic properties) make us concern the further pulverization of the material. Finally, the high density of the fraction [75-150] μm makes its transportation financial-worthy, while the non-transportation of the fine-grained fraction reduces the consequent environmental cost.

Grain Fraction [>150] μm:

The high LOI values of the [>150μm] fraction are attributed to the experimental combustion of those particles that had not been incinerated during the power production process. Throughout the exposure of the fraction [>150μm] at high temperatures the volatiles release, thus forming porosity in the main mass of its particles that subsequently results in the increase of their SSA and the decrease of their density. The percentage presence of CaO, CaO_f and SO_3 is relatively low, while the components of the -difficult to crumble- materials (SiO_2, Al_2O_3) occur in significant quantities. The critical temperatures for the physical and chemical conversion of the FA particles are higher than in the fraction [75-150] μm and they are comparable to those of the fraction [<75] μm. This fact sufficiently explains the concentration of specific components in the crystalline (and not in the glass) phase.

The [>150μm] grain fraction, mainly causes the high LOI values of the total amount of lignite fly ash and therefore obstructs the extended utilization of the material in cement industry applications. Furthermore, this fraction does not release all its energy content during the power production process. The small contribution of this fraction to the quality of the final cement product should also be taken into consideration. The non-participation of this fraction in the cement production process can result in energy saving during the production process of cement, thus reducing the environmental disturbance and contributing towards an upgraded quality of the final products.

CONCLUSIONS

The grain fraction of [75-150] μm presents the more intense glass phase and the weakest crystalline presence. This particular fraction obtains the better pozzolanic properties. In order to take advantage of its properties, the further grinding of its particles (under the subsequent release of the pozzolanic and silicon ingredients) is suggested, so as to crumble the superficial glass and to significant increase their specific surface area. This fraction can be used for the fabrication of cement in order to lead to the energy saving during the production process, to the significant decrease of the financial cost and to the effective reduction of the environmental disturbance. However, the conduction of further research (mainly oriented towards the strength of the final cement composites) is definitely required. Regarding the cement industry applications, the discard of the fraction [<50μm] is recommended due to the intense percentage presence of CaO and SO_3 in its particles. Nevertheless, the usage of this FA fraction is suggested for road construction and soil reconditioning applications. Although the usage of the fraction [>150μm] could obviously save energy during the stage of

clinker formation, its non-participation in the cement production process is (for a plenty of reasons) suggested.

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